PRODUCTION OF LATEX RECLAIM AND ITS UTILISATION IN POLYMER BLENDS

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by **Ms.Reena Susan George** under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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DECLARATION

I hereby declare that the thesis entitled **"PRODUCTION OF LATEX RECLAIM AND ITS UTILISATION IN POLYMER BLENDS"** is the original work carried out by me under the supervision of **Dr.Rani Joseph**, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, and no part of this thesis has been presented for any other degree from any other institution.

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LIST OF ABBREVIATIONS USED IN THIS THESIS

Polymers

CGR	Cryogenic-ground rubber
EPDM	Ethylene-propylene-diene rubber
HSR	High styrene resin
LR	Latex reclaim
NR	Natural rubber
PP	Polypropylene
SBR	Styrene-butadiene rubber

Additives

DCP	Dicumyl peroxide
DEG	Diethylene glycol
HAF	High abrasion furnace black
MBTS	Dibenzthiazyl disulphide
S	Sulphur
SP	Styrenated phenol
TMTD	Tetramethyl thiuram disulphide
ZnO	Zinc oxide

Other abbreviations

ASTM	American Society for Testing Materials
BS	British Standards

E	Activation energy
cc	Cubic centimeter
gm	Gram
h	Hours
IS	Indian Standards
ISNR	Indian Standard Natural Rubber
Kg	Kilogram
KJ	Kilojoule
M_c	Number average molecular weight of rubber chains between crosslinks
mg	Milligram
M gm	Meter gram
min	Minutes
ML((1+4)100°C)	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100°C.
mm	Millimeter
MPa	Mega pascal
n	Power law index
N	Newton
Nm	Newton meter
P_o	Initial plasticity
Phr	Parts per hundred rubber/plastic
PRI	Plasticity retention index

R	Gas constant
rpm	Revolutions per minute
S	Second
SEM	Scanning electron microscope
T	Temperature
UTM	Universal testing machine
τ	Shear stress
τ_w	Shear stress at the wall
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_w$	Shear rate at the wall
$\dot{\gamma}_{wa}$	Apparent shear rate at the wall
η	Viscosity

Chapter 1

INTRODUCTION

In recent years, the polymer industry has been confronted with the need to minimize the effects of fluctuations in the availability and pricing of raw materials, while maintaining product performance. One of the solutions for this problem is to recycle and reuse the rubber products after their useful life. This has been practised by the rubber industry for many years, almost entirely by conversion of the waste products to reclaimed rubber.[1-22] Reclaiming process imparts the necessary degree of plasticity to vulcanized rubber and thereby enabling it to be blended with virgin natural or synthetic rubber.[23-37] Reclaiming process is not exactly devulcanization. The combined sulphur still present after reclaiming is an evidence for this. Reclaiming process involves degradation of the vulcanizate structure, induced by chemical and thermal means followed by mechanical working.

Ample literature is available on the reclaiming of waste rubber.[38] Some of the important reclaiming processes are: Heater or pan process, digestor (neutral or alkali) process, high pressure steam process, Engelke thermal process, lancaster-banbury process, dispersion process, lurgi-ficker process, acid process, cryogenic process and reclaimator process.

Among them, reclaimator process is probably the best documented reclaiming process and was patented by the US Rubber Reclaiming Company in 1946. Reclaimator is a screw extruder with a hopper at one end into which a premixed crumb/oil blend is automatically fed at a predetermined rate. The machine generates its own heat for devulcanization by mechanical working of this blend under pressure before discharging the resulting reclaim in less than five minutes. The temperature of the rubber is controlled by heating and cooling jackets around the machine. As the reclaim is discharged from the machine, it is cooled by water sprays and passed to a screw conveyor where it is mixed with the required mineral fillers to comply with reclaim purchase specifications. To ensure complete mixing, the product from the screw conveyor is fed into a mixing hopper from which it is finally extracted through a perforated die, cut into small pieces by a rotating knife and conveyed to the refining section.

Reclaim rubber generally has the following properties. It is cheaper than a new rubber. It mixes faster than new rubber because all the fillers of the original product are already incorporated and the power consumed for mixing is less. During mixing, less heat develops and this is important with compounds having high loadings of carbon black and other reinforcing pigments. Reclaim rubber gives faster processing during extrusion and calendering. It provides better dimensional stability of unvulcanized compounds, lower die swell of extrudates and less shrinkage of calendered articles. But the mechanical properties of reclaimed rubber are very inferior to those of the virgin rubber due to the degradation of rubber during reclaiming. Hence it is added in small percentage to virgin rubbers. The amount of reclaimed rubber that can be added to virgin rubbers without significant drop in properties is usually very low (below 10% or so).[24,33,35,39-42]

The latex industry has expanded over the years to meet world demand for examination gloves, condoms etc. Due to the strict specifications in the quality of latex products, as high as 15 percent of the products are sometimes rejected and these rejects create a major disposal problem for the rubber industry. At the same time, the local authorities prohibit open burning of such waste due to the environmental pollution. Since latex products waste represents a source of high quality rubber hydrocarbon it is a potential candidate for generating reclaimed rubber of much superior quality. Rubber Research Institute of India has reported a method for reclaiming latex products.[43] In this process waste condoms were powdered initially by passing through a hot two roll mill (80-90°C) to a size of about 40 mesh. The powdered material was admixed with 10 phr of naphthenic oil and 1 phr of Renacit-7 in a cold mill. The resulting compound was heated in an air oven at 140°C for 30 minutes. The reclaimed rubber obtained by this process is found to form a smooth band on the mill and contains about 82 per cent of rubber hydrocarbon. However it was found that only small amounts of such reclaim could be added to raw rubber without affecting the mechanical properties adversely. The addition of reclaimed rubber of about 25 per cent in filled natural rubber caused a decrease in tensile strength, elongation at break, resilience, tear strength and abrasion resistance. Compression set of raw rubber was not much affected by the addition of about 25% latex reclaim but an increase in heat build up and hardness was observed. However, the compound containing this reclaim showed better processing characteristics. One another method for reclaiming latex waste products is reported from Rubber Research Institute of Malaysia.[44] However the details of this process are not available.

From the foregoing it is clear that the utilisation of reclaimed rubber is at present limited to preparation of elastomer blends with the raw rubber only and reclaim is added only in very small percentage of the raw rubber. This is mainly due to the degradation of the rubber hydrocarbon during the reclaiming process.

Polymer Blends

Almost all polymers in industrial and transportation applications are used as polymer blends. Moreover, the science and technology of polymer blends is advancing at a rapid rate. One of the main advantages of polymer blends is the great regulatable variability of their properties despite the limited number of initial components. The easiest method to develop polymer compositions having the required properties involves physical blending of two or more polymers.

All materials attract interest on the basis of their property--processing--cost performance relationship. The properties of miscible blends will follow relationships that are functions of composition and to some extent the degree of interaction between the blend components.[45,46] Immiscible blend properties will depend on the phase morphology and phase interaction as well as composition. Compatibility is the fundamental property deciding the practical utility of a polymer blend.[47-49] In miscible polymer blends the property (P) depends on average properties of the constituents and can be described by the following equation:

$$P = P_1C_1 + P_2C_2 + IP_1P_2$$

where, P is the property of the blend, P_1 and P_2 the properties of the isolated components and C_1 and C_2 the respective concentrations of the constituents. I is an interaction parameter which can be positive, zero or negative as shown in Fig.1.1. When I is positive the property is synergistic, when I is zero the property is additive and when I is negative the property is nonsynergistic.

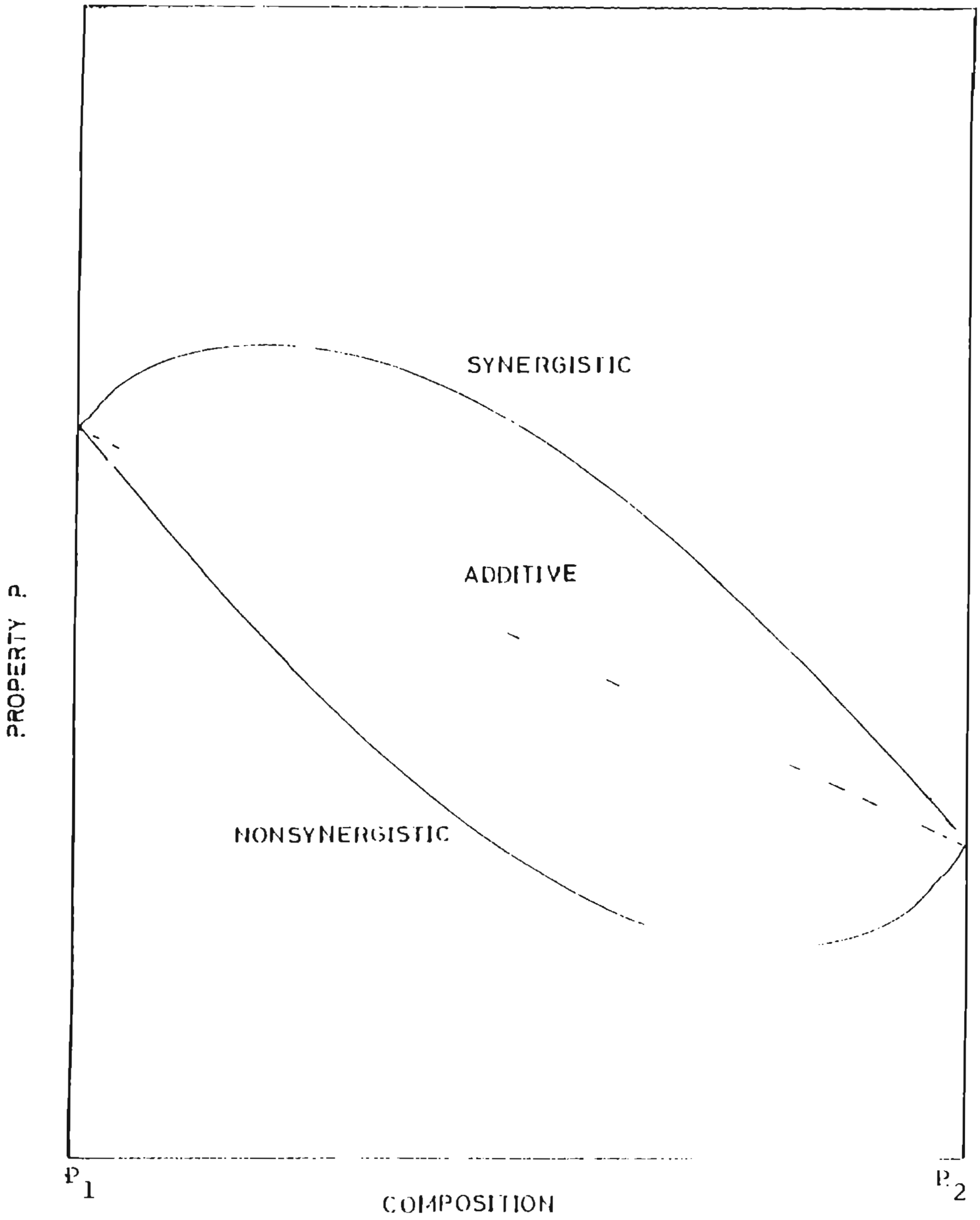

Fig.1.1: Variation of property with composition for a binary polymer blend

The most important factor governing the ultimate properties of a polymer blend is intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). Also, poor adhesion between the components at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface leading to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialised, the applicability of such polymer blends is limited because of the inferior macroscopic properties. So successful blending of incompatible polymer systems is gaining importance both in the academic and industrial field.

Microscopical methods are most suitable to assess the homogeneity of polymer blends because they provide information on overall homogeneity and phase morphology. Optical microscope and scanning electron microscope have been widely used to observe the surface morphology of polymeric materials.[50-52] The most important application of scanning electron microscope in polymer industry is in fracture studies.[53-62] Since the appearance of fracture surfaces reflects a large extent of microstructure and properties of materials used.

Methods of producing polymer blends

The simplest and most direct method is mechanical blending. This may be accomplished on two roll mill or internal mixers, eg. Banbury. The nature of the resulting dispersion depends on the time of mixing, the shear field in equipment, temperature, rheological properties of the component polymers etc. Also there is a possibility of chemical effects produced by the milling operation.

When the individual components can be obtained in latex form, they may be conveniently combined by blending the latices. The polymer is then recovered by coagulation or spray drying. This method results in an intimate, uniform dispersion. However, one drawback is the difficulty in completely removing the nonpolymer material (emulsifier etc.) present in the latices.

Mixing of polymer solutions is in practice mainly used for coatings, because it allows rapid and easy mixing of the components at low energy costs, leads to simple applications at normal temperatures and neither causes degradative colour changes nor premature crosslinking reactions. But, for the preparation of the solid polymer blends, this method requires removal of the solvent, which usually leads to phase separation. Furthermore, the use of solvents implies problems connected with their price, toxicity, flammability, pollution and the economics of the whole process. Usually only laboratory samples of solid polymer blends are prepared by this method.

Blends may also be prepared by dissolving a polymer in the monomer of the other component and then polymerising the second component. This may result in appreciable grafting of the polymer in addition to good dispersion.

Processing characteristics of polymer blends

Rheological studies of polymer blends are important because of the reasons outlined below.

1. Most processing techniques involve some form of directed flow of polymer solutions or melts. Therefore processing defects can be identified and thus the conditions can be adjusted to minimise the defect.

2. The design of process and equipment by deriving qualitative and to some extent quantitative relations between such factors as output, power consumption, machine dimensions, material properties and operational variables such as temperature and pressure can be done.

3. The best polymer which can be used under a given set of conditions can be selected.

4. Flow of polymer solutions plays an important role in the identification and characterisation of their molecular structure.

Processing of rubbers involves those operations that come between the initial mastication of rubbers and the vulcanization of the otherwise finished article, that is operations of mixing, calendering, frictioning, extrusion, moulding etc. In all these cases rheological properties are predominant than any other properties.[63-65]

A fascinating variety of methods and instruments have been devised to measure viscosity and other flow properties of liquids in all cases.[67] Nearly all viscometric systems fall into two classes, those in which flow is caused by a difference in pressure from one part of the liquid to another and those in which flow is caused by controlled relative motion of the confining solid boundaries of the liquid. In the first class, are the capillary types, in the second are the rotational types.

Of the many devices available to study the rheological properties of polymer melts, capillary rheometer is the most important one[68] because it can be used to cover the shear rate ranges encountered in factory processes such as compression moulding (1-10 s^{-1}), milling and calendering (10-100 s^{-1}), extrusion (100-1000 s^{-1}), and injection moulding (1000-10000 s^{-1}).

Blending of polymers is often utilised to obtain a better processing material. This improvement may consist of lowering of stock viscosity, or producing a material that is less prone to fracture or crumbling when subjected to flow. The elastic behaviour and the related phenomena of die swell and shrinkage can also be altered by blending. Generally it is expected that the processing behaviour of the polymer blend will be intermediate between that of the components. However, polymer blends sometimes display anomalous rheological properties. The viscosity of a polymer blend may exhibit minima or maxima as a function of the composition. Very complex dependencies on composition have been observed.

Elastomer blends

Elastomer blends have been used in the rubber industry for a long time now and they are regarded as being quite normal, but more recently the word, elastomer alloy[69,70] has come to have special meanings in the elastomer related industry and their significance is somewhat different to that in the past. From the viewpoint of applied research, elastomer blends therefore represent a very attractive way of finding new materials with the required combinations of properties.

The most pertinent polymeric properties pertaining to elastomer blends are homogeneity of mixing (phase morphology) and cure compatibility. The complete miscibility of polymers requires that the free energy of mixing be negative, which can only be achieved by exothermic mixing or a large entropy of mixing.[71,72] Therefore, most blends of elastomers are immiscible because mixing is endothermic and the entropic contribution is small because of the high molecular weights. Fortunately, miscibility is not a requirement for most rubber applications. Homogeneity at a fairly fine level is necessary for optimum performance but some degree of microheterogeneity is usually desirable to preserve the individual properties of the respective polymer components.

Due to the high structural regularity of natural rubber, natural rubber based elastomer blends is widely used in industrial applications. They have superior building tack, green stock strength, better processing, high resilience and excellent dynamic properties. For reducing the compound cost and to conserve raw materials and energy the utilisation of reclaim rubber is widely accepted in elastomer blends. Reclaim based elastomer blends are widely used in battery cases, soles and heels, boots and shoes, jar rings, kneeling mats, garden hose, baby-carriage tyres etc. The addition of reclaim rubber in the form of cryo-ground rubber which is obtained by the cryogenic process has been practised[16] and was found that the cryoground rubber can be bonded in a two roll mill and compounded with common rubber ingredients. Phadke et al.[23] observed that cryoground rubber compounds are vulcanizable and can be blended with natural rubber either in powder form or as a compound. When blended with natural rubber in powder form, cryoground rubber acts as an inert filler and the reduction in the viscosity is more pronounced in the blends containing cryoground rubber in powder form which is attributed to the wall-slip mechanism.[73]

The styrene-butadiene rubber and natural rubber blends are widely used in the manufacture of tyre parts, sports goods, moulded and extruded products, footwear sheetings, sponge, coated fabric etc. The utilisation of dry rubber reclaim in styrene-butadiene rubber was also reported[3] and was found that the cure rate of styrene-butadiene rubber can be improved by using reclaim rubber. Angerer et al.[74] studied the flow behaviour of styrene-butadiene rubber and rubber crumb by means of a Goettfert high pressure capillary rheometer. They observed an increase in apparent viscosity with increasing filler concentration. But at extrusion pressures of about 30 MPa and higher, the flow curves of the mixtures approached those of the pure rubber and even intersected at a point of inversion. Angerer also studied the influence of capillary dimension on the flow curves, using styrene-butadiene rubber-EPDM mixtures blended with crumb from scrap tyre treads. He observed that with narrow and short capillaries, the flow behaviour proved to be independent of the filler concentration. Also, at low shear rates, a discrimination of the flow characteristics according to the filler loading was observed only with capillaries above a certain width and length. At high shear rates, with such a capillary, an inversion of the rating of the flow curves was found.

The morphology of the elastomer blends containing reclaim rubber was studied by Phadke et al.[35] From this study, it was found that addition of upto about 20 weight percent reclaim rubber in natural rubber compounds does not alter the fracture mechanism while further increasing the reclaim rubber in the blend produces cracks on the fracture surface and results in lower strength properties.

Polyolefin thermoplastic elastomer blends

Thermoplastic elastomers based on blends of polyolefins are an important family of engineering materials.[75-78] Their importance arises from a combination of rubbery properties along with their thermoplastic nature in contrast to thermoset elastomers. Polyolefins are based on coordination catalysts that do not easily lend themselves to block or multisegmented copolymer synthesis. However, since polyolefins have many important attributes favourable to useful elastomeric systems, there was considerable incentive to produce thermoplastic elastomers based on simple α-olefins by some means. Low density, chemical stability, weather resistance, and ability to accept compounding ingredients without compromising physical properties are highly desirable. These considerations led to the development of polyolefin thermoplastic elastomer blends.

To produce a thermoplastic elastomer from non-thermoplastic elastomer materials by blending technology, it is critical to control the morphology of the system. This has been accomplished by choice of the mixing methods, mixing conditions, rheological properties of the blend components, controlling the surface energy and chemical reactions during mixing.

As a class of materials, thermoplastic elastomers based on polyolefin blends exhibit a number of highly useful properties. They can be processed using standard injection moulding, blow moulding extrusion and thermoforming methods. Their chemical composition results in good resistance to many solvents. They have good resistance to ozone and can be stabilized for good outdoor aging. By dynamically vulcanizing the elastomer phase, physical properties are improved due to the stable chemical crosslinks.[79-84]

The incorporation of cryo-ground rubber reclaim in plastics has been practised by Phadke et al.[85] From this study, it was found that the addition of this partially crosslinked rubber recliam in thermoplastics ensures lower mechanical properties due to the poor adhesion between cryo-ground rubber and polypropylene matrix.

Deanin et al.[86] also reported a decrease in mechanical properties when a thermoplastic is blended with reclaimed rubber even at low percentages. Michel Duhaime et al.[87] studied the reactive blending of polyethylene and scrap rubber. In this study, prior to blending, the rubber phase and the LLDPE phase were modified with small amounts of chemical functionality capable of interacting in the melt blending process. Impact and tensile properties of these reactive blends were compared with simple mechanical melt blends of similar compositions. All blends, whether reactive or unreactive, showed a decrease in overall mechanical properties at all proportions of rubber phase content.

Microcellular polymer blends

Solid polymers are replaced by microcellular polymers with 20 to 40 per cent reduction in material without compromising their function or required strength. Microcellular polymers are closed cell foams which can be achieved by a uniform gas diffusion through a solid polymer.[88,89] Microcellular sheets based on natural rubber and high styrene resin are widely used in footwear based polymer industry. For minimising the consumption of our natural resources and for reducing the compound cost, reclaim rubber is incorporated in microcellular sheets.[90] Further, Vipin Kumar[88] has reported that the strength of microcellular sheets is directly proportional to the density of the matrix.

Objectives and scope of the present work

From the foregoing discussions, it is clear that reclaiming of rubber products and its reutilisation in blends with raw elastomer has not achieved its full potential mainly due to the high cost of the reclaiming process and the low percentage of the reclaim that can be blended with raw elastomers. The primary objective of this study has been to develop a cost effective process for developing reclaimed rubber without much degradation so that it can be blended with virgin elastomers in appreciably higher amounts than what is practised now. With these objectives in mind we propose to develop a novel process for reclaiming of waste latex products. Waste latex products are chosen because it has a higher potential to generate good quality rubber hydrocarbon since it is (1) only lightly crosslinked, (2) not filled, (3) not degraded and (4) not masticated. We also propose to fully explore the possible applications of latex reclaim in various fields.

Objectives of the proposed work

1. To develop a process to convert waste latex products to a processible form with the minimum possible degradation.

2. To investigate the possibility of using the latex reclaim along with virgin rubbers as elastomer blends.

3. To investigate the application of the latex reclaim in other useful areas such as developing thermoplastic blends, microcellular sheets etc.

This thesis is divided into the following Chapters.

Chapter 1	Introduction.
Chapter 2	Experimental Techniques.
Chapter 3	
Part I	Development of Latex Reclaim from Waste Latex Products.
Part II	Studies on Natural Rubber/Latex Reclaim Gum Compounds.
Part III	Studies on Natural Rubber/Latex Reclaim Blends.
Part IV	Rheological and Extrudate Behaviour of Natural Rubber/Latex Reclaim Filled Compounds using a Capillary Rheometer.

Chapter 4

Part I The Utilisation of Latex Reclaim for Developing Blends with Styrene-Butadiene Rubber.

Part II Investigation of the Processibility of Styrene-Butadiene Rubber/Latex Reclaim Blends using a Torque Rheometer.

Chapter 5

Part I Studies on Polypropylene/Latex Reclaim Blends.

Part II Rheological and Extrudate Behaviour of Polypropylene/Latex Reclaim Blends using a Capillary Rheometer.

Chapter 6 Development of Microcellular Sheets with Latex Reclaim.

Chapter 7 Summary and Conclusions.

REFERENCES

1. D.S.Le Beau, Rubber Chem. Technol., 40, 217 (1967).

2. P.M.Norling, T.C.P.Lee and A.V.Tobolsky, Rubber Chem. Technol., 38, 1198 (1965).

3. R.A.Swor, L.W.Jensen and M.Budzol, Rubber, Chem. Technol., 53, 1215 (1980).

4. S.Yamashita, Nippon Gomu Kyokaishi, 6, 357 (1981); Int. Polym. Sci. Technol., 8(12), T/77 (1981).

5. G.Grane, R.A.Elefritz, E.L.Kay and J.R.Laman, Rubber Chem. Technol., 5, 577 (1978).

6. K.Tomihisa, Nippon Gomu Kyokaishi, 52, 308 (1979); Int. Polym. Sci. Technol., 12, 31 (1979).

7. Y.Onouchi, S.Inagaki, H.Okamoto and J.Furukawa, Nippon Gomu Kyokaishi 55, 439 (1982); Int. Polym. Sci. Technol., 9(10), T/58 (1982).

8. J.A.Backman, G.Grane, E.L.Kay and J.R.Laman, Rubber Chem. Technol., 47, 597 (1974).

9. G.Grane and E.L.Kay, Rubber Chem. Technol., 48, 50 (1975).

10. N.R.Braton and J.A.Koutsksky, Chem. Eng. News, 52(6), 21 (1974).

11. A.Ratcliffe, Chem. Eng., 79(7), 62 (1972).

12. A.A.Harshaft, Environ. Sci. Technol., 6(5), 412 (1972).

13. J.A.Backman, G.Grane, E.L.Kay and J.R.Laman, Rubber Age, 104(4), 43 (1973).

14. S.Yamashita, N.Kawabata, S.Sagan and K.Havashi, J. Appl. Polym. Sci., 21, 2201 (1977).

15. N.Kawabata, B.Okuvama and S.Yamashita, J. Appl. Polym. Sci., 26, 1417 (1981).

16. A.Acetta and J.M.Vergnaud, Rubber Chem. Technol., 54, 302 (1981).

17. A.Acetta and J.M.Vergnaud, Rubber Chem. Technol., 55, 961 (1982).

18. Y.Saeki and G.Suzuki, Rubber Age, 2, 33 (1976).

19. N.Kawabata and S.Yamashita, Int. Polym. Sci. Technol., **7**(3), T/55 (1980).

20. J.W.Larsen and B.Chang, Rubber Chem. Technol., **49**, 1120 (1976).

21. N.Kawabata, T.Murakami and S.Yamashita, Int. Polym. Sci. Technol., **7**(5), T/29 (1980).

22. W.Szelingier and A.Luczak, Int. Polym. Sci. Technol., **19**(5), T/95 (1992).

23. A.A.Phadke, S.K.Chakraborty and S.K.De, Rubber Chem. Technol., **57**, 19 (1984).

24. N.P.Chopey, Chem. Eng., **80**, 54 (1973).

25. R.H.Wolk, Rubber Age, **104**, 103 (1972).

26. A.A.Phadke and A.K.Bhowmick, J. Appl. Polym. Sci., 32(4), 4063 (1986).

27. J.Boruta and M.Behol, Angew. Makromol. Chem., No.176-177, 173 (1990).

28. J.N.Lynch and B.D.La Grone, Rubber Chem. Technol., 60, 202 (1987).

29. J.Stark, Rubber World, 200(1), 16 (1989).

30. I.Baruta, Int. Polym. Sci. Technol., 18(4), T/34 (1991).

31. A.A.Phadke, A.K.Bhowmick and S.K.De, Rubber Chem. Technol., 58, 4063 (1985).

32. V.N.Kalinichenko, G.A.Blokh, A.Ya Vasker and N.P.Sulyaeva, Int. Polym. Sci. Technol., 11(7), T/87 (1984).

33. M.D.Burgogne, G.R.Leaker and Z.Krekic, Rubber Chem. Technol., 49, 375 (1976).

34. P.Elfferding, Int. Polym. Sci. Technol., 9(10), T/30 (1982).

35. A.A.Phadke, A.K.Bhattacharya, S.K.Chakraborty and S.K.De, Rubber Chem. Technol., 56, 726 (1983).

36. L.N.Sharapova, A.A.Chekanova, N.D.Zakharov and E.Yu Borisova, Int. Polym. Sci. Technol., 10(2), T/4 (1983).

37. E.M.Solov'ev, V.B.Pavlov and N.S.Enikolopov, Int. Polym. Sci. Technol., 14(8), T/10 (1987).

38. G.Cheater, A.E.Eagles, D.Matthews, S.H.Morrel, W.Whalley, B.Whittaker and B.J.Willooughby, A study of the reclamation and reuse of waste tyres, Rubber and Plastics Research Association of Great Britian (1976).

39. G.Adam, A.Sebenik, V.Osredkar, F.Ranogajec and Z.Veksli, Rubber Chem. Technol., 64, 133 (1991).

40. V.F.Drozodovskii, Int. Polym. Sci. Technol., 20(8), T/64 (1993).

41. K.Fujimoto, T.Nishi and T.Okamoto, Int. Polym. Sci. Technol., 8(8), 65 (1981).

42. L.Slusarski and R.Sendlewski, Int. Polym. Sci. Technol., 11(4), T/6 (1984).

43. K.T.Thomas, N.M.Claramma, Baby Kuriakose, E.V.Thomas, Paper presented in the International Conference on Rubber and Rubber-Like Materials, Nov. (6-8), Jamshedpur, India, 511 (1986).

44. Y.Aziz, Kautschuk Gummi Kunststoffe, 45, 862 (1992).

45. J.Kovar, J.Fortelny and M.Bodhanecky, Int. Polym. Sci. Technol., 9(11), T/50 (1982).

46. E.Martuscelli, R.Palumbo and M.Kryszewski, Polymer blends, New York (1980).

47. L.A.Utraki, Polym. Plast. Technol. Eng., 22(1), 27 (1984).

48. Sarah Yarger Kienzle, Plast. Eng., 41 (1987).

49. M.Xanthos, S.S.Dagli, Polym. Eng. Sci., 31(13), 929 (1991).

50. R.C.Thamm, Rubber Chem. Technol., 50, 24 (1977).

51. D.N.Schulz, L.E.Calihan and D.P.Tate, Rubber Chem. Technol., 49, 126 (1976).

52. J.C.Andries, C.K.Rhee, R.W.Smith, D.B.Ross and H.E.Diem, Rubber Chem. Technol., 52, 823 (1979).

53. J.E.O'Conner, Rubber Chem. Technol., 50, 945 (1977).

54. V.M.Murty, A.K.Bhowmick and S.K.De, J. Mat. Sci., 17, 709 (1982).

55. V.M.Murty and S.K.De, Rubber Chem. Technol., 55, 287 (1982).

56. S.K.Chakraborty, D.K.Setua and S.K.De, Rubber Chem. Technol., 55, 1370 (1982).

57. W.D.Bascom, Rubber Chem. Technol., 50, 327, 875 (1977).

58. Anil K.Bhowmick, Sanjay Basu and Sadhan K.De, J. Mat. Sci., 16, 1654 (1981).

59. P.K.Pal, A.K.Bhowmick and S.K.De, Int. J. Polym. Mat. 9, 139 (1982).

60. Baby Kuriakose and S.K.De, J. Mat. Sci., 20, 1864 (1985).

61. N.M.Mathew and S.K.De, Polymer, 23, 632 (1982).

62. N.M.Mathew, A.K.Bhowmick, B.K.Dhindaw and S.K.De, J. Mat. Sci., 17, 2594 (1982).

63. R.Brezik, Int. Polym. Sci. Technol., 11(12), T/76 (1984).

64. R.H.Norman and P.S.Johnson, Rubber Chem. Technol., 54(3), 493 (1981).

65. Yu F.Shutilin, A.I.Omitrenkov, M.P.Parinova and V.S.Shein, Int. Polym. Sci. Technol., 15(9), T/24 (1988).

66. V.C.Fott and R.W.Smith, Rubber Chem. Technol., 46, 1193 (1973).

67. J.A.Brydson, Flow properties of polymer melts, second edition, George Godwin Ltd., London, chapter 3 (1981).

68. D.J.Williams, Polymer Science and Engineering, Prentice-Hall Inc.,(1971).

69. A.Y.Coran and R.Patel, Rubber Chem. Technol., 63, 599 (1990).

70. A.Y.Coran and S.Lee, Rubber Chem. Technol., 65, 231 (1992).

71. C.M.Roland, Rubber Chem. Technol., 62, 456 (1989).

72. O.Olabisi, L.M.Robenson and M.T.Shaw, Polymer-Polymer Miscibility, Academic Press, Inc., New York, chapter 2 (1979).

73. A.A.Phadke, Plast. Rubber Process. Appln., 6, 273 (1986).

74. G.Angerer and W.G.Wolff, Rheol. Acta, 15, 57 (1976).

75. E.N.Kresge, J. Appl. Polym. Sci., 39, 37 (1984).

76. A.Y.Coran, Thermoplastic Elastomers, N.R.Legge, G.Holden and H.E.Schroeder, Eds., Hanser, New York, chapter 7 (1987).

77. J.R.Wolfe, Jr., Thermoplastic Elastomers, N.R.Legge, G.Holden and H.E.Schroeder, Eds., Hanser, New York, chapter 6 (1987).

78. C.P.Rader, Handbook of Thermoplastic Elastomers, B.M.Walker and C.P.Rader, Eds., Van Nostrand Reinhold, New York, chapter 4 (1988).

79. A.Y.Coran and R.P.Patel, Rubber Chem. Technol., 53, 141 (1980).

80. A.Y.Coran, R.P.Patel and D.Williams, Rubber Chem. Technol., 55, 116 (1982).

81. A.Akhtar, P.P.De, and S.K.De, Int. Polym. Sci. Technol., 16(6), T/55 (1989).

82. Baby Kuriakose and S.K.De, J. Appl. Polym. Sci., 32, 5509 (1986).

83. V.S.Glukhovskoi, G.I.Popova, E.S.Kretinina, T.M.Rogova and M.I.Sokolov, Int. Polym. Sci. Technol., 16(10), T/80 (1989).

84. C.S.Ha, D.J.Ihm and S.C.Kim, J. Appl. Polym. Sci., 32(8), 6281 (1986).

85. A.A.Phadke and S.K.De, Polym. Eng. Sci., 26(15), 1079 (1986).

86. R.D.Deanin and S.M.Hashemielya, Polym. Mat. Sci. Eng., 57, 212 (1987).

87. J.R.Michel Duhaime and Warren E.Baker, Plast. Rubber Process. Appln., 15, 87 (1991).

88. Vipin Kumar, Prog. Rubber Plast. Technol., 9(1), 54 (1993).

89. Vipin Kumar and Nam P.Suh, Polym. Eng. Sci., 30(20), 1323 (1990).

90. Jacob K.Varkey, N.M.Mathew and P.P.De, Indian J. Nat. Rubber Res.,2(1), 13 (1989).

Chapter 2

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

Materials

Polymers

1. Natural Rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala. The Indian standard specifications for this grade of rubber are given below:

Parameters	Limit
Dirt content, % by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass, max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, (P_o), min.	30.00
Plasticity retention index, (PRI), min.	60.00

2. Styrene-Butadiene Rubber (SBR)

SBR used was synaprene 1502 grade supplied by Synthetics and Chemicals Ltd., Bareilly. Styrene content, % by mass - 23.50; Mooney viscosity (ML(1+4) 100°C) - 52.00

3. Polypropylene (PP)

PP used was Koylene M0030 grade supplied by Indian Petrochemical Corporation Ltd., Gujarat, India. Density at 23°C, gm/cm^3 - 0.905; Melt flow index at 230°C (MFI) -10.00

4. High Styrene Resin (HSR)

HSR used was Synaprene 1958 grade supplied by Synthetics and Chemicals Ltd., Bareilly. Styrene content, % by mass - 49.

5. Latex Gloves

Waste latex gloves (Examination gloves) was supplied by AVT Rubber Products Ltd., Kakkanad, Kerala,India.

6. Latex Condoms

Waste condoms was supplied by Hindustan Latex Ltd., Trivandrum, Kerala, India.

Polymer Additives

1. Zinc Oxide (ZnO)

ZnO was supplied by M/s.Meta Zinc Ltd., Bombay, India having the following specifications.

Specific gravity	5.5
Zinc oxide content	98%
Acidity	0.4% max
Heat loss (2 hrs at 100°C)	0.5% max

2. Stearic Acid

Stearic acid used in the study was supplied by Godrej Soaps (Pvt.) Ltd., Bombay, India and has the following specifications:

Melting point	50-69°C
Acid number	185-210
Iodine number	9.5 max
Specific gravity	0.85 ± 0.01
Ash content	0.1% max

3. Dibenzthiazyl Disulphide (MBTS)

MBTS was supplied by Bayer Chemicals, Bombay, India having the following specifications.

Specific gravity	1.34
Melting point	165°C

4. Tetramethyl Thiuram Disulphide (TMTD)

TMTD used was supplied by Polyolefins Industries Ltd., Bombay, India having the following specifications.

Melting point	136°C
Specific gravity	1.4

5. Sulphur

Sulphur was supplied by Standard Chemical Company (Pvt.) Ltd., Madras, India having the following specifications.

Specific gravity	2.05
Acidity	0.01% max
Ash	0.01% max
Solubility in CS_2	98% max

6. Di-cumyl Peroxide (DCP)

DCP used was supplied by Bengal Water Proof Ltd., Panihati having 40% active ingredient.

7. Dinitroso Pentamethylene Tetramine (DNPT)

DNPT was supplied by Deepak Nitrite, Bombay, India having 40% active ingredient.

8. Renacit-VII

Renacit-VII used was supplied by Bayer India Ltd.

9. High Abrasion Furnace Black (HAF N-330)

HAF (N-330) was supplied by M/s.Carbon and Chemicals Ltd., Kochi, India, having the following specifications.

Iodine adsorption	80 mg/g
DBP absorption	105 cm^3/100 g
Mean particle diameter	32 nm

10. Precipitated Silica

It was obtained from Lunar Chemicals, Kanpur, India. The specific gravity was 1.95.

11. China Clay

It was supplied from English Indian Clays, Trivandrum, India. It had a specific gravity of 2.6.

12. Micro Crumb

Ground microcellular sole scrap having 200 mesh size was used for this study.

13. Aromatic Oil

It was supplied by M/s.Hindustan Petroleum Ltd., India having the following specifications.

Colour - Black coloured oil

Viscosity gravity constant (VGC) - 0.98-1.0.

14. Naphthenic Oil

It was supplied by M/s.Hindustan Petroleum Ltd., India having the following specifications.

Colour - Light coloured oil

Viscosity gravity constant - 0.85-0.9

15. Other Additives

Accinox ZC(N-1,3 dimethyl N'-phenyl P-phenylene diamine); specific gravity - 1.02, diethylene glycol, vulcafor F (An activated thiazole); specific gravity - 1.46, wax, styrenated phenol, titanium dioxide, wood rosin were of commercial grade. Sodium sulphite, strontium chloride, cadmium acetate, starch, iodine, sodium stearate used were of analytical grade.

Solvents

Acetic acid, formaldehyde and toluene used were of analytical grade. Commercial grade toluene also was used.

Experimental Methods

1. Mixing and Homogenization

a) Using the mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002x100)". Then it was given 2 passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 70 ± 5°C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order activators, fillers, accelerators and curing agents. Before the addition of accelerators and sulphur the batch was thoroughly cooled.

After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. For the preparation of compounds of elastomer blends, NR was masticated to the mooney viscosity level of the other elastomer and then the other additives were added as described above unless otherwise specified.

b) Using the Brabender Plasticorder

A Brabender plasticorder (torque rheometer) model PL 3S was used for various investigations. It is a device for measuring the torque during processing under pre-selected conditions of shear and temperature. The mixing chamber of 40 cc capacity is the central part of the machine which is heated by oil circulating thermostat heating tanks. The mixer temperature can be adjusted with the contact thermometer in the heating tank. High temperature silicone oil is used as heating liquid and the temperature on the mixer can be varied upto 300°C. The measuring head is equipped with a stock temperature thermocouple coupled with a temperature recorder for temperature measurement. The mixing or shearing of the material in the mixing chamber is done by two rotors.

Various types of rotors can be used, depending upon the nature of the polymers. A speed controlled DC drive thyristor allows the rotor speed adjustment between 0 to 150 rpm. The measurement is based on the fact that the resistance which is put up by the material against the rotors in the chamber is made visible as a means of viscosity in the dynamometer. The torque is plotted continuously against time. Torque upto 20,000 meter grams can be measured by the torque rheometer.

In the present study, Brabender plasticorder was used for blending polypropylene with natural rubber/latex reclaim to study the effect of latex reclaim on mechanical properties of these blends. It was also used to assess the rheological behaviour of thermoplastic/elastomer blends based on PP and latex reclaim, SBR/latex reclaim blends and NR/latex reclaim blends.

Thermoplastic/elastomer blends were prepared in the Brabender plasticorder equipped with roller mixing heads according to ASTM D 3184 (1980) and 3182 (1982). Blending parameters were selected based on torque temperature data of the individual components and the particular blend. The basic principle followed in every blending was to ensure the melting of the polymers and to keep polymer degradations to minimum.

2. Cure Characteristics

The cure characteristics of the elastomers and elastomer blends were determined using a Goettfert Elastograph model 67.85. It is a microprocessor controlled rotorless curemeter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of defined size is kept in the lower half of the cavity which is oscillated through a small deformation angle (±0.2°). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. The following data can be taken from the torque - time curve.

i) Minimum torque: Torque obtained by the mix after homogenizing at the test temperature before the onset of cure.

ii) Maximum torque: This is the torque recorded after the curing of the mix is completed.

iii) Scorch time: This is the time taken for attaining 10% of the maximum torque.

iv) Optimum cure time: This is the time taken for attaining 90% of the maximum torque.

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

3. Moulding of Test Specimens

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding, electrically heated press having (18x18 inch) platens at a pressure of 120 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150°C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hrs and were used for subsequent physical tests. For samples having thickness more than 5 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

For compression moulding of thermoplastic/ elastomer blends, specially designed moulds with provision for cooling under pressure were used. In the case of thermoplastic/elastomer blends, moulding temperature and time were determined by trial and error methods according to ASTM D 3182 (1982).

4. Physical Test Methods

At least five specimens per sample were tested for each property and mean values are reported.

a) Tensile stress-strain behaviour

Tensile properties of the elastomer and elastomer blends were determined according to ASTM D 412 (1980) using dumb-bell specimens on a Zwick universal testing machine (UTM) model 1445. All the tests were carried out at 28±2°C. Samples were punched out from compression moulded sheets using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min for elastomeric specimens. The tensile properties of the thermoplastic/elastomer blends were determined according to ASTM D 638 on the Zwick UTM using a crosshead speed of 50 mm/min. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

b) Tear resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheet parallel to the mill grain direction. The test was carried out on a Zwick UTM model 1445. The speed of extension was 500 mm/min. and the test temperature was 28±2°C.

c) Split tear strength

The split tear strength determination of microcellular sheets was carried out as per IS: 10702-1985. 25x100x7±0.2 mm test pieces were cut along and across the direction of the compression moulded sheet. Then each test piece was prepared by splitting it midway between the top and the bottom surface for a distance of 30 mm from one end and thus forming two tongues at the end. The tongues of the test piece were clamped in the jaws of the Zwick UTM and the jaws were allowed to separate at a constant rate of 75 mm/min. The maximum load was noted and the arithmetic average of the tests in kg was recorded as the split tear strength.

d) Hardness

The hardness (Shore A) of the moulded samples was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981) for rubber vulcanizates and with IS: 3400 (Part II) 1965 for microcellular samples. The tests were performed on mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens.

e) Compression set

The rubber samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C according to ASTM D 395 (1982) method B. The samples were taken out from the compression set apparatus and cooled at room temperature for half an hour and the final thickness was measured. The microcellular samples (9.5 mm thick and 30 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 24 hours at 27±1°C and then the samples were taken out and allowed to recover for an hour and the final thickness was measured.

The compression set was calculated as follows:

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100$$

where t_o and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used.

f) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader. Sample having a diameter of 6±0.2 mm and a thickness of 6 to 10 mm, was kept on a rotating sample holder and 10 N load was applied and for microcellular sample only 5 N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece getting abraded away by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows:

$$V = \frac{\Delta m}{\rho}$$

where, Δm = mass loss, ρ = density of the sample and V = abrasion loss.

g) Rebound resilience

Dunlop tripsometer (BS 903, Part 22, 1950) was used to measure rebound resilience. The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as follows:

$$\text{Rebound resilience (\%)} = \frac{1-\mathrm{Cos}\phi_2}{1-\mathrm{Cos}\phi_1} \times 100$$

where ϕ_1 and ϕ_2 are the initial and final rebound angles respectively, ϕ_1 was 45° in all cases.

h) Heat build up

The Goodrich flexometer conforming to ASTM D 623-67 (method A) was used for measuring heat build up. The test was carried out with the cylindrical samples of 2.5 cm height and 1.9 cm diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.9 kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature riseΔT°C at the end of 20 minutes was taken as the heat build up.

i) Ageing studies

Physical properties like tensile strength, elongation at break, modulus and tear strength were measured after ageing according to ASTM D 573 procedure.

The initial plasticity and plasticity retention index of the samples were measured according to ASTM D 3194-73 method. A test portion of about 30 gm rubber sample was taken and passed three times between mill rolls at room temperature with the opening adjusted so that the final sheet thickness is approximately 1.7 mm. Immediately the sheet was doubled and the two halves were pressed lightly together, avoiding the formation of air bubbles. The test pieces were cut from the doubled sheet with the punch and their thickness was measured until six test pellets were obtained with a thickness of 3.4 mm having a volume of 0.40 cm^3. These test pieces randomly divided into sets of three, one was tested before ageing and the other was tested after ageing. The ageing was done in an air oven kept at 140°C, for 30 minutes. After ageing, the samples were removed from the oven and allowed to cool to room temperature for 30 minutes. Then the sample was placed between a bleached unglazed acid free tissue paper and then inserted between the heated platens of the wallace rapid plastimeter. The median values of the three results of the unaged and aged test pieces were used for the calculation of initial plasticity (P_o) and plasticity retention index (PRI).

P_o = Initial plasticity of the unaged samples.

$$\text{PRI} = \left(\frac{\text{aged plasticity}}{\text{unaged plasticity}}\right) \times 100$$

$$= \left(\frac{P_{30}}{P_o}\right) \times 100$$

The change in hardness of microcellular samples was determined according to IS: 3400 (part III) - 1965 method. The cut test pieces (50x50 mm) from the microcellular sheets were heated in an air oven at 100±1°C for 24 hours. The test pieces were then removed and cooled for 1 hour at 27±1°C. The change in hardness was expressed as follows:

Change in hardness due to ageing = $R_2 - R_1$

where R_2 and R_1 are the final and initial readings of shore A hardness respectively.

Heat shrinkage of microcellular samples was determined according to IS: 6664-1972 procedure. The test samples (125x5x5 mm) were conditioned at a temperature of 27±2°C for at least 24 hours, prior to testing. The length of the test piece was accurately measured. The test piece was kept in an air oven at 100±1°C for 1 hour. The test piece was removed from the oven and allowed to cool for 2 hours at 27±2°C. The final length of the test piece was measured and the heat shrinkage was calculated as follows:

$$\text{Heat shrinkage, percent} = \frac{L_o - L_1}{L_o} \times 100$$

where, L_o = length of the test piece in mm before heating and L_1 = length of the test piece in mm after heating.

j) Density

The densities of the polymer samples were measured by the method of displacement of liquid (ASTM D 792). In this method the weight of the specimen in air was first noted and then the specimen was immersed in water and its loss of weight in water was determined. The density is given by,

$$\text{Density} = \frac{\text{Weight of specimen in air}}{\text{Weight loss of specimen in water}}$$

k) Water absorption

Water absorption of the microcellular test pieces (5x5x5 mm) was carried out according to IS: 6664-1972 procedure. The test pieces were conditioned at a temperature of 27±2°C for at least 24 hours prior to testing. The weight of samples was accurately measured and immersed in distilled water for a period of 24 hours at 27±2°C. Then the samples were removed from water and wiped out using a blotting paper. Test pieces were accurately weighed within 2 minutes of the removal from distilled water. The water absorption was calculated as follows:

$$\text{Water absorption, \% by mass} = \frac{M_1 - M_o}{M_o} \times 100$$

where, M_1 and M_o are the mass in gm of the test piece after and before immersion in distilled water respectively.

l) Flexing resistance

Flexing resistance of the microcellular samples was determined from Ross flexing machine according to IS: 3400 (part XVI) - 1974 method. Test specimen of 25 mm in width, 150 mm in length and 6.3 mm in thickness was prepared from the microcellular sheet so that the longitudinal dimension was parallel with the direction of the grain. The test specimen should be pierced by using a piercing tool and the cut made by it should be parallel to the width of test specimen at a point 62 mm from the clamped end. The test specimens were clamped to the holder arm of the flexing machine in such a position that when the specimens were flexed at 90°, the cuts were at the centre point of the arc of flexure. Then the machine was started and run at a rate of 100±5 cycles per minute. The number of cycles was recorded by the use of counter. Frequent observations should be made, recording the number of cycles and the increase in cut length for the purpose of determining the rate of increase in cut length. Number of cycles for the initiation of the crack from the pierced hole should also be recorded.

The results from observation of two test specimens were averaged and reported as (i) the number of cycles for the initiation of crack and (ii) the number of cycles for each 100 percent increase in cut growth upto and including 600 percent.

m) Expansion ratio

The expansion ratio of the microcellular sheets was calculated according to the following formula:

$$\text{Expansion ratio} = \frac{\text{Area of the microcellular sheet}}{\text{Area of the mould}} \times 100$$

n) Thermogravimetric analysis

The thermogravimetric analysis of the samples was done using a Shimadzu-50 Thermogravimetric analyser. About 10 mgs of the sample was taken in a platinum crucible and the experiment was done in air atmosphere at a heating rate of 10°C/min. The weight loss of the sample was taken and then plotted against temperature.

5. Rheological evaluation

a) Using a Brabender Plasticorder

Brabender plasticorder (torque rheometer) has been widely used for measuring processibility of polymers, rheological properties of polymer melts, blending of polymers etc.[1,2] The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow under preselected conditions of shear and temperature.

The Brabender plasticorder model PL 3S was used in this study for evaluating the rheological behaviour of polymer blends. The nature of shear in the plasticorder is similar to that encountered in practical processing operations such as extrusion or milling. Blyler and Daane[3] observed that the power law relationship between rotor torque and rotor speed is reminiscent of the power law relationship often found between shear stress and shear rate and with a few assumptions derived the equation,

$$M = C(n)\ KS^n$$

where, M is the torque, n the power law index, C(n) a function weakly dependent on n, K a constant and S the rotor speed.

The slope of the plot of log M vs. log S gives the power law index. Also torque/rpm of the Brabender plasticorder represents viscosity and the activation energy for viscous flow can be measured from it if log (torque/rpm) is plotted against 1/T. The activation energy at constant rpm obtained by this procedure should correspond to the flow activation energy at constant shear rate.

b) Using a Capillary Rheometer

Capillary rheometer is widely used for determining the rheological properties of polymer melts[4] since they cover a shear rate range of interest in practical processing upto 10,000 S^{-1} with good rheological behaviour of polymers and polymer blends were measured using a capillary rheometer attached to Zwick UTM, model 1474. The extrusion assembly consists of a barrel made up of hardened steel, underneath the moving cross-head of the machine. A hardened steel plunger which was accurately ground to fit inside the barrel was held to the load cell with the help of a latch assembly. The barrel was thermally insulated from the rest of the machine to prevent heat losses due to conduction. The capillary was made up of tungsten carbide steel, having a length to diameter ratio (l_c/d_c) of 40 was used. The temperature inside the barrel and capillary could be varied between ambient to 400°C with an accuracy of 1°C. The barrel was electrically heated and accurately controlled. The cross-head speed could be varied in the range of 0.05-500 mm/min.

The barrel of the capillary rheometer was filled with 8 gm of the sample in the form of pieces. Then it was forced down to the capillary by a plunger attached to the moving cross-head. After a warming period of 5 minutes, the sample was extruded through the capillary at different speeds, viz., 0.05, 0.1, 0.2, 0.5, 10.0 and 20 mm/min. Forces corresponding to specific plunger speeds could be measured by the pressure transducer attached to the plunger and were recorded using a strip-chart recorder. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall by using the following equations,

$$\tau_w = \frac{F}{4A_p(l_c/d_c)}$$

$$\dot{\gamma}_{wa} = \frac{32Q}{\pi d_c^3}$$

$$\dot{\gamma}_w = \left(\frac{3n + 1}{4n}\right) \dot{\gamma}_{wa}$$

where F = force applied at a particular shear rate

A_p = cross sectional area of the plunger

l_c = length of the capillary

d_c = diameter of the capillary

Q = volumetric flow rate, calculated from the velocity of the plunger and

n = flow behaviour index defined by $\frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})}$ was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from experimental data

Melt elasticity measurements were done by calculating the extrudate swell ratio, d_e/d_c where d_e and d_c are the diameter of the extrudate and the die respectively. The high polymer liquids show pronounced elastic properties during flow. The normal stress built up in such materials can exceed shear stresses by a larger order of magnitude and cause losses of pressure at the inlet and outlet of the capillary results in extrudate swell and in extreme cases other undesirable flow phenomena.

Extrudate swelling of two phase blends is composed of two parts (i) matrix swell and (ii) form recovery of dispersed drops. Bogue and White[5] suggested the use of the parameter recoverable shear strain γ_R for describing and distinguishing the fluid elasticity of different viscoelastic fluids as a function of shear stress. γ_R can be calculated from the expression,

$$\gamma_R = 2\ [(d_e/d_c)^6 - 2]^{\frac{1}{2}}$$

γ_R increases with increasing shear stress.

The measurement of extrudate swell ratio is correlated with normal stress functions according to the

Tanners equation.[6]

$$\tau_1 - \tau_2 = 2\tau_w\,[2(d_e/d_c)^6 - 2]^{\frac{1}{2}}$$

In the present investigations the extrudate emerging from the capillary was collected at different shear rates taking care to avoid any deformation. The diameter of the extrudate was measured at several points after 24 h of extrusion using a binocular stereomicroscope. The average value of five readings was taken as the diameter of the extrudate (d_e) and the extrudate swell ratio was calculated.

The extrudate from capillary rheometer may also provide useful visual evidence of non-laminar flow or surface imperfections. The extrudate appearance may be used to assess the quality of flow behaviour during processing and also to obtain evidence of rupture behaviour and the shear rate at which flow instabilities commence.

The viscosity of a polymer decreases as the temperature increases over a small region of temperature. The temperature dependence of viscosity can be represented by the equation,

$$\eta = A \exp. E/RT$$

where A is a constant, E the activation energy, R the gas constant and T the absolute temperature. A plot of η against 1/T gives an Arrhenius plot.

c) Mooney viscosity measurements

The mooney viscosities of the raw rubbers were measured on the Mooney Viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc rotating (2 rev/min) in a cylindrical cavity set at 100°C and filled with rubber under test. In running a viscosity test, the sample was allowed to warm up for one minute after the platens were closed and the motor was then started. Reading after 4 minutes was reported as the Mooney viscosity of rubber [ML (1+4) at 100°C]. The procedure given in ASTM D 1646 (1981) was followed.

6. Morphology Studies

a) Using Optical Microscope

The morphology of rubber compounds was investigated using an optical microscope (Versamet-2 Union 7596). For optical microscopy compounds were dissolved in toluene and the solutions were cast into thin films. They were then cut into a convenient size and mounted on a microscope slide. Photographs were taken at a magnification of 66.

The morphology of microcellular sheets was done using a Nikon phase contrast microscope model Alphaphot-2. For this, a compression moulded test piece was cut into a convenient size and mounted on a microscope slide. Photographs were taken at a magnification of 50.

b) Using Scanning Electron Microscope (SEM)

SEM JEOL JSM 35C was used to investigate the morphology of fractured surfaces. In this technique an electron beam is scanned accross the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors and magnified. An image of the investigated microscopic region of the specimen is thus photographed.

If the specimen under investigation is not a good conductor, it should be coated with a thin layer of conducting material like platinum or gold. This is done by placing the specimen in a high vacuum evaporator and vaporising the conducting material held in a tungsten basket (vacuum dispersion).

The SEM observations reported in the present study were made on the fracture of tensile test and tear test specimens. The fractured surfaces of the samples were carefully cut without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made within 24 hours of coating. The gold coated samples were kept in a desiccator before the SEM observations were made.

7. Chemical Test Methods

a) Determination of chemical crosslink density

The concentration of chemical crosslinks was estimated from the equilibrium swelling data as follows. Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.20 gm weight were punched out from the central portion of the compression moulded sheet and allowed to swell in solvent (toluene). The swollen sample was taken out from the solvent after equilibrium swelling and weighed.

The deswollen weight of the samples was taken after drying the sample in an oven for 1 hour. The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding[7] from the following equation,

$$V_r = \frac{(D - FT)\,\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_o\,\rho_s^{-1}}$$

where,

T = weight of the test specimen

D = deswollen weight of the test specimen

F = weight fraction of insoluble components

A_o = weight of the absorbed solvent corrected for the swelling increment

ρ_γ = density of the rubber

and ρ_s = density of solvent.

The value of ρ_r and ρ_s taken were,

ρ_r (NR) = 0.921 g/cm^3

ρ_s(Toluene) = 0.886 g/cm^3

The crosslink density (½ Mc) was then determined from V_r using the Flory-Rehner equation[8,9],

$$\tfrac{1}{2}\,Mc = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{2\,\rho_r\,V_s\,(V_r)^{1/3}}$$

where V_s = molar volume of solvent (for toluene V_s = 106.2 cc/mol).

χ = parameter characteristic of interaction between rubber and solvent (for NR - Tolune, χ = 0.420).

b) Swelling index determination

Samples of about 0.5 gm weight were cut from the compounds and kept in solvent (toluene) at laboratory temperatures for 36 hours. The samples were taken out, quickly dried with a filter paper and weighed. The percentage change in weight was calculated and expressed as swelling index.

c) Free sulphur estimation

Free sulphur was estimated according to ASTM D 297-72A procedure. The principle of this method is based on the reaction of free sulphur with sodium sulphite to give sodium thiosulphate which is finally titrated against standard iodine solution.

$$S + Na_2SO_3 \rightarrow Na_2S_2O_3$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Two grams of finely divided sample was digested gently with 100 ml of aqueous sodium sulphite solution (50 gm/litre) for 16 hours in the presence of 5 ml of sodium stearate suspension in water (1 gm/litre) to assist wetting and approximately 1 gm of paraffin wax to avoid aerial oxidation. 100 ml of strontium chloride (5 gm/litre) solution was added to precipitate fatty acids and 10 ml of cadmium acetate solution (30 gm/litre) to remove accelerators. Rubber and the precipitate were separated by filtration. It was then washed twice with 75 ml portions of cadmium acetate solution (1.2 gm/litre). To the filtrate 10 ml of 40% formaldehyde solution was added with vigorous stirring and subsequently acidified with glacial acetic acid (10 ml). The solution was cooled below 15°C by adding enough crushed ice and titrated with 0.02 N iodine solution using starch as indicator.

A reagent blank was run and this value was subtracted from the titre value of the sample.

$$\text{Free sulphur \%} = \frac{(x-y) \times N \times 0.032 \times 100}{W}$$

where, x is the volume of iodine solution required for titration of the sample in ml, y is the volume of iodine solution required for titration of the blank in ml, N is the normality of iodine solution and W is the weight of the sample taken.

d) Acetone extract determination

The procedure adopted here is according to BS 1673 Part 2, 1967. About 1 gm of the sample of 1.6 mm thickness was weighed to the nearest milligram and wrapped in a filter paper in such a manner that the pieces were separated from each other. The test pieces were kept in the Soxhlet type apparatus and sufficient acetone was poured to fill the extraction cup. The apparatus was assembled and the extraction vessel was heated continuously on a thermostatically controlled water bath for not less than 12 hours and not more than 16 hours, the rate of evaporation being controlled to give 5 to 8 extractions per hour. After the extraction period was over, the combined acetone from the extraction flask and cup was recovered by distillation. After most of the acetone was recovered, the contents of the flask was dried in an oven at 70°C for about 1 hour to remove the last traces of acetone. The flask was cooled to room temperature in a desiccator and weighed. Heating, cooling and weighing were repeated until concordant values were obtained.

$$\text{Acetone extract \%} = \frac{B-C}{A} \times 100$$

where A = weight of the sample taken in gm

B = weight of extraction flask and extracted residue in gm

and C = weight of empty flask in gm.

e) Volatile matter determination

Volatile matter of the samples was determined according to IS specifications for analysis of dry rubber. About 30 gm of the sample was cut and wrapped air tight in a polyethylene bag. Then 10 gm was weighed from this and passed through the mill rolls set 0.5 mm apart and a friction ratio 1:1.4. Then the test portions were placed on an aluminium tray and kept inside the oven at 100°C for 4 hours. At the end of heating each test portion was inserted in a polyethylene bag and clipped quickly. The test pieces were allowed to cool for half an hour and then removed from the bag and weighed.

$$\text{Volatile matter (\%)} = \frac{A-B}{A} \times 100$$

where A = weight of test piece in gm and

B = weight of test piece after drying in gm.

f) Ash content determination

Ash content was determined according to ASTM D 1278 68a, 1969. About 5 gm of the sample was weighed, wrapped in an ashless filter paper and placed in a silica crucible which had been previously ignited for 15 minutes and weighed. Then the crucible was introduced into a muffle furnace at 550°C for 4-5 hours heating. When ashing was completed, the crucible was allowed to cool in a desiccator and then weighed.

$$\text{Ash content (\%)} = \frac{A-B}{C} \times 100$$

where A = weight of crucible plus ash in gm
B = weight of empty crucible in gm and
C = weight of sample taken in gm.

g) Rubber hydrocarbon content determination

The rubber hydrocarbon content was calculated using BS 903: Part B 11: 1960 method. It was determined by difference after the other constituents have been determined.

Rubber hydrocarbon content (%) = 100 - (Acetone extract + Volatile matter + Ash content).

REFERENCES

1. Z.Bartha, P.Erdos and J.Matis, Int. Polym. Sci. Technol., 10(6), 50 (1983).

2. J.E.Goodrich and R.S.Porter, Polym. Eng. Sci., **7**, 45 (1967).

3. L.L.Blyler and Daane, Polym. Eng. Sci., **7**, 178 (1967).

4. D.J.Williams, Polymer Science and Engineering, Prentice-Hall Inc.,(1971).

5. C.D.Han, Rheology in polymer processing, Academic Press, New York, chapter 5 (1976).

6. R.I.Tanner, J. Polym. Sci., **A28**, 2067 (1970).

7. B.Ellis and G.N.Welding, Techniques of Polymer Science, Soc. Chem. Ind., London, 46 (1964).

8. P.J.Flory and J.Rehner, J. Chem. Phys.,11, 512 (1943).

9. P.J.Flory and J.Rehner, J. Chem. Phys.,11, 521 (1943).

Chapter 3

Part I: DEVELOPMENT OF LATEX RECLAIM FROM WASTE LATEX PRODUCTS

The recycling of scrap and used rubber has been practised by the rubber industry for many years, almost entirely by conversion to reclaimed rubber.[1-8] Reclaimed rubber is the product obtained by chemical and/or thermal treatment of waste rubber products. It can not however, be considered simply as devulcanized rubber, since some main chain breakdown and other side reactions probably occur. It has been reported that thiols and amines can open sulphur crosslinks and can act as reagents for promoting devulcanization. But they are not commercially used due to their high cost and bad odour.

Due to the unstable nature of the latex compound and the strict specifications in the quality of latex products such as examination gloves and condoms, the rejection in the latex industry comes to as high as 10 to 15% of the rubber consumed. These rejects have created a major disposal problem for the rubber industry. However, these rejects represent a source of high quality rubber for reclamation and reuse. Two methods for reclaiming latex products are reported in the literature, one developed by the Rubber Research Institute of Malaysia[9] and the other by the Rubber Research Institute of India.[10] But the latex reclaim in both these cases does not possess the properties expected of its high quality. Obviously, the reclamation process degrades the rubber to a great extent. The primary aim of this work has been to develop a process for reclaiming latex products waste that does not adversely affect the quality of the rubber.

EXPERIMENTAL

In the first process, the waste latex products such as examination gloves and condoms were passed through a laboratory two roll mill with a nip of 1 mm at room temperature for 10 minutes so that the material undergoes mechanical breakdown. Further plastication was achieved using a reclaiming agent and a process oil while applying some mechanical shear. Renacit-VII(pentachlorothiophenol, 1 gm/100 gm sample) was added and the homogenization was done for another 3 minutes. Aromatic oil (5 ml/100 gm sample) was then added and after another 3 minutes of milling, the rubber was removed from the mill. The properties of the reclaimed rubber such as mooney viscosity and initial plasticity were measured.

In the second process, the above method was modified by increasing the number of passes through the mill and the initial milling time was increased to 15 minutes. Then Renacit-VII and aromatic oil were added according to the procedure mentioned above. The mooney viscosity, initial plasticity (p_o) and plasticity retention index (PRI) of this sample were evaluated.

As the third trial, the sample was allowed to swell in commercial toluene for 24 hours and then ground to fine powder. After removing the solvent, the mooney viscosity and initial plasticity were measured. Inorder to reduce the wastage of solvent, the latex products were dipped in commercial toluene and then immediately taken out from the solvent. The excess toluene was allowed to drain off from the sample. This was collected and reused. About 10 ml of toluene could wet 100 gm of latex product. The samples were then kept in a closed container for different times, viz., 8 hours, 16 hours, 24 hours. In all the above cases, after the prescribed time, 100gm of the sample was taken and passed through a laboratory two roll mill with 1 mm nip at room temperature for 3 minutes. The fine rubber particles were made into a compact mass on the mill and 0.5 gm of Renacit-VII was added. After 3 minutes of homogenization, 3 ml of aromatic oil was added and the milling was continued for another 2 minutes. The properties of the reclaimed rubber like mooney viscosity, initial plasticity and plasticity retention index at different swelling time were measured. The properties like volatile matter, acetone extract, ash content, free sulphur content and rubber hydrocarbon content were also determined according to relevant ASTM standards. The thermogravimetric analysis of the latex reclaim and the latex products were made using a TGA-50 Shimadzu thermogravimetric analyser.

RESULTS AND DISCUSSION

Table 3.1 shows the mooney viscosity and the initial plasticity values of the latex reclaim obtained from the first process. It is found that mooney viscosity and initial plasticity are high. This may be due to the inadequate chain breakdown. The mooney viscosity, initial plasticity and plasticity retention index values of the reclaimed rubber obtained by the second process is given in Table 3.2. From the mooney viscosity and initial plasticity values it is clear that the material has not attained adequate plasticity. Table 3.3 shows the mooney viscosity and initial plasticity of the latex reclaim obtained from the third process using different swelling times in toluene. It is found that the lowest values of

Table 3.1: Properties of latex reclaim (Process I)

Properties of latex reclaim	
Mooney viscosity, ML(1+4) 100°C	124
Initial plasticity, P_o	68

Table 3.2: Properties of latex reclaim (Process II)

Properties of latex reclaim	
Mooney viscosity, ML (1+4) 100°C	115
Initial plasticity, P_o	63
Plasticity retention index, PRI	32

Table 3.3: Properties of latex reclaim (Process III)

Swelling time	Properties of latex reclaim	
	Mooney viscosity, ML(1+4) 100°C	Initial plasticity, P_o
8	78	54
16	68	48
24	54	40

Table 3.4: Properties of latex reclaim (Process III, 24 hours swelling time)

Properties of latex reclaim	
Volatile matter, % by mass	0.12
Acetone extract, % by mass	4.86
Ash content, % by mass	3.98
Rubber hydrocarbon content, % by mass	91.04
Free sulphur content, % by mass	0.14
Mooney viscosity, ML(1+4) 100°C	54
Initial plasticity, P_o	40
Plasticity retention index, PRI	58

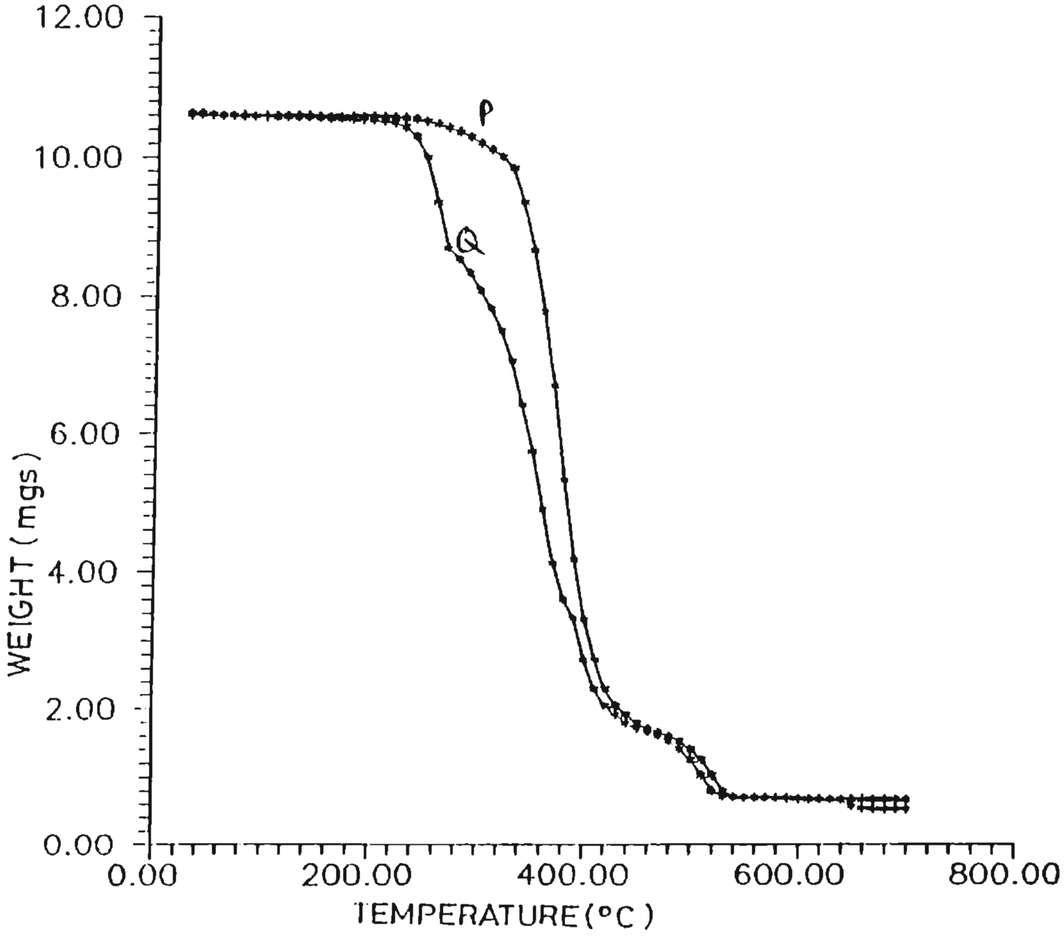

Fig.3.1: TGA graph of waste latex product (P) and latex reclaim from the final Process (Q).

mooney viscosity and initial plasticity values are obtained for the samples kept for 24 hours in the closed container. Since these values are in the processible range, it can be easily incorporated into natural or synthetic rubber. The volatile matter, ash content, acetone extract and plasticity retention index values of the reclaim shown in Table 3.4 are also comparable to those of pure natural rubber.

Fig. 3.1 shows the TGA graph of the latex reclaim and the waste latex product. From this figure, it is clear that there is not much change in the temperature sensitivity of the latex reclaim compared with the original latex product. Compared to latex product, the weight loss of the reclaim sample occurs at a lower temperature. This shows that considerable amount of mechanical breakdown has occured in the latex sample during the reclaiming process.

CONCLUSION

The study shows that the method of reclaiming latex products outlined in the chapter is a promising one for generating good quality rubber.

Part II: STUDIES ON NATURAL RUBBER/LATEX RECLAIM GUM COMPOUNDS

The utilisation of dry rubber reclaim in rubber industry is widely practised to reduce the compound cost and to conserve raw materials and energy.[11-18] However, due to the deterioration in technical properties with the addition of reclaimed rubber the use of dry rubber reclaim constitutes only a very low percentage of total rubber consumption.[19-26]

In contrast to dry rubber reclaim, latex reclaim contains rubber hydrocarbon of very high quality and hence could be added in higher percentages to raw rubber. This study proposes to find the effect of adding latex reclaim in various percentages in gum natural rubber compounds. The vulcanization and physical properties of raw natural rubber, latex reclaim and their blends were studied and compared along with their morphology.

Fractography was done using a scanning electron microscope (SEM). The processing characteristics of the natural rubber, latex reclaim and their blends were studied using a Brabender plasticorder.

EXPERIMENTAL

Natural rubber was masticated on a laboratory mixing mill and the latex reclaim in the form of a sheet was added at different percentages and the blends were compounded as per the formulations given in Table 3.5. Natural rubber and latex reclaim alone were also compounded on a mixing mill as per formulations given in Table 3.5.

The optimum cure time of the compounds was determined on a Goettfert Elastograph. The compounds were then vulcanized upto their respective optimum cure times in an electrically heated hydraulic press at 150°C. The tensile and tear properties were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/min according to ASTM standards. Samples for compression set and hardness were moulded and tested as per relevant ASTM standards. The ageing resistance of the vulcanizates was studied after ageing the samples at 100°C for 24 and 48 hours in a laboratory air oven.

The average chemical crosslink density of the vulcanizates was estimated from equilibrium swelling data.[27] The crosslink density ½ Mc was determined from V_r using the Flory-Rehner equation.[28,29]

Table 3.5: Formulations and vulcanizate properties of NR/LR blends

Materials	A	B	C	D	E	F	G	H	I	J	K
NR	100	90	80	70	60	50	40	30	20	10	0
Latex reclaim	0	10	20	30	40	50	60	70	80	90	100
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
MBTS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Accinox ZC	1	1	1	1	1	1	1	1	1	1	1
<u>Cure Characteristics</u>											
T_{10} (Scorch time in minutes)	2.6	2.5	2.5	2.4	2.4	2.3	2.2	1.8	1.7	1.4	0.9
T_{90} (Optimum cure time in minutes)	4.9	4.8	3.9	3.7	3.6	3.2	2.9	2.7	2.5	2.2	1.8
Maximum torque (Nm)	0.21	0.22	0.24	0.26	0.28	0.30	0.32	0.34	0.36	0.38	0.41
<u>Vulcanizate Properties</u>											
Crosslink density (gm mol/cc) $\times 10^{-5}$	4.56	4.73	4.93	5.19	5.35	5.57	5.76	5.93	6.12	6.26	6.39
Compression set (%)	26.19	25.78	25.26	24.26	24.13	23.92	23.54	22.98	22.02	21.63	19.78
Hardness (Shore A)	40	44	46	48	50	52	54	56	58	60	61

The morphology of gum natural rubber compound, its blends with latex reclaim was investigated using an optical microscope.

The SEM studies of the tear tracture (NR, 50/50 NR/LR & LR) and tensile fracture (original and aged samples of NR, 90/10, 50/50 & 20/80 NR/LR and LR) surfaces were made using a SEM model JEOL JSM 35C.

Processability of the gum natural rubber compound, its blends with latex reclaim was evaluated at different temperatures (80, 100 and 120°C) and at different shear rates (20, 40 and 60 rpms) on a Brabender Plasticorder.

RESULTS AND DISCUSSION

Fig. 3.2 shows the cure characteristics of the gum natural rubber compound, 50/50 natural rubber/latex reclaim blend and latex reclaim alone. The optimum cure time (T_{90}), scorch time (T_{10}) and the maximum torque obtained from the cure curves are shown in Table 3.5. There is a gradual reduction in the cure time and scorch time with the addition of latex reclaim. This is possibly due to the presence of crosslink precursors and/or unreacted curatives

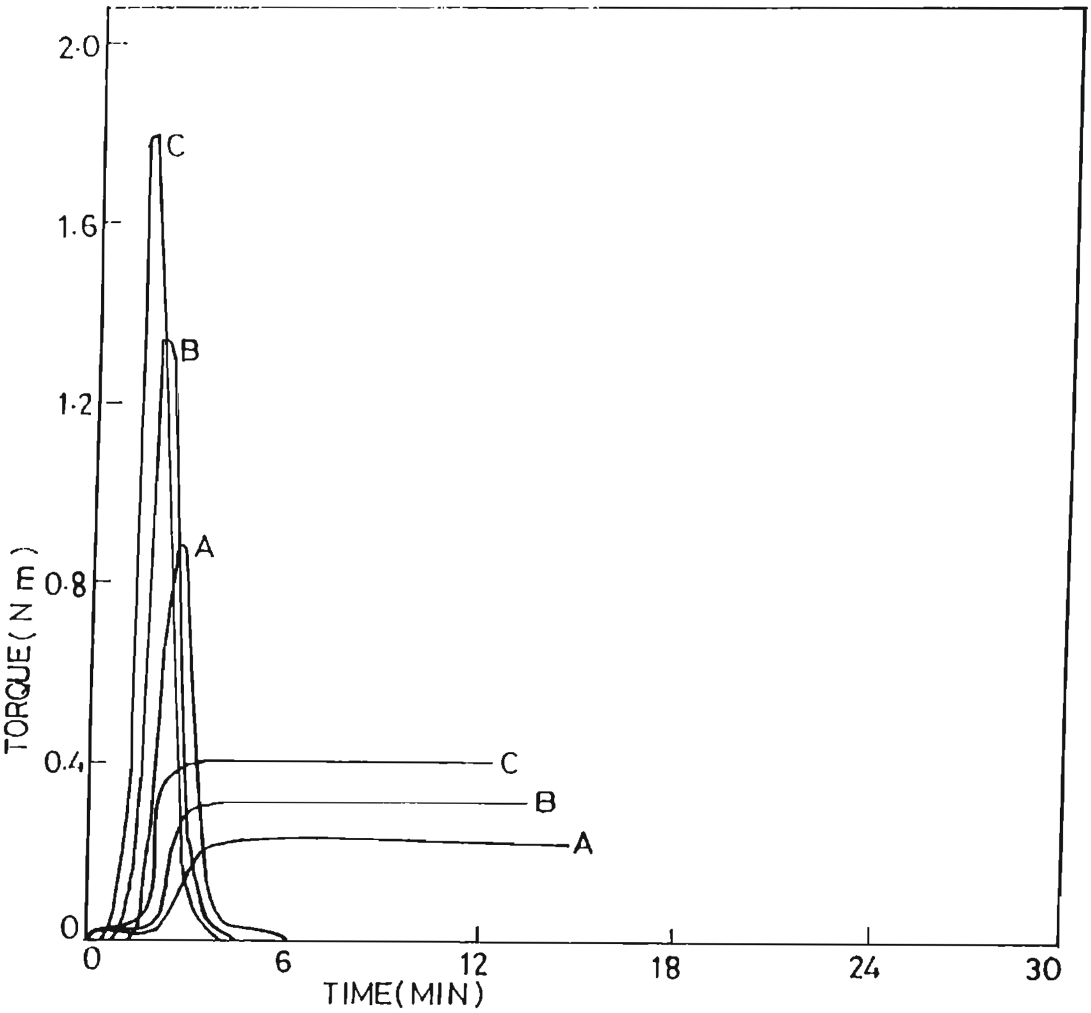

FIG.3.2: Cure curves of gum compounds

A. NR; B. NR/LR (50/50); C. LR

in the latex reclaim.[20] The maximum torque is found to increase with increasing percentage of latex reclaim. This may be attributed to the higher crosslink density in the blends compared to gum natural rubber vulcanizate. The 100% latex reclaim shows the highest value of maximum torque.

The average crosslink density of the vulcanizates is shown in Table 3.5. It shows that the crosslink density increases with the amount of latex reclaim. This confirms the presence of crosslink precursors and/or unreacted curatives in the latex reclaim.

Fig. 3.3 shows the variation in tensile strength with the addition of latex reclaim. The tensile strength shows only marginal changes upto about 50 per cent reclaim. This shows that the quality of rubber hydrocarbon in the latex reclaim is good and there is good bonding between reclaim and the virgin rubber. The ageing resistance of the blends is also found to be comparable to that of the gum natural rubber vulcanizate.

Fig. 3.4 shows the variation in tear strength of the blends with the percentage of latex reclaim. The

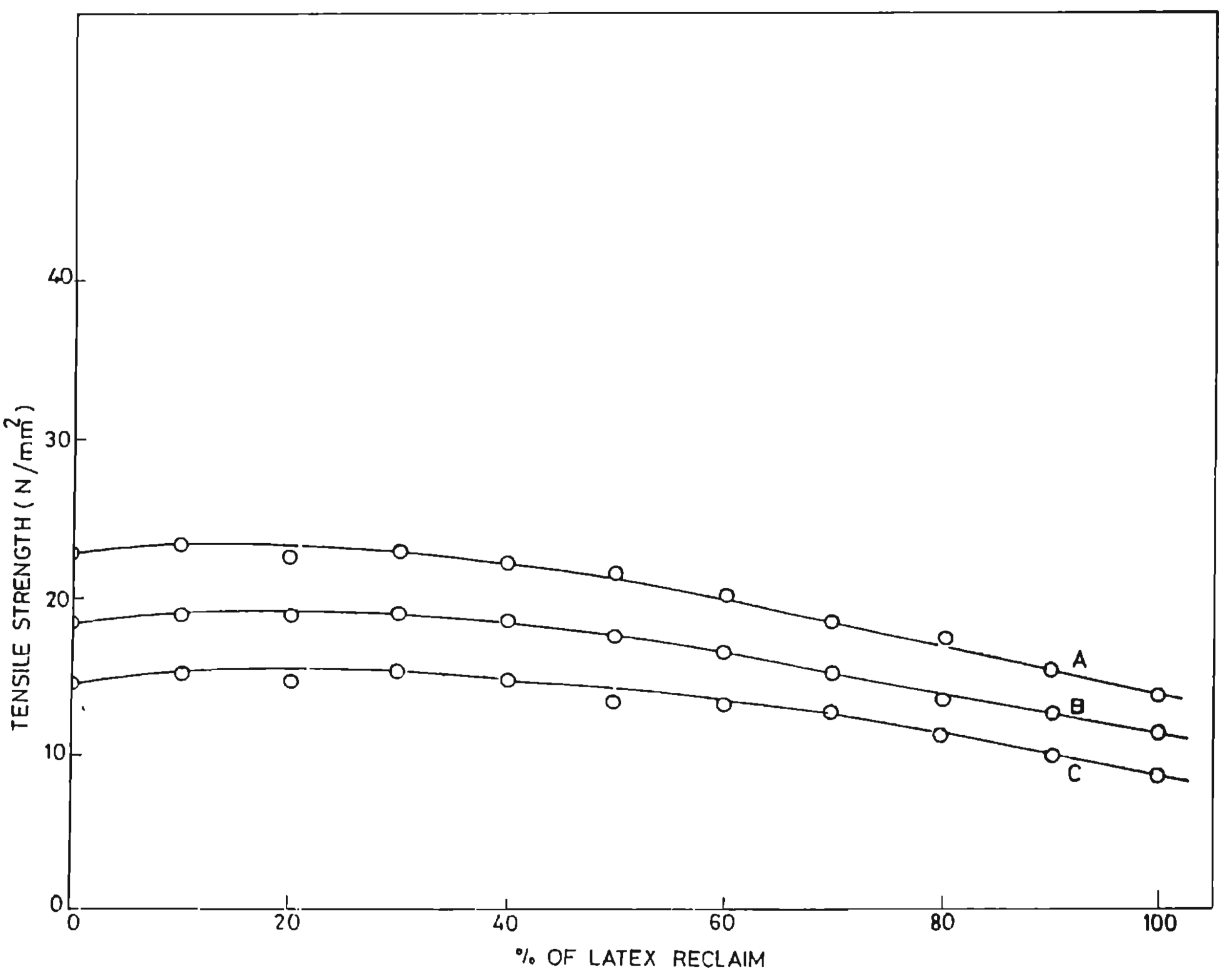

FIG.3.3: Variation in tensile strength with latex reclaim of NR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

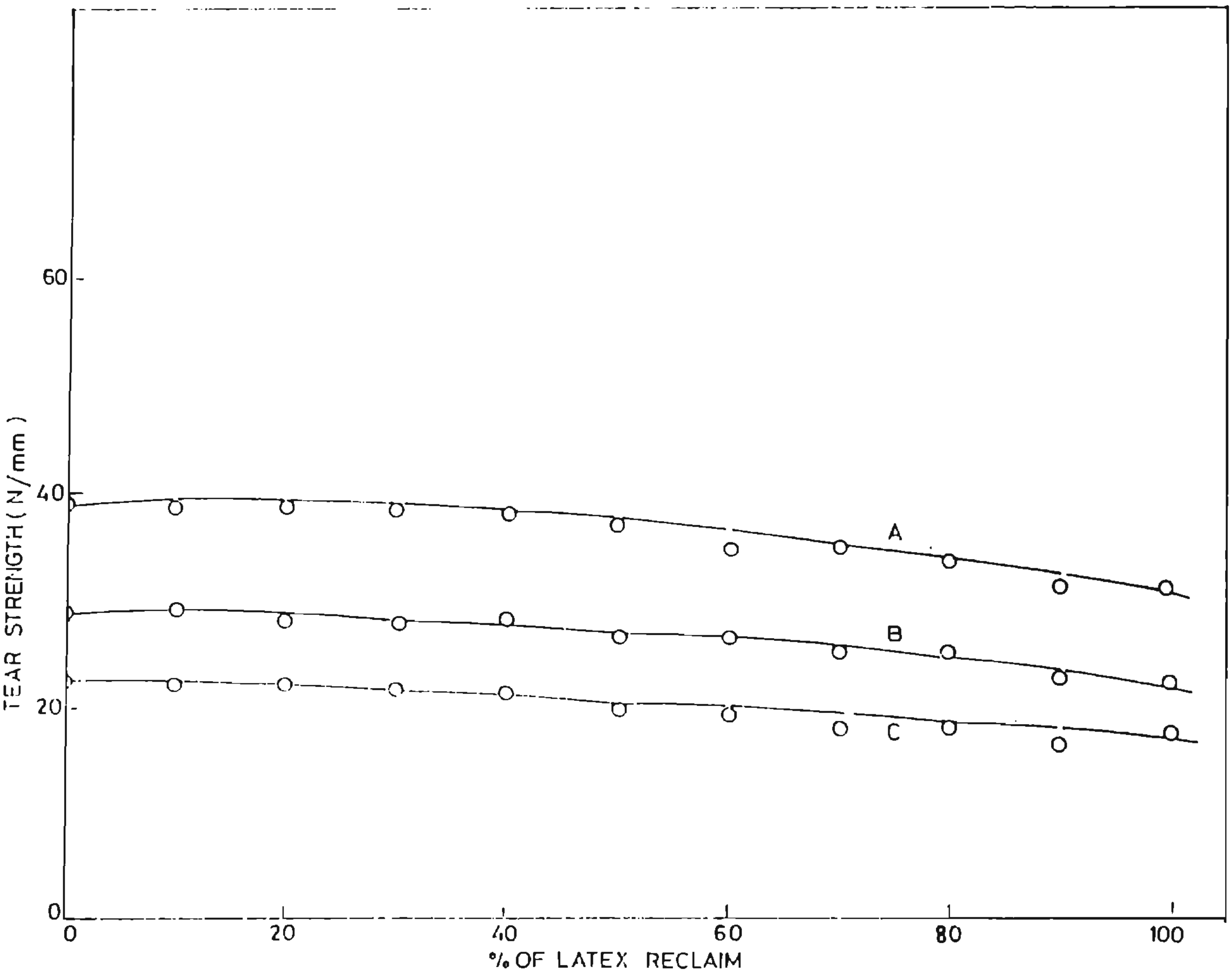

FIG.3.4: Variation in tear strength with latex reclaim of NR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

behaviour is similar to that of tensile strength showing only marginal decrease upto about 50 per cent reclaim. The ageing resistance of the samples containing latex reclaim is also comparable to that of natural rubber gum vulcanizate. This again shows the high quality of hydrocarbon derived from the latex reclaim and its good bonding with natural rubber.

Fig. 3.5 shows the variation in elongation at break with the addition of latex reclaim and its retention after ageing. The significant reduction in elongation at break may be due to the increased crosslink density in the blends as well as due to the reduction in molecular weight resulting from the reclamation process.

Fig. 3.6 shows the variation in modulus with the amount of latex reclaim and the retention in modulus with ageing. There was a gradual increase in modulus with the addition of latex reclaim. This may be attributed to the increased amount of crosslink density in the blends and the reduction in elongation of the vulcanizates containing latex reclaim.

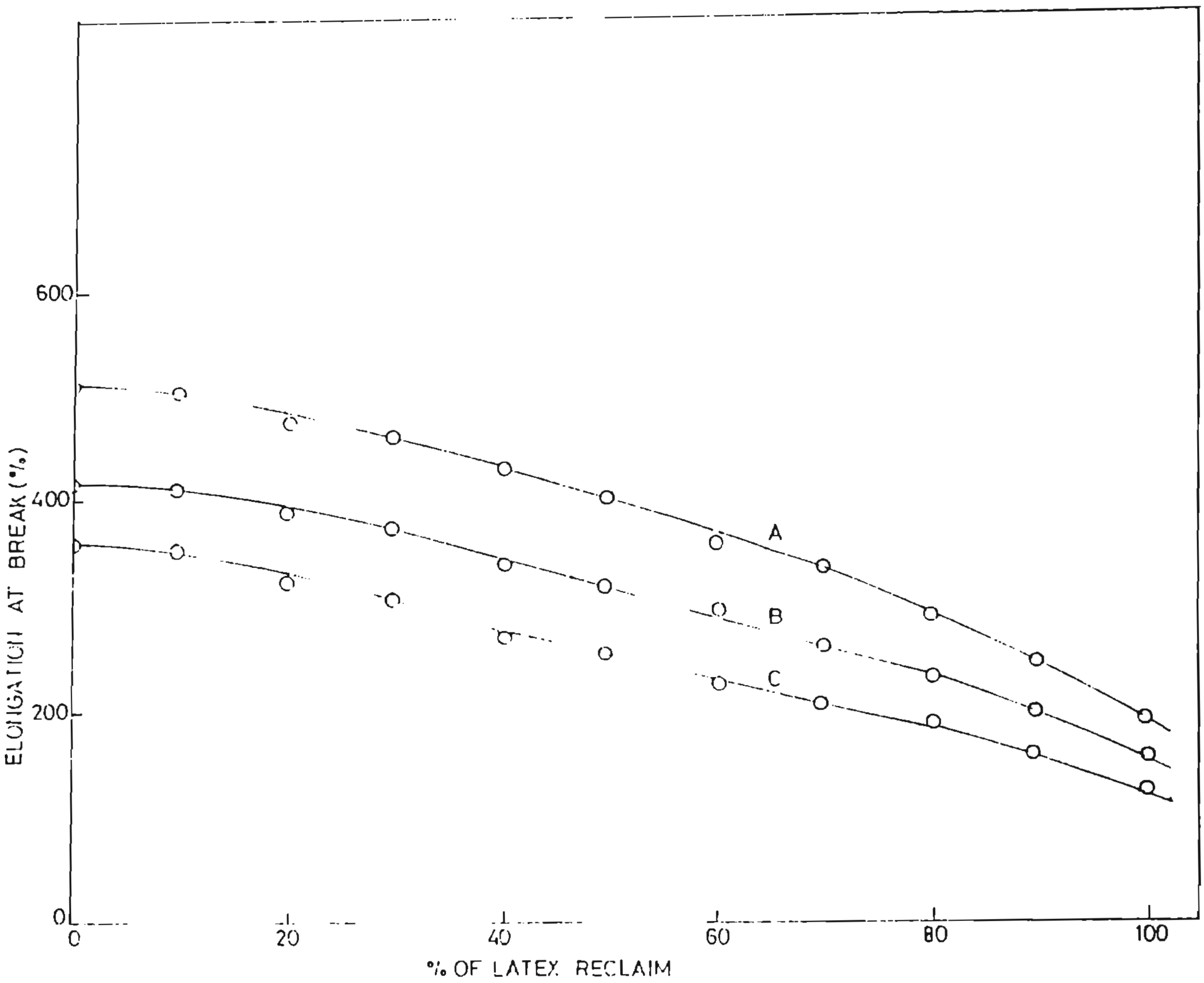

FIG.3.5: Variation in elongation at break with latex reclaim of NR/LR blends
A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

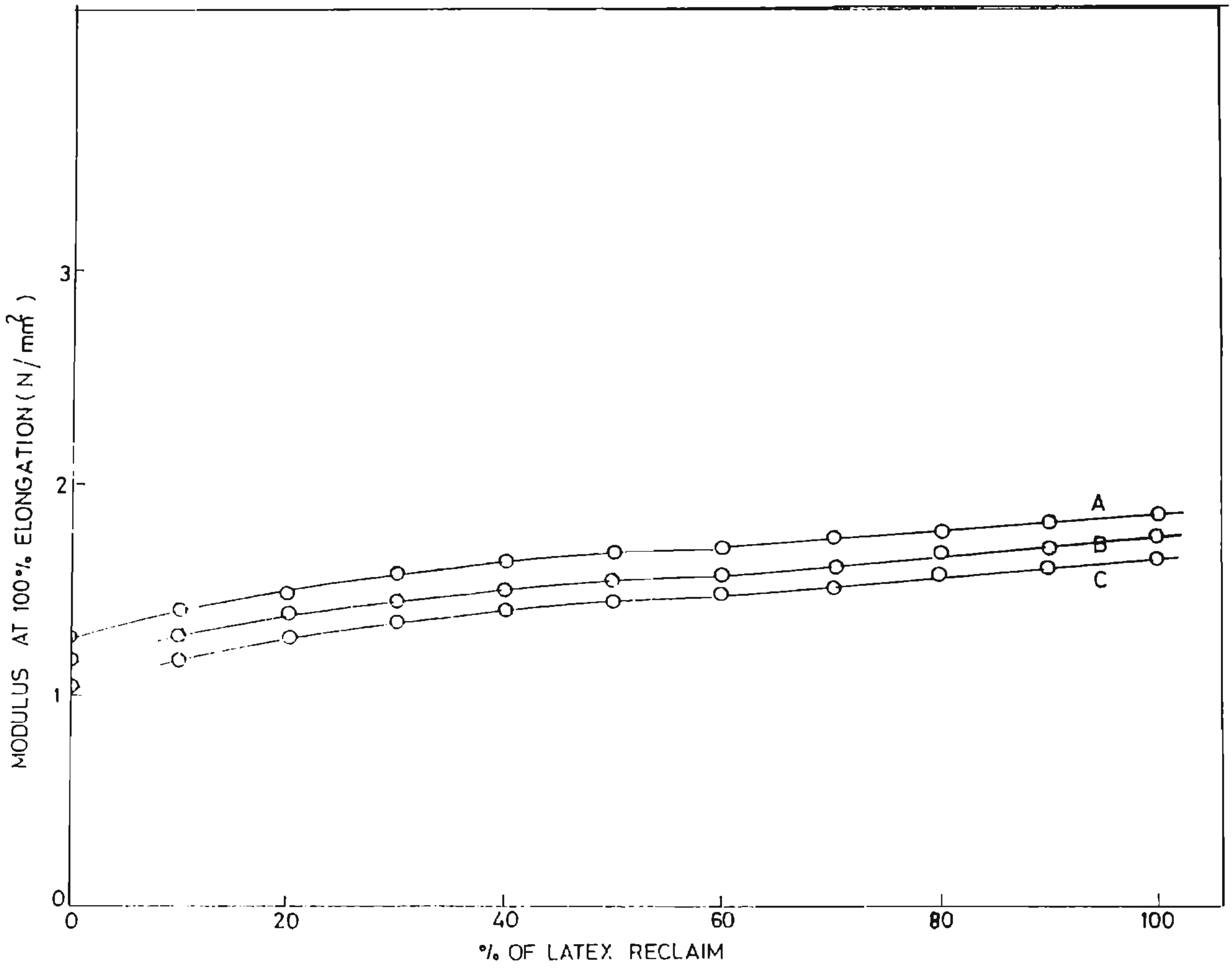

FIG.3.6: Variation in modulus with latex reclaim of NR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

The hardness is found to significantly increase with increase in the amount of latex reclaim as expected (Table 3.5). The compression set is found to decrease with the addition of latex reclaim which further confirms the increased crosslink density in the blends.

Figs. 3.7-3.13 show the optical photographs of natural rubber gum compound, its blends with latex reclaim (90/10, 70/30, 50/50, 30/70 & 10/90) and latex reclaim compound. These show that when the percentage of latex reclaim in the blend is up to about 50 percent, the particles are uniformly distributed in the compound and forms a part of the natural rubber phase. When the percentage of latex reclaim in the blend is above 50 percent the particle of the reclaim are found to be of larger size. Even at this high percentage of latex reclaim, natural rubber form the continuous phase and the latex reclaim existing as larger sized particles. This obviously explains the deterioration in mechanical properties at higher concentrations of reclaim.

Fig.3.14 shows the SEM photograph of the tear fracture surface of gum natural rubber vulcanizate. It shows that the tear paths are short with a smooth torn surface. Fig.3.15 shows the tear fracture surface of 50/50 natural rubber/latex reclaim gum vulcanizate. It shows that the tear proceeds in a short stick-slip manner. This ensures good tear strength properties.[30] It may be attributed to the higher total crosslink density of the vulcanizate. Fig.3.16 shows the tear fracture surface of gum latex reclaim vulcanizate. In this figure, the tear proceeds in a long stick-slip manner and gives an irregular torn surface when compared with gum natural rubber vulcanizate. This results in lower tear strength when compared with gum natural rubber vulcanizate (Fig.3.4).

Fig.3.17 shows the tensile fracture surface of gum natural rubber vulcanizate. It shows that bright spots are agglomerated along the fracture paths. This may be due to crystalline regions formed on stretching of the gum vulcanizate.[31] Occurrence of crystalline regions in certain distinct planes seems to be the most characteristic feature of the tensile ruptured surfaces of a natural rubber gum vulcanizate.[32] Addition of latex reclaim in gum natural rubber compounds (Figs.3.19 and 3.21) also show spots with highly charged agglomerates and the crystallinity is not continuous. It is also noted that the shear lines are less on the fracture surface of the vulcanizates containing upto about 50 percent latex reclaim. This explains the marginal reduction in tensile strength of the vulcanizate up to the addition of 50 weight percent latex reclaim. Figs.3.23 and 3.25 show the tensile fracture surface of 20/80 natural rubber/latex reclaim and latex reclaim vulcanizates. It shows more shear lines and hence is slightly different from the fracture surface of gum natural rubber vulcanizate. This results in lower tensile strength of the samples when compared with natural rubber vulcanizate.

Fig.3.18 shows the aged tensile fracture surface of gum natural rubber vulcanizate. It shows more tiny cracks on the fracture surface when compared with original sample. This results in lower tensile strength of the aged samples. Figs.3.20 and 3.22 show the aged tensile fracture surface of 90/10 and 50/50 natural rubber/latex reclaim vulcanizates. The cracks on the fracture surface are comparable with the aged natural rubber gum vulcanizate. This behaviour results in marginal change in tensile properties on the addition of about fifty weight percent of latex reclaim in aged natural rubber vulcanizate. Figs.3.24 and 3.26 show the aged tensile fracture surface of 20/80 natural rubber/latex reclaim and latex reclaim

FIG.3.7: NR

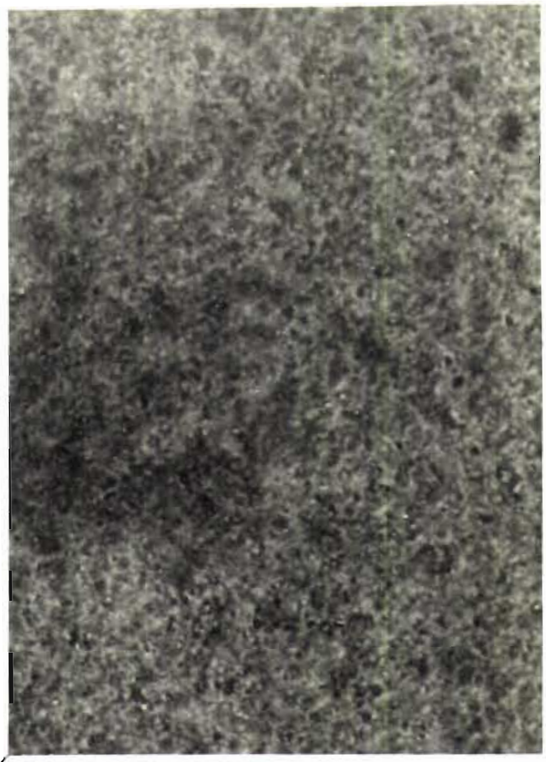

FIG.3.8: NR/LR (90/10)

Optical microscope photographs of gum compounds

FIG.3.9: NR/LR (70/30)

FIG.3.10: NR/LR (50/50)

Optical microscope photographs of gum compounds

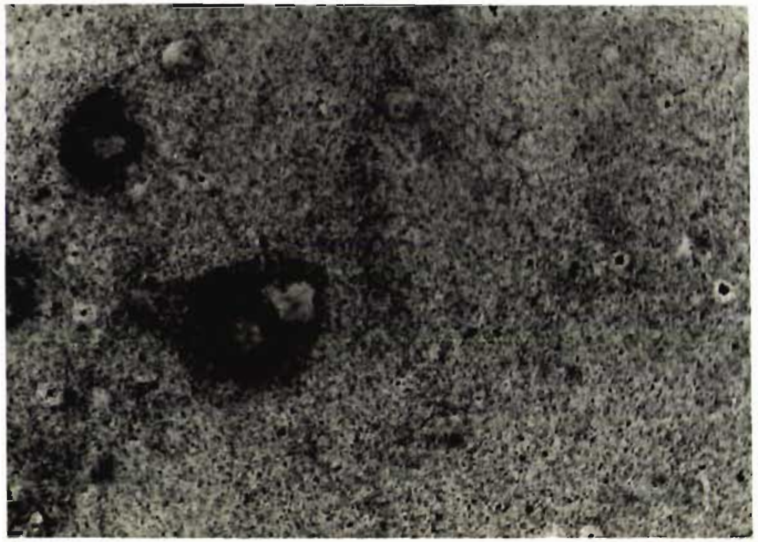

FIG.3.11: NR/LR (30/70)

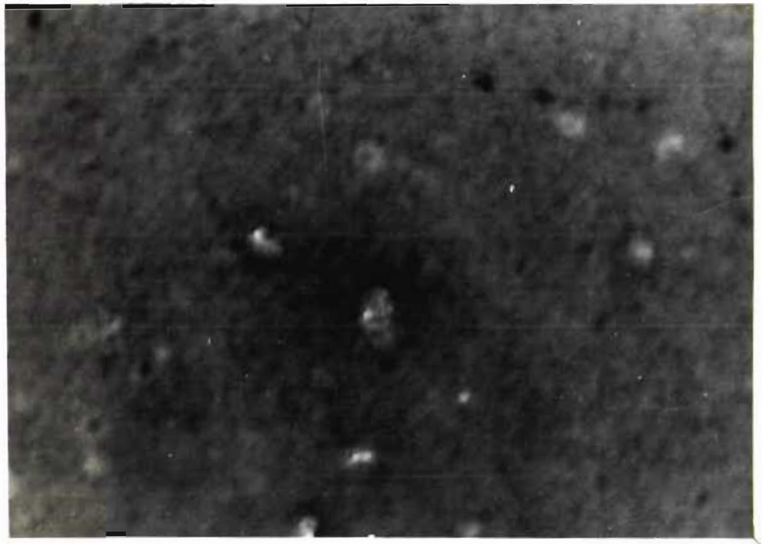

FIG.3.12: NR/LR (10/90)

Optical microscope photographs of gum compounds

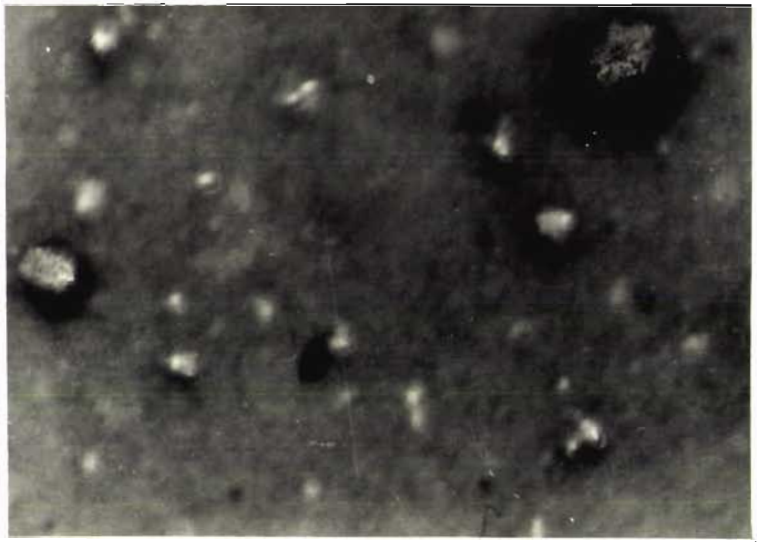

FIG.3.13: Optical microscope photograph of LR compound

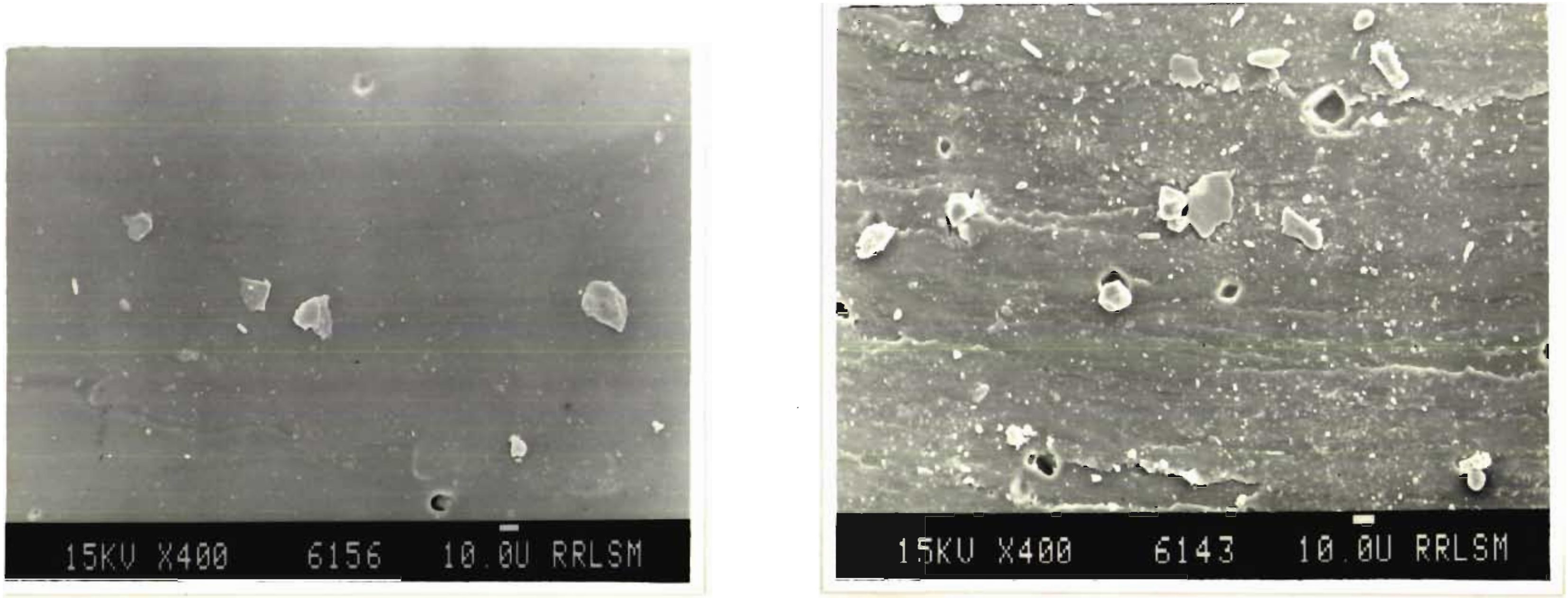

FIG.3.14: NR

FIG.3.15: NR/LR (50/50)

SEM photographs of the tear fracture surface of gum vulcanizates

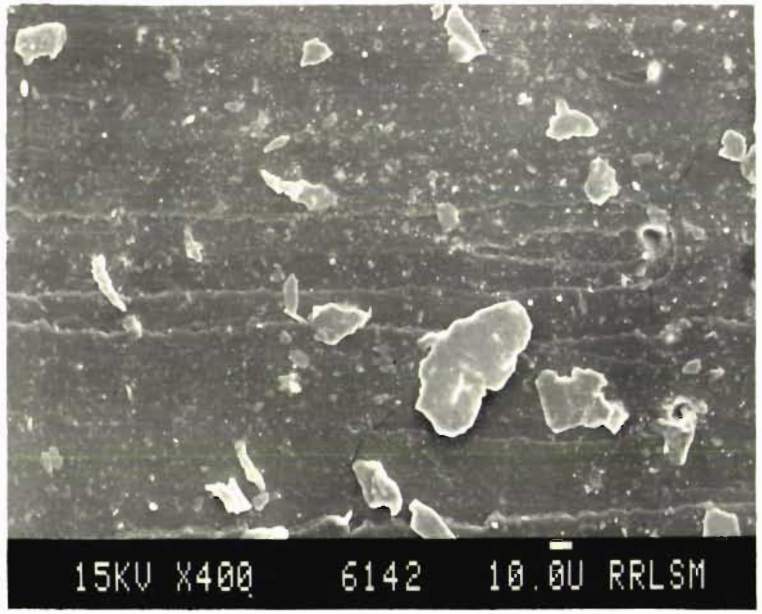

FIG.3.16: SEM photograph of the tear fracture surface of gum LR vulcanizate

FIG.3.17: ORIGINAL

FIG.3.18: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of gum NR vulcanizate

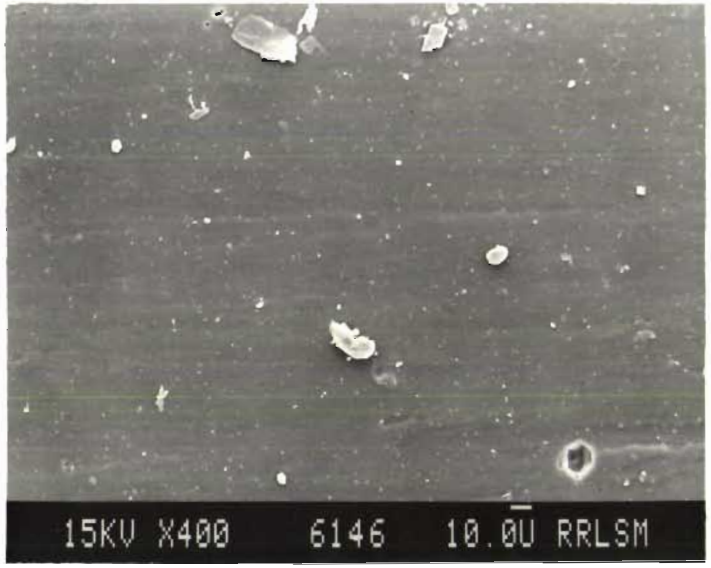

FIG.3.19: ORIGINAL

FIG.3.20: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of NR/LR (90/10) vulcanizate

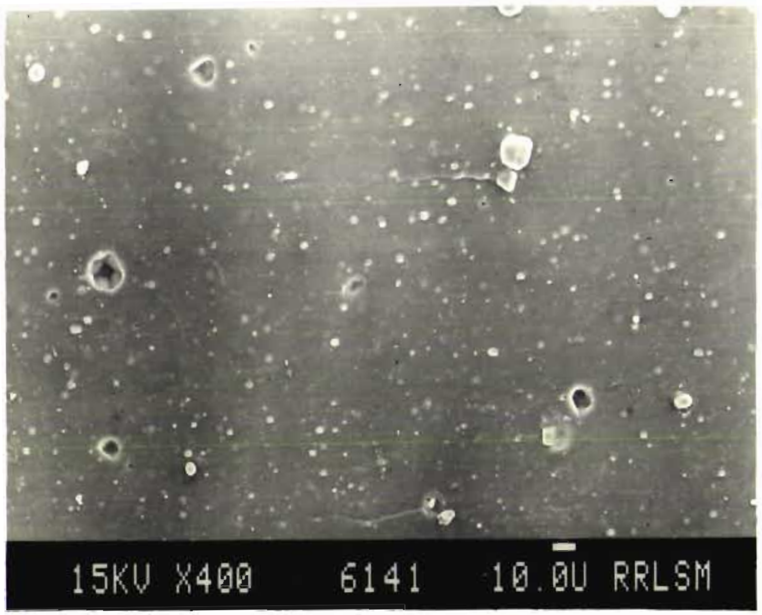

FIG.3.21: ORIGINAL

FIG.3.22: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of NR/LR (50/50) vulcanizate

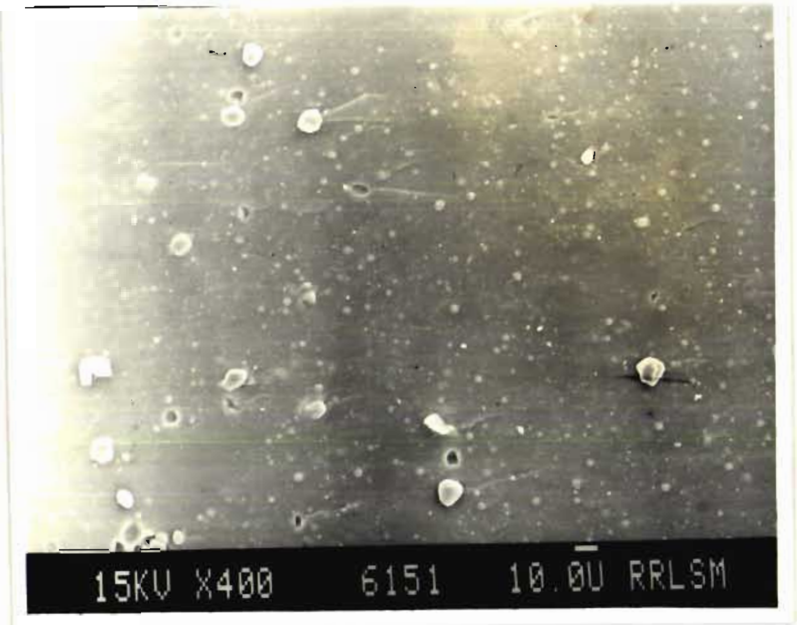

FIG.3.23: ORIGINAL

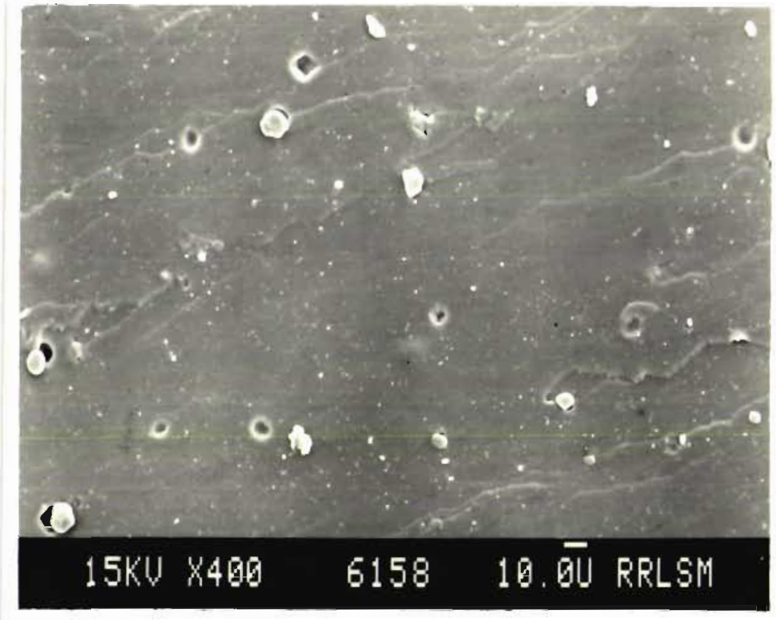

FIG.3.24: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of NR/LR (20/80) vulcanizate

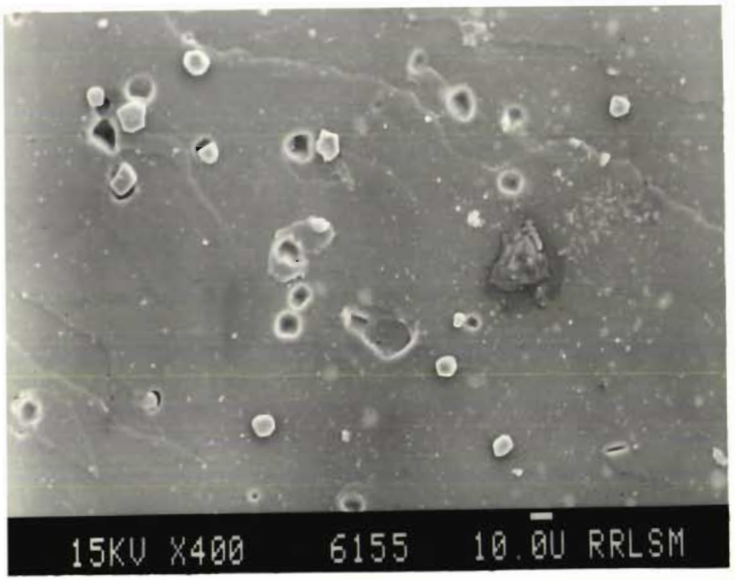

FIG.3.25: ORIGINAL

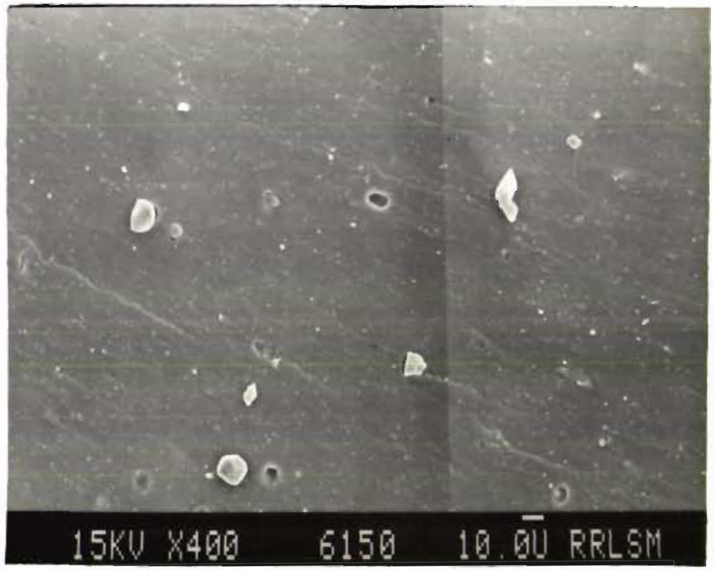

FIG.3.26: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of gum LR vulcanizate vulcanizates. It shows more cracks on the fracture surface and hence is slightly different as in the case of unaged samples when compared with gum natural rubber vulcanizate. This results in lower tensile strength of the aged samples when compared with that of gum natural rubber vulcanizate.

In all the aged samples the flow of the matrix is more when compared with original samples. It is also noted that there is no loose aggregates or separation of the particles from the original as well as from the aged tensile fracture surfaces.

The processability studies of natural rubber gum compound, its blends with latex reclaim (80/20, 60/40, 40/60 and 20/80) and latex reclaim compound were done at different temperatures (80, 100 and 120°C) and at different shear rates (20, 40 and 60 rpm). Fig.3.27 illustrates the effect of viscosity (torque/rpm) of the compounds with shear rate at a temperature of 80°C. It shows that the viscosity of the natural rubber compound decreases with the addition of latex reclaim.

Fig.3.28 shows the variation of torque with shear rate. The power law index values were calculated as the

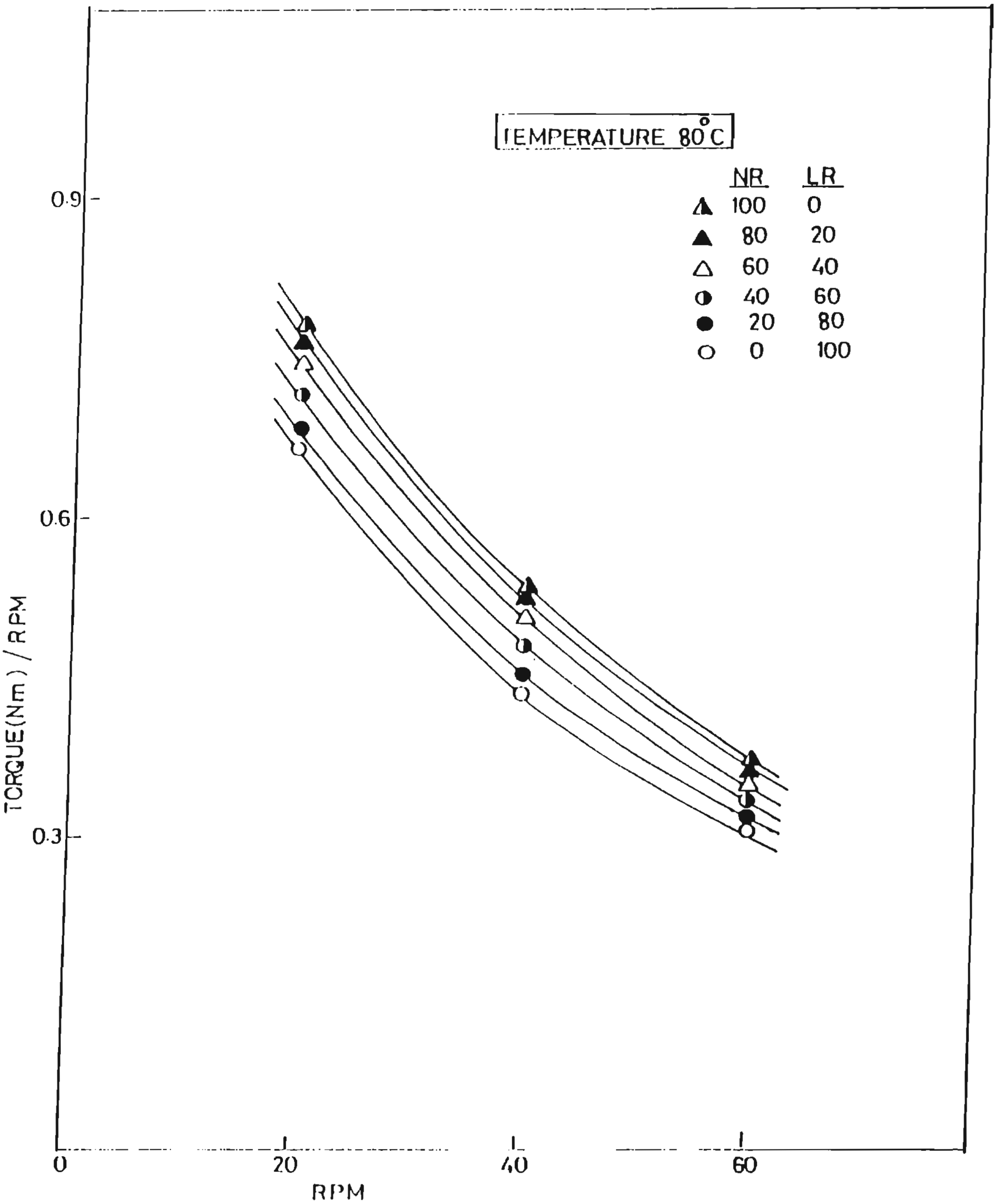

FIG.3.27: Variation in viscosity with shear rate of NR/LR blends at 80°C

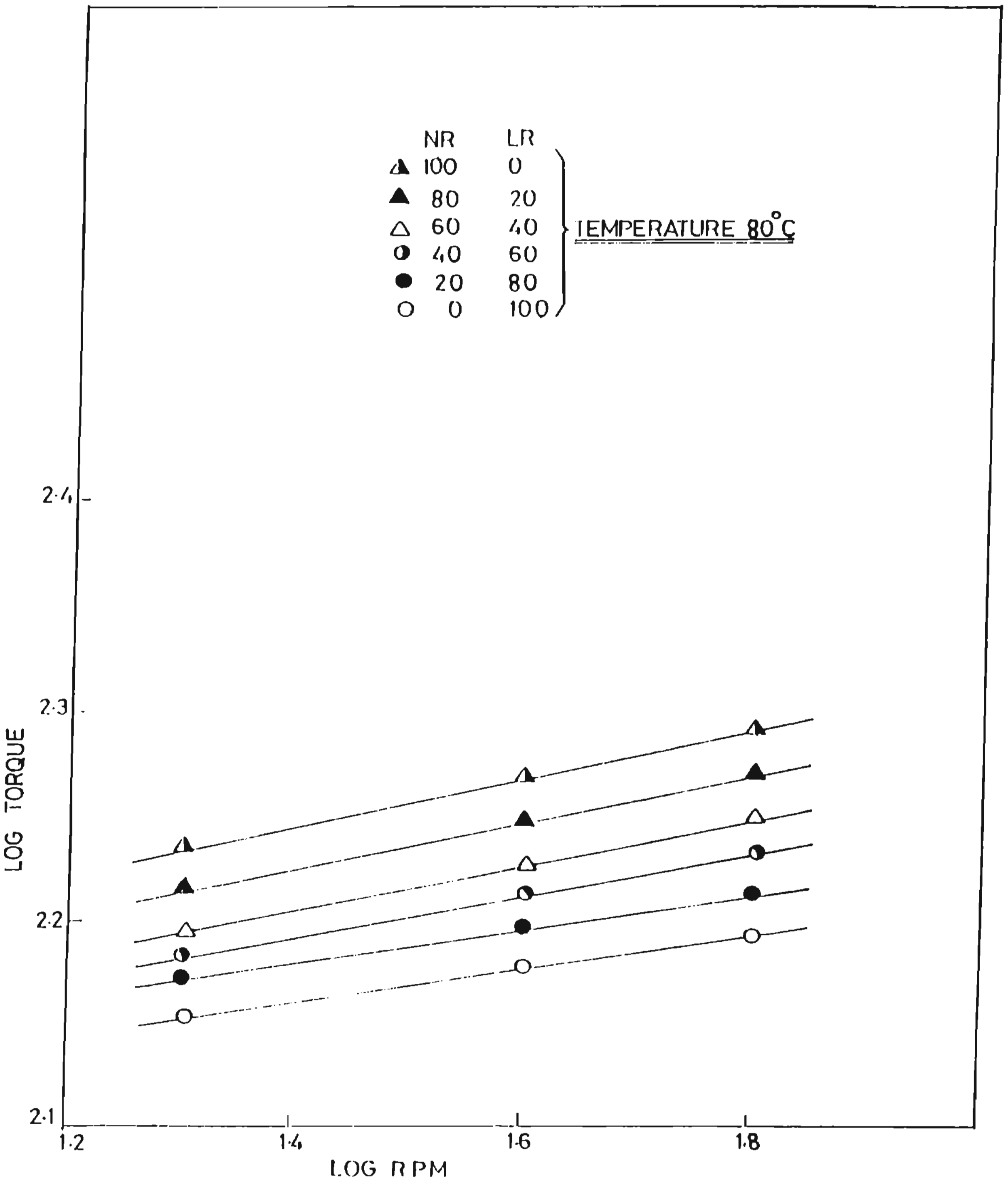

FIG.3.28: Variation in torque with shear rate of NR/LR blends at 80°C

slope of the log (torque) vs. log (rpm) lines.[33,34] Variation of power law index with temperature (80, 100 and 120°C) of the compounds is shown in Table 3.6. The value of the power law index decreases with increase in temperature and with the percentage of latex reclaim. This means that the blends become more pseudoplastic as expected.

Fig.3.29 permits the calculation of activation energies of viscous flow of the compounds. Inorder to understand the influence of temperature on viscosity of the compounds at a particular shear rate, Arrhenius plots at constant rpms were made.[35] In this figure logarithm of torque/rpm was plotted as a function of reciprocal temperature. The activation energy (E) of the flow was calculated from the slope [E /R] of these lines and is given in Table 3.7. It provides valuable information on the sensitivity of the material towards the change in temperature. From the table it is clear that all the blends have an activation energy intermediate between those of the components. It is further noticed that the heat sensitivity of the natural rubber compounds is not adversely affected on the addition of latex reclaim in higher percentages.

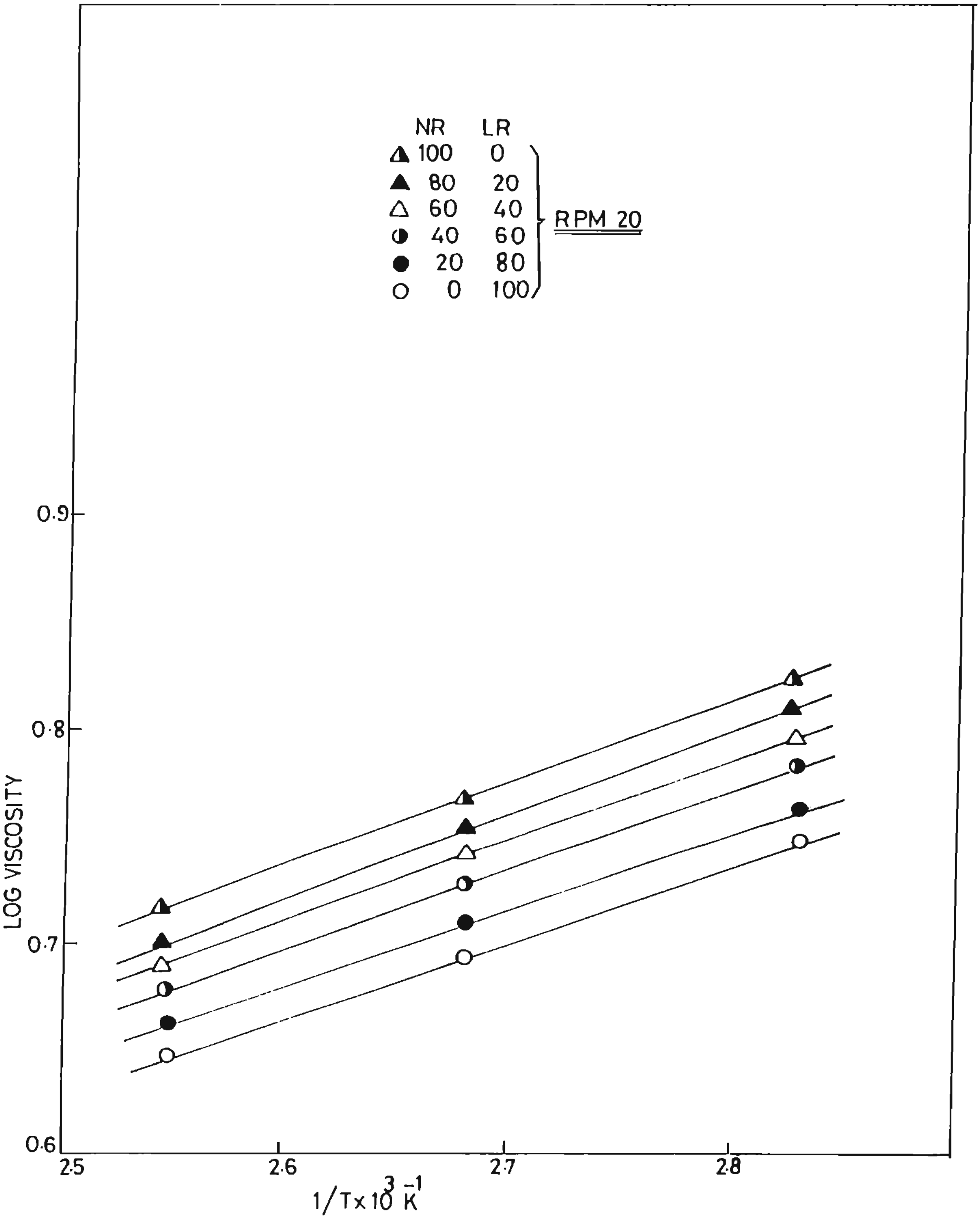

FIG.3.29: Variation in viscosity with temperature of NR/LR blends at 20 rpm

Table 3.6: Flow behaviour index values (n) of NR/LR gum compounds

Blend composition (Percentage of latex reclaim)	Power law index at a temperature of		
	80°C	100°C	120°C
0	0.23	0.22	0.21
20	0.22	0.20	0.19
40	0.21	0.19	0.18
60	0.19	0.18	0.17
80	0.18	0.17	0.16
100	0.17	0.16	0.15

Table 3.7: Activation energy of viscous flow of NR/LR gum compounds

Blend composition (Percentage of latex reclaim)	Activation energy in kJ mol^{-1} at		
	20 rpm	40 rpm	60 rpm
0	4.2	4.0	3.8
20	4.0	3.9	3.7
40	3.7	3.6	3.4
60	3.4	3.2	3.0
80	3.2	3.0	2.8
100	2.9	2.8	2.7

CONCLUSION

1. The latex reclaim can replace raw natural rubber upto about 50 percent of its weight without any deterioration in mechanical properties.

2. The morphology studies show that there is uniform distribution of the latex reclaim in natural rubber compounds and has good bonding with natural rubber up to about 50 percent of reclaim.

3. The SEM studies show that the tensile and tear failure mechanism of NR, latex reclaim and their blends is essentially similar.

4. The viscosity of the gum natural rubber compounds decreases with the addition of latex reclaim.

5. The power law index values decrease with increase in reclaim content which means that the blends become more pseudoplastic with the addition of reclaim.

6. The heat sensitivity of the gum natural rubber compounds is not seriously affected by the addition of latex reclaim.

Part III: STUDIES ON NATURAL RUBBER/LATEX RECLAIM BLENDS

Natural rubber is the preferred polymer in many areas because of its superior building tack, green stock strength, better processing, high resilience and excellent dynamic properties. The utilisation of scrap materials is an important factor in the expansion of the raw materials based industry, the reduction of demand for primary raw materials and economization of financial resources. Considerable work has been done on reuse of scrap polymeric materials since it offers processing as well as economic advantages.[2,5,7,12,19,25,26]

The previous section of this chapter showed that the high quality rubber hydrocarbon prepared from the waste latex products has good interparticle bonding with gum natural rubber and can replace raw natural rubber upto about 50% of its weight without affecting their mechanical as well as processing properties. One way of reducing the compound cost and modifying their properties is by the incorporation of fillers to rubber compound. This study reports the effect of adding the latex reclaim in carbon black filled natural rubber compounds in different percentages. The curing and physical properties of natural rubber/latex reclaim blends were studied. 100% natural rubber and 100% latex reclaim filled compounds were also prepared for comparison. The tear fracture and tensile fracture mechanism (original and aged) of the samples was investigated using a scanning electron microscope. The abraded surface pattern of the vulcanizates was also studied using a SEM for supporting their mechanical behaviour.

EXPERIMENTAL

Natural rubber was masticated on a laboratory mill and the latex reclaim in the form of a sheet was added at different percentages and the blends were compounded as per the formulations given in Table 3.8. Natural rubber and latex reclaim alone were also compounded on a mixing mill as per the formulations given in Table 3.8.

The optimum cure time of the compounds was determined on a Goettfert Elastograph. The compounds were then vulcanized upto their respective optimum cure times in an electrically heated hydraulic press at 150°C. Dumbell shaped test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/min.

Table 3.8: Formulations of NR/LR blends

Materials	A	B	C	D	E	F	G	H	I	J	K
NR	100	90	80	70	60	50	40	30	20	10	0
Latex reclaim	0	10	20	30	40	50	60	70	80	90	100
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
MBTS	0.6	0.54	0.48	0.42	0.36	0.30	0.24	0.18	0.12	0.06	0.06
TMTD	0.20	0.18	0.16	0.14	0.12	0.10	0.08	0.06	0.04	0.02	0.02
Sulphur	2.50	2.25	2.00	1.75	1.50	1.25	1.00	0.75	0.50	0.25	0.25
Carbon black	40	40	40	40	40	40	40	40	40	40	40
Aromatic oil	5	5	5	5	5	5	5	5	6	7	9
Accinox ZC	1	1	1	1	1	1	1	1	1	1	1

Angular test specimens were punched out of the compression moulded sheets and tear resistance of the vulcanizates was measured on the Zwick UTM. Samples for compression set, hardness, abrasion resistance, heat build up and resilience were moulded and tested as per relevant ASTM standards. The ageing resistance of the vulcanizates was studied after ageing the samples at 100°C for 24 and 48 hours in a laboratory air oven.

The swelling index of the vulcanizate was determined to monitor the variation in total crosslink density.

$$\text{The swelling index} = \left(\frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}}\right)100$$

The scanning electron microscope photographs of the tear and tensile fracture surfaces and abraded surfaces of the vulcanizates were made using a SEM model JEOL JSM 35C. The fracture and the abraded surfaces of the test specimens were carefully cut from the test pieces and were then sputter coated with gold within 25 hrs of testing. The gold coated surfaces were examined through the scanning electron microscope.

Processability of the filled natural rubber compound, its blends with latex reclaim (80/20, 60/40, 40/60 and 20/80) and latex reclaim compound was evaluated at different temperatures (80, 100 and 120°C) and at different shear rates (20, 40 and 60 rpms) on a Brabender Plasticorder.

RESULTS AND DISCUSSION

Table 3.9 shows the cure characteristics of the compounds. The scorch safety of the compounds containing latex reclaim marginally decreases with reclaim content as indicated by T_{10} values. This is possibly due to the presence of crosslink precursors and/or unreacted curatives in the latex reclaim since curatives were added only for natural rubber in this study. The optimum cure time, T_{90}, is also found to decrease with the addition of latex reclaim.

The swelling index is found to decrease with increase in the amount of latex reclaim as shown in Table 3.9. This shows that the crosslink density of the compounds increases with latex reclaim content.

Fig.3.30 shows the variation in tensile strength with the addition of latex reclaim. The tensile strength

Table 3.9: Cure characteristics and vulcanizate properties of NR/LR blends

Cure characteristics	A	B	C	D	E	F	G	H	I	J	K
<u>Cure characteristics</u>											
T_{10} (Scorch time in minutes)	2.1	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.0
T_{90} (Optimum cure time in minutes)	3	2.9	2.85	2.8	2.7	2.6	2.4	2.2	2.1	2.0	1.9
<u>Vulcanizate properties</u>											
Swelling index	336	332	327.5	315.28	309.10	302.50	294	288	279	271	262
Hardness (Shore A)	50	51	52	53	54	55	57	58	60	62	63
Abrasion resistance (cc/h)	5.3	5.5	5.6	5.7	5.8	5.9	6.3	6.4	6.6	6.8	7.4
Heat build up (°C)	22.3	24.8	25.5	26.7	27.5	28.4	29.5	30.3	31.2	32.4	33.1
Resilience (%)	61.7	60.00	59.03	57.7	56.7	55.4	52.87	50.4	48.6	45.8	42
Compression set (%)	30.12	29.65	29.32	28.95	28.56	27.92	27.42	26.88	26.21	25.49	24.66

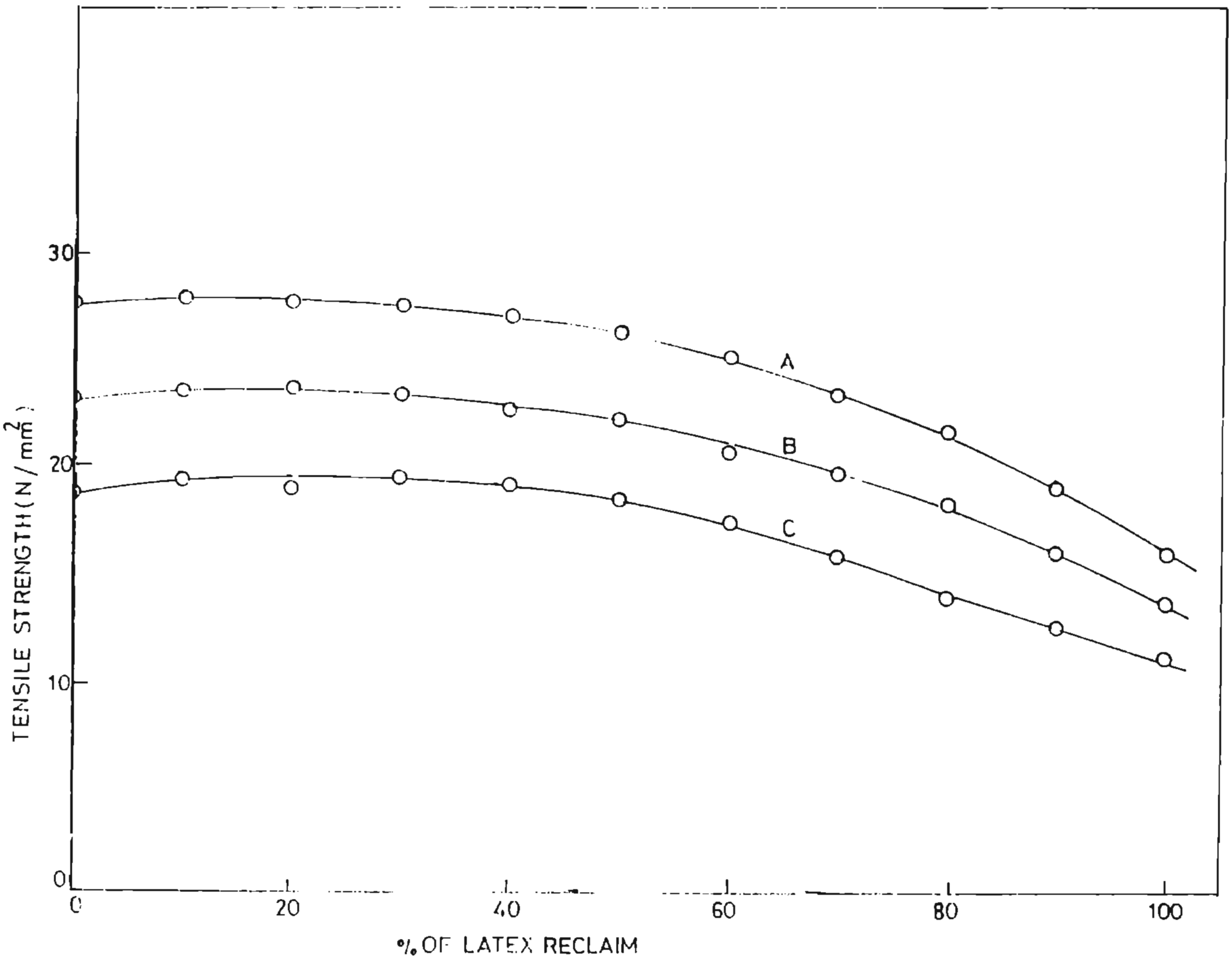

FIG.3.30: Variation in tensile strength with latex reclaim of NR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

shows only marginal variations up to about 50 percent reclaim content and thereafter decreases with the addition of latex reclaim similar to the gum compounds.[36] The ageing resistance of the blends is also found to be comparable to that of the carbon black filled natural rubber vulcanizate as shown in Fig.3.30.

Fig.3.31 shows the variation in tear strength with the amount of latex reclaim. The variation in tear strength is also similar to that of the tensile strength. This shows the high quality of rubber hydrocarbon derived from the latex reclaim as well as its good bonding with natural rubber. The ageing resistance of the samples containing latex reclaim is also comparable to that of carbon black filled natural rubber vulcanizate as shown in Fig.3.31.

The variation in elongation at break with the amount of latex reclaim and its retention after ageing is shown in Fig.3.32. The significant reduction in elongation at break may be due to the increased crosslink density in the blends as well as due to the reduction in molecular weight resulting from the reclamation process.

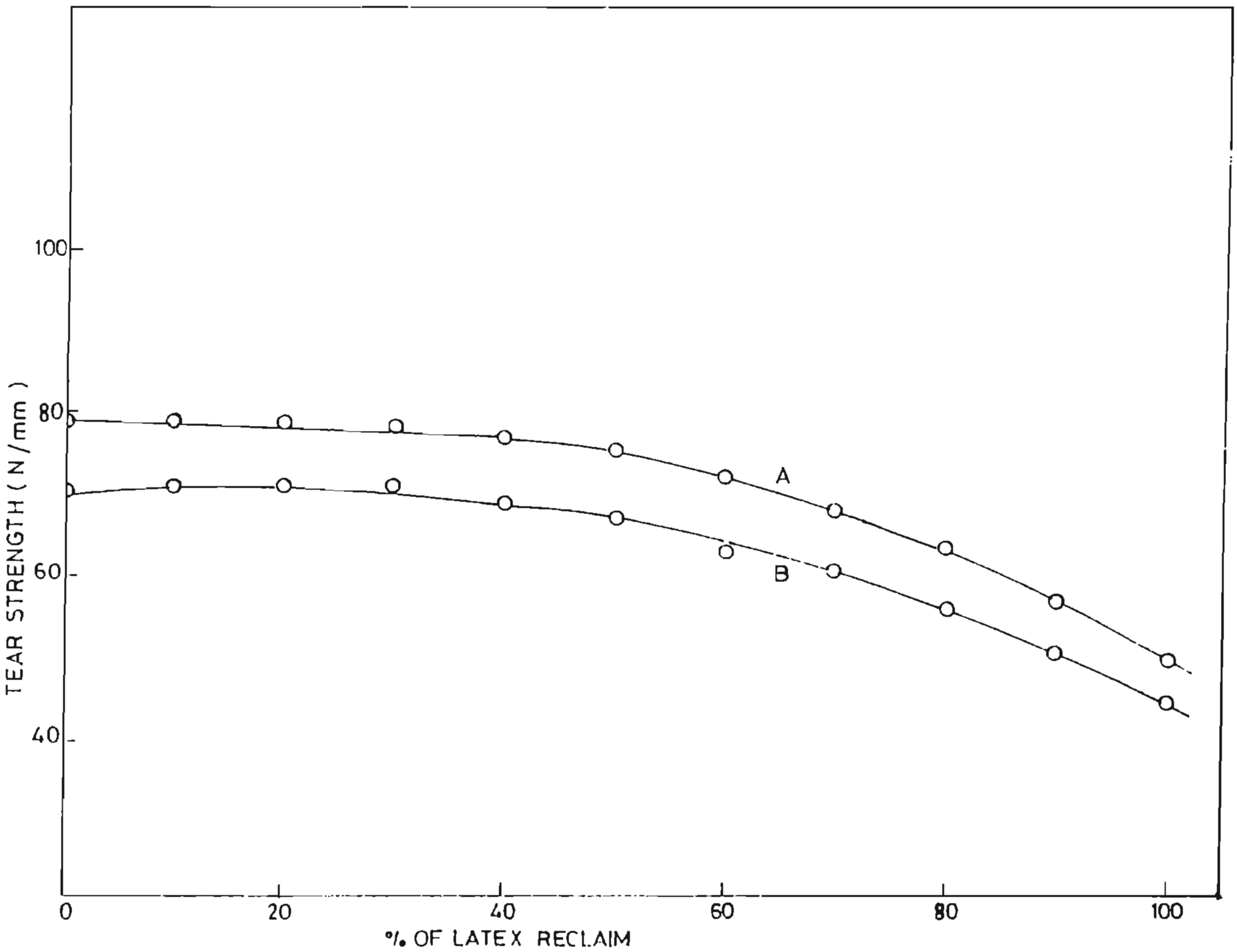

FIG.3.31: Variation in tear strength with latex reclaim of NR/LR blends

A. Original;   B. Aged 24 h, 100°C

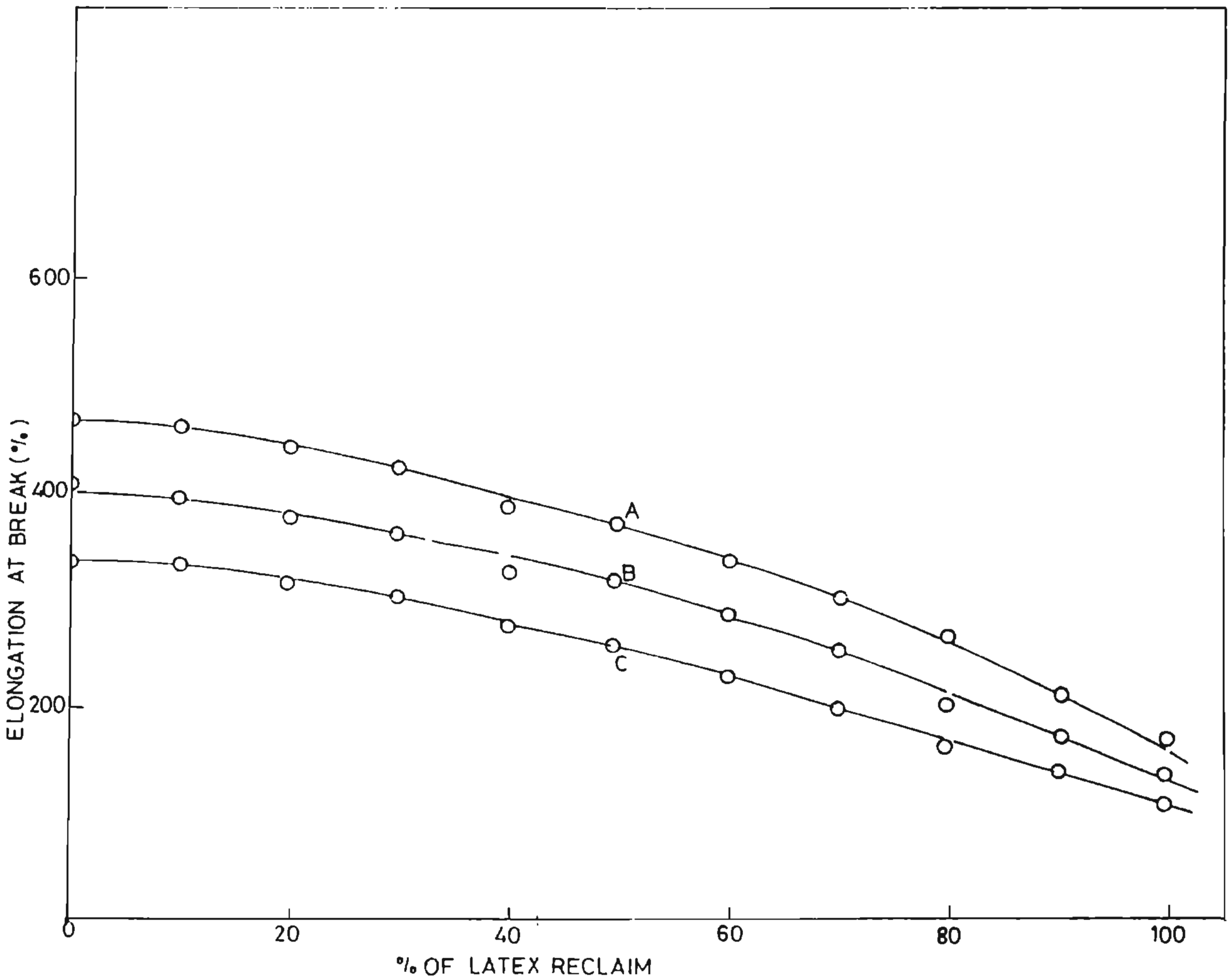

FIG.3.32: Variation in elongation at break with latex reclaim of NR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

Fig.3.33 shows the variation in modulus with the amount of latex reclaim and the retention in modulus with ageing. There is a gradual increase in modulus with the addition of latex reclaim. This may be attributed to the increased amount of crosslink density in the blends and the reduction in elongation of the vulcanizates containing latex reclaim.

The hardness increases with increase in the amount of latex reclaim as expected (Table 3.9). The compression set decreases with the addition of latex reclaim (Table 3.9) which further confirms the increased crosslink density in the blends.

The heat build up slightly increases with increasing amount of latex reclaim and abrasion resistance registers only marginal changes initially and decreases at higher concentrations of latex reclaim (Table 3.9).

The variation in resilience is inversely proportional to that of heat build up as expected.

Fig.3.34 shows the SEM photograph of the tear fracture surface of filled natural rubber vulcanizate. It

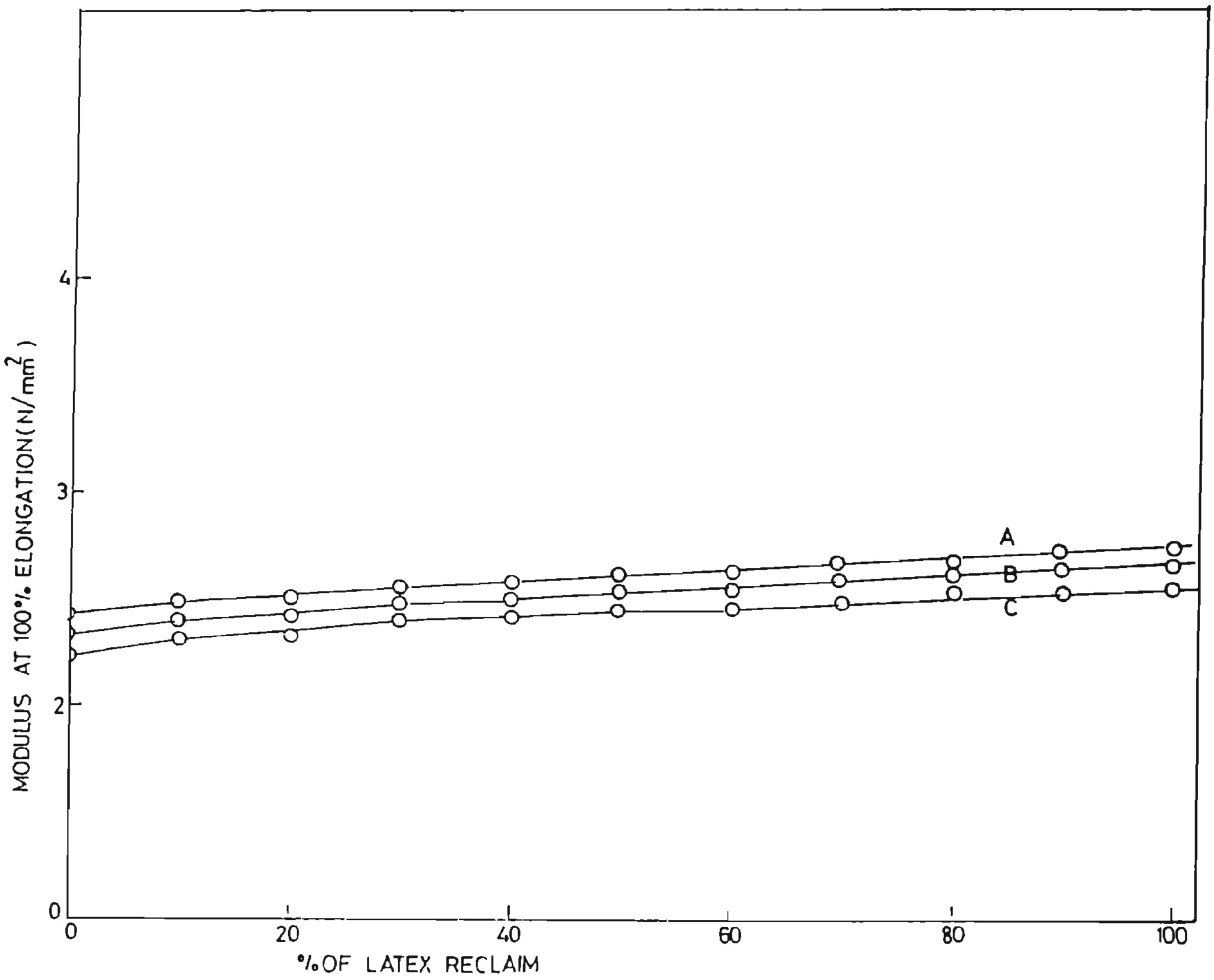

FIG.3.33: Variation in modulus with latex reclaim of NR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

shows that the tear lines are in parabolic shape which are distributed randomly on the fracture surface. This accounts for the higher tear resistance of the black filled natural rubber vulcanizate as compared to the gum natural rubber vulcanizate.[30] Reinforcing high abrasion furnace black provides improved wetting and adhesion characteristics and prevents tear from proceeding straight.

The tear fracture surface of the 50/50 filled natural rubber/latex reclaim vulcanizate is shown in Fig.3.35. It shows that a large number of parabolic and short round tear lines on the fracture surface. This could explain slightly lower tear strength shown by the 50/50 natural rubber/latex reclaim blend compared to filled natural rubber vulcanizate. Since the formation of the parabolic tear lines on the fracture surface has been attributed to the interaction of the main fracture front with subsidiary fracture fronts initiated from flaws just ahead of the crack.[37]

Fig.3.36 shows the tear fracture surface of filled latex reclaim vulcanizate. In this also, the tear lines appear as parabolic but they are broad which gives a rough torn surface resulting in lower tear strength compared to natural rubber vulcanizate.

Fig.3.37 shows the SEM photograph of the tensile fracture surface of filled natural rubber vulcanizate. Very tiny shear lines are seen on the fracture surface. Addition of filler raised the crystallinity, covering almost the whole of the matrix. This results in the increase in strength properties of the filled vulcanizate when compared with gum vulcanizate. Fig.3.39 shows the tensile fracture surface of the 70/30 natural rubber/latex reclaim filled vulcanizate. In this, more tiny cracks are observed on the fracture surface but the mechanism of failure is similar when compared to filled natural rubber vulcanizate. This results in only marginal changes in tensile strength of this sample when compared to natural rubber vulcanizate.

Figs.3.41 and 3.43 show the tensile fracture surfaces of 40/60 natural rubber/latex reclaim and latex reclaim filled vulcanizates. The cracks are more visible and broad when compared with natural rubber vulcanizate. Further, more irregular bright spots are seen on the fracture surface on the addition of latex reclaim in natural rubber vulcanizate. This results in lower tensile strength when compared with natural rubber vulcanizate.

Fig.3.38 shows the tensile fracture surface of the aged natural rubber vulcanizate. Shear lines are truncated and more when compared with original samples resulting in lower tensile strength. In Fig.3.40, the aged fracture surface of 70/30 filled natural rubber/latex reclaim vulcanizate shows that the fracture is brittle in nature and gives good strength properties. Addition of sixty weight percent of latex reclaim in filled natural rubber vulcanizate (Fig.3.42) gives the aged tensile fracture surface with broadly curved shear lines. This results in a lower tensile strength when compared with filled natural rubber vulcanizate. Fig.3.44 shows the aged tensile fracture surface of filled latex reclaim vulcanizate. In this case also, the shear lines are curved but gives a crumbled fracture surface. The fracture mechanism of the aged latex reclaim vulcanizate is similar to that of natural rubber vulcanizate.

The abraded surface of filled natural rubber vulcanizate is shown in Fig.3.45. It gives a well defined ridge pattern and close spacing of the ridges. The formation of the ridges by microtearing and subsequent removal of the material from the surface influence the tensile strength, tear strength and cut growth resistance

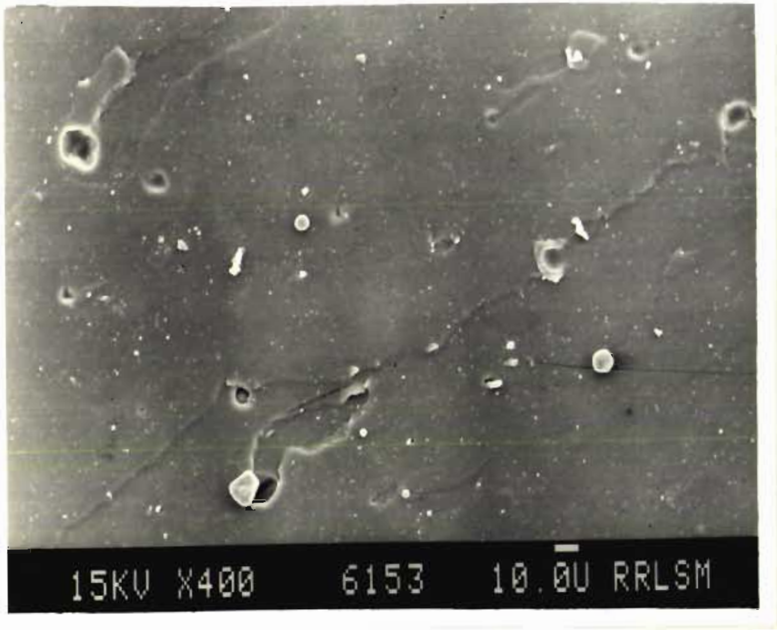

FIG.3.34: NR

FIG.3.35: NR/LR (50/50)

SEM photographs of the tear fracture surface of filled vulcanizates

FIG.3.36: SEM photograph of the tear fracture surface of filled LR vulcanizate

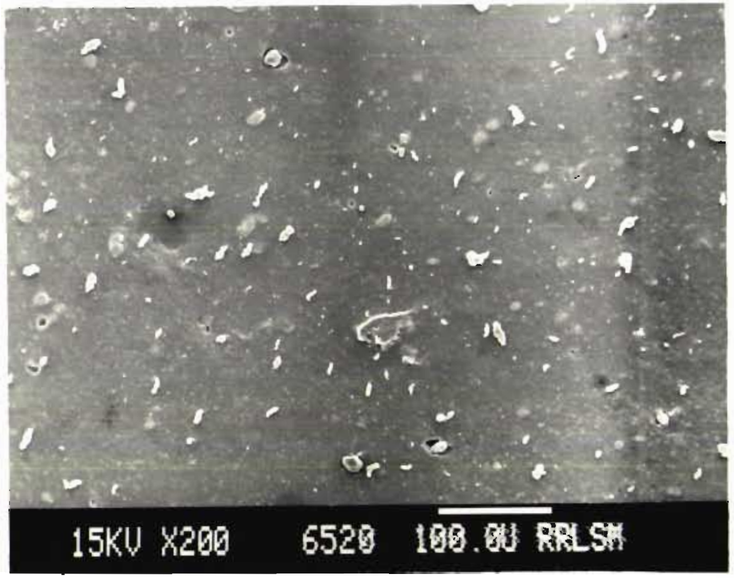

FIG.3.37: ORIGINAL

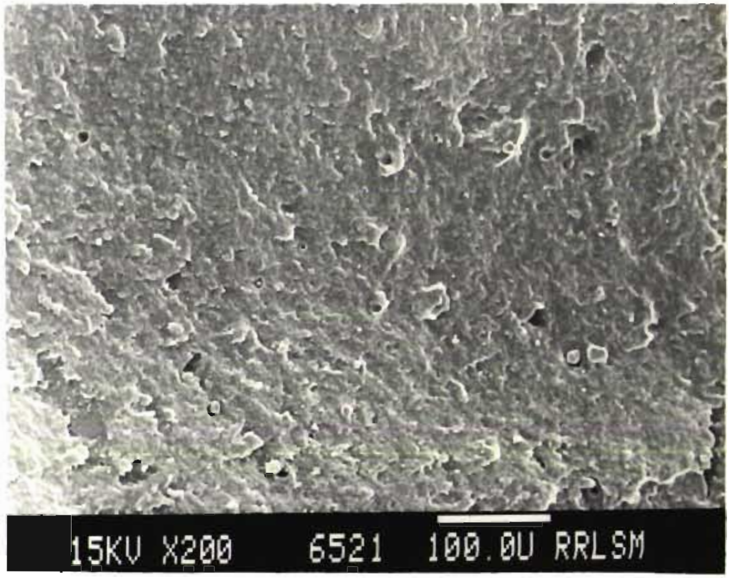

FIG.3.38: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of filled NR vulcanizate

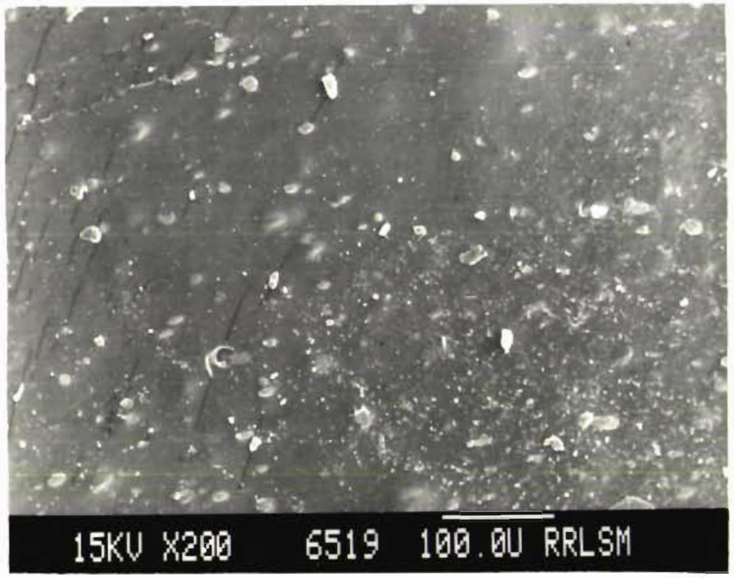

FIG.3.39: ORIGINAL

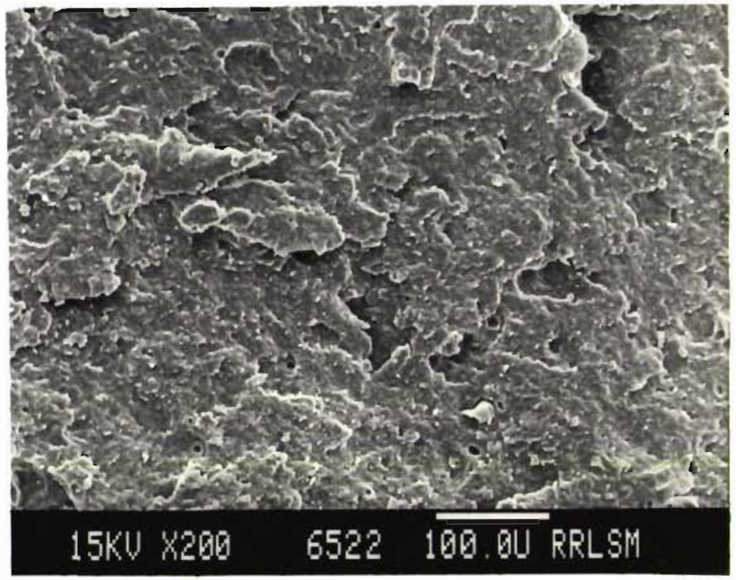

FIG.3.40: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of NR/LR (70/30) vulcanizate

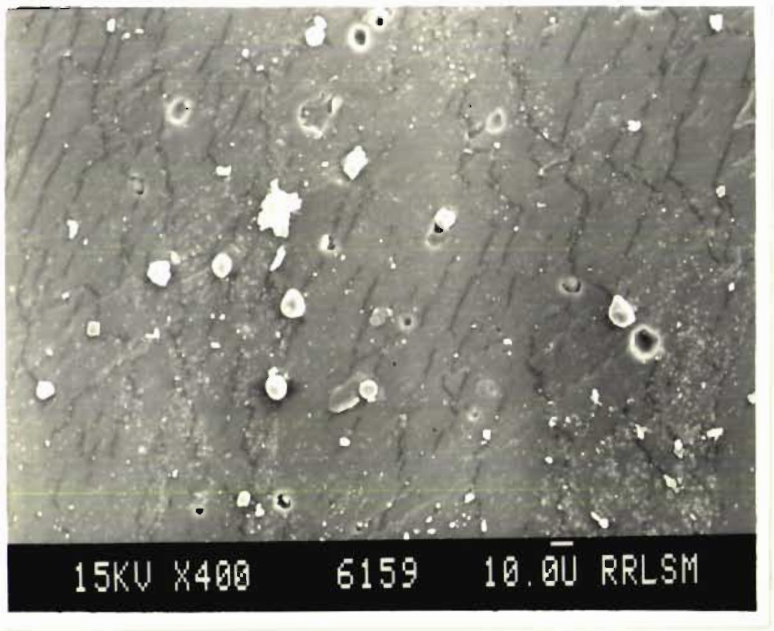

FIG.3.41: ORIGINAL

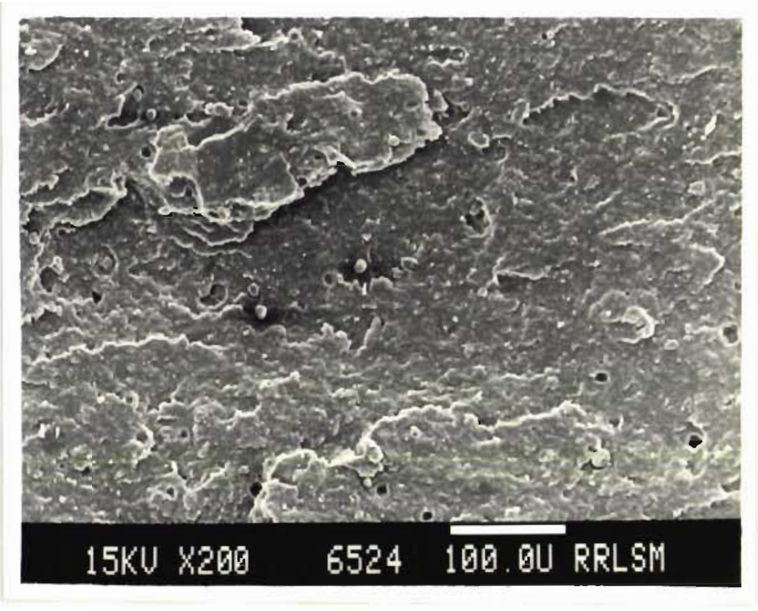

FIG.3.42: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of NR/LR (40/60) vulcanizate

FIG.3.43: ORIGINAL

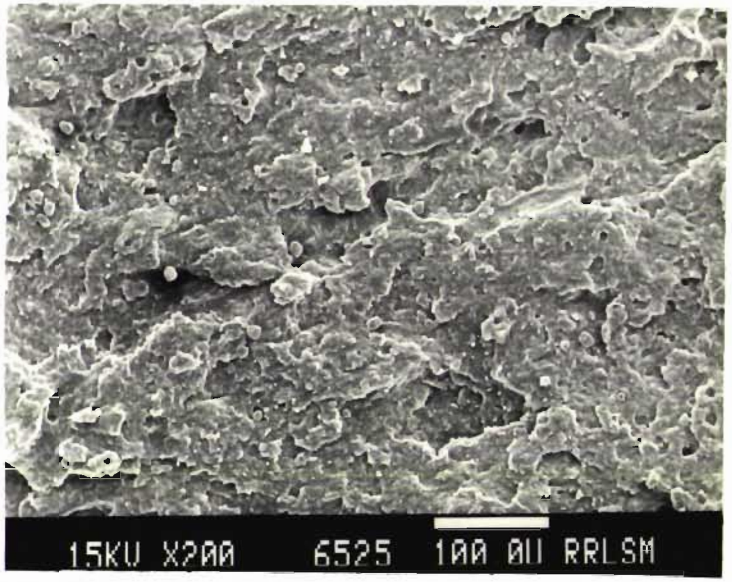

FIG.3.44: AGED 24 h, 100°C

SEM photographs of the tensile fracture surface of filled LR vulcanizate

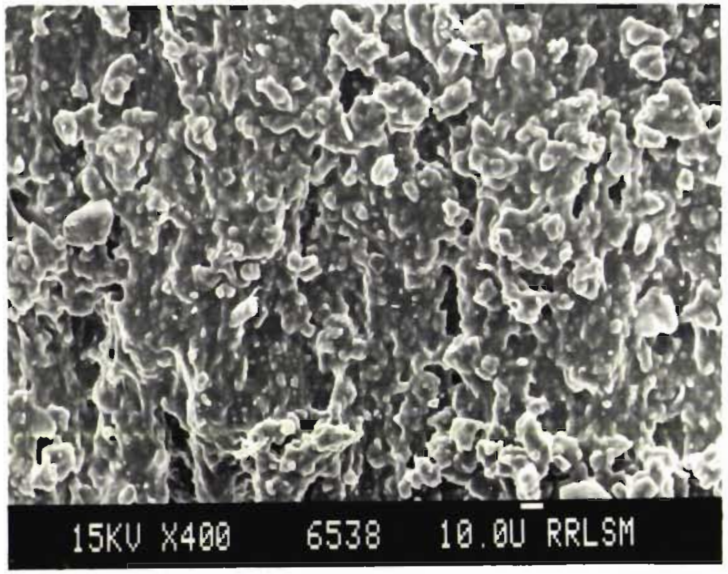

FIG.3.45: NR

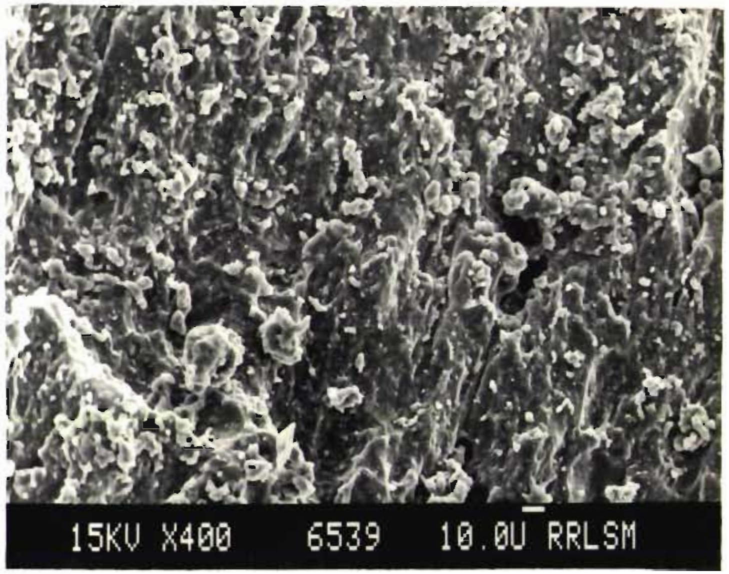

FIG.3.46: NR/LR (50/50)

SEM photographs of the abraded surface of filled vulcanizates

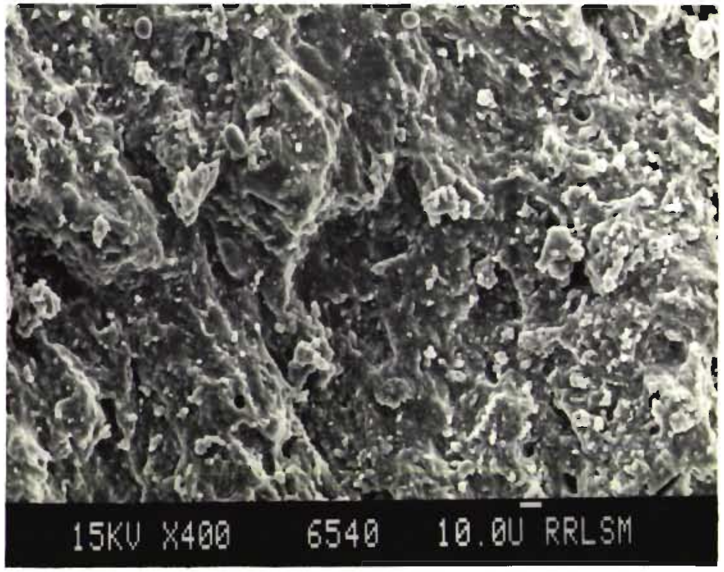

FIG.3.47: SEM photograph of the abraded surface of filled LR vulcanizate

of the matrix.[38] Fig.3.46 shows the abraded surface of the natural rubber/latex reclaim 50/50 blend. It shows that the ridges are comparatively less closely spaced than pure natural rubber vulcanizate. Hence, this blend shows a slightly lower abrasion resistance than natural rubber vulcanizate (Table 3.9), since the close spacing of the ridges are indicative of high resistance to abrasion.[39] The abraded surface of latex reclaim is shown in Fig.3.47. It shows that ridges are more deformed compared with pure natural rubber vulcanizate. Hence, this sample is less resistant to the frictional forces of abrasion than natural rubber vulcanizate (Table 3.9).

Fig.3.48 illustrates the effect of viscosity (torque/rpm) of the compounds with shear rate at a temperature of 80°C. The viscosity is strongly dependent on the shear rate and the compounds are highly pseudoplastic as expected. It may also be observed that the viscosity of the compounds decreases with the addition of latex reclaim.

The variation of torque with shear rate is shown in Fig.3.49. The power law index was calculated as the slope of the log (torque) vs. log (rpm) lines.[33,34]

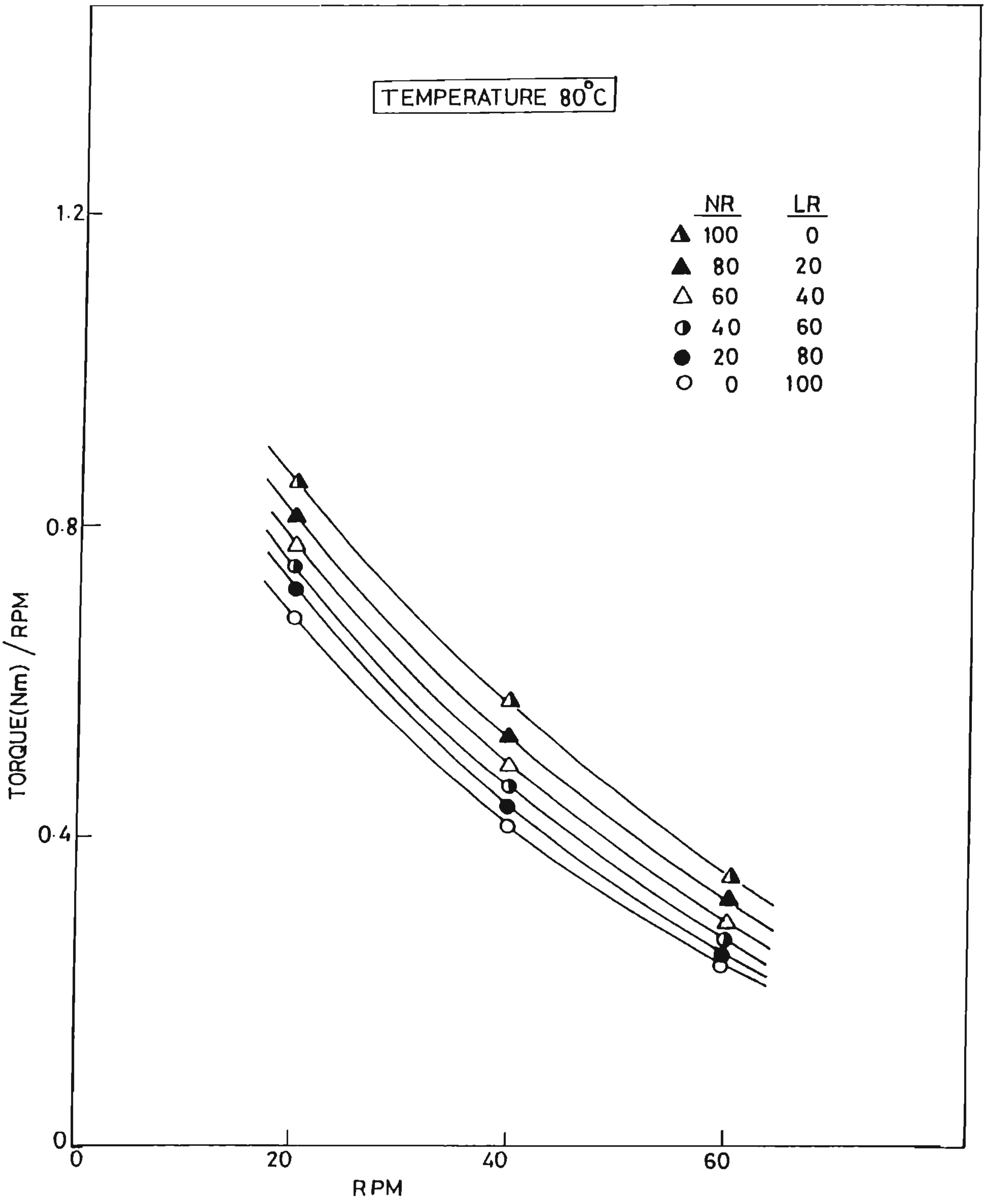

FIG.3.48: Variation in viscosity with shear rate of NR/LR blends at 80°C

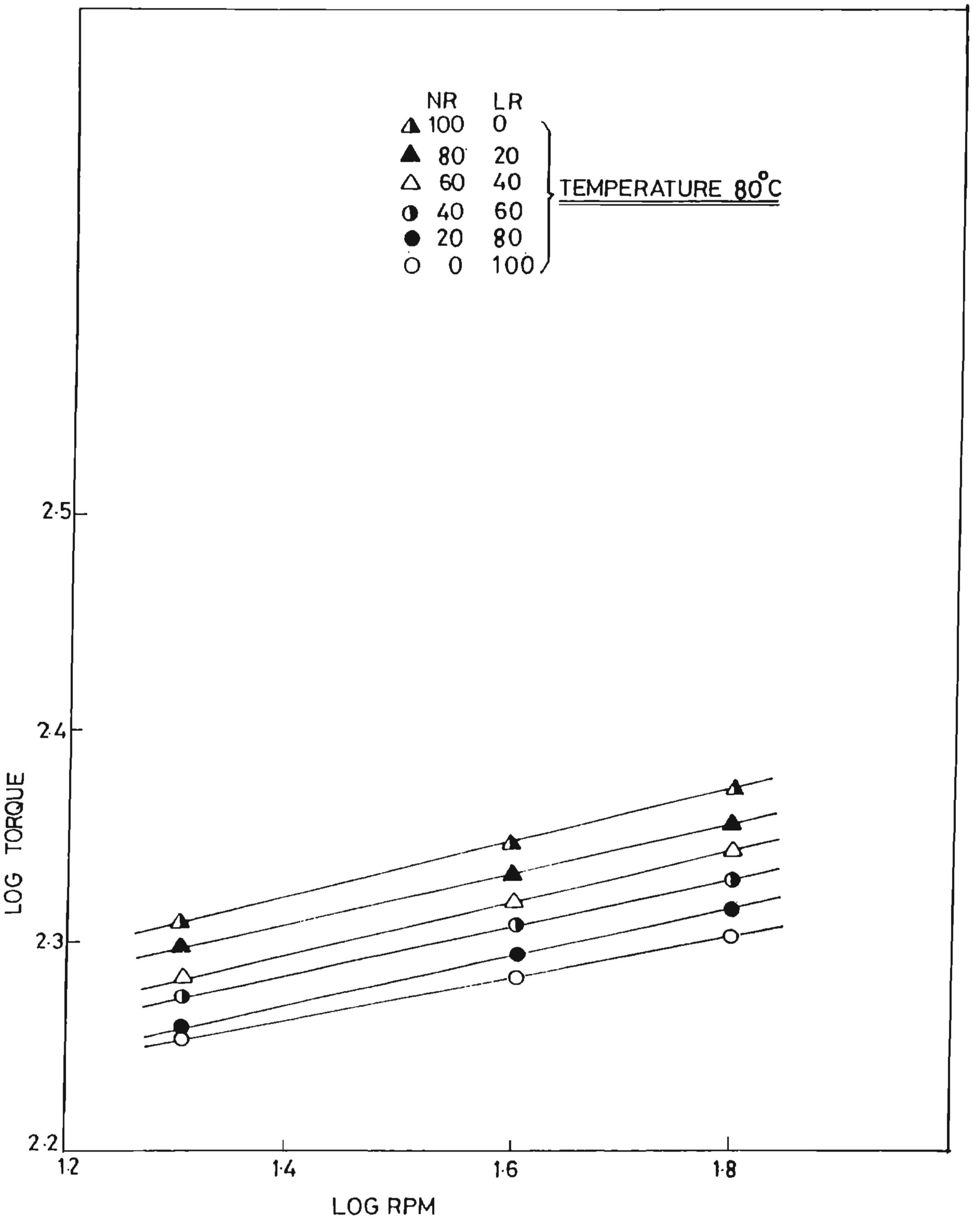

FIG.3.49: Variation in torque with shear rate of NR/LR blends at 80°C

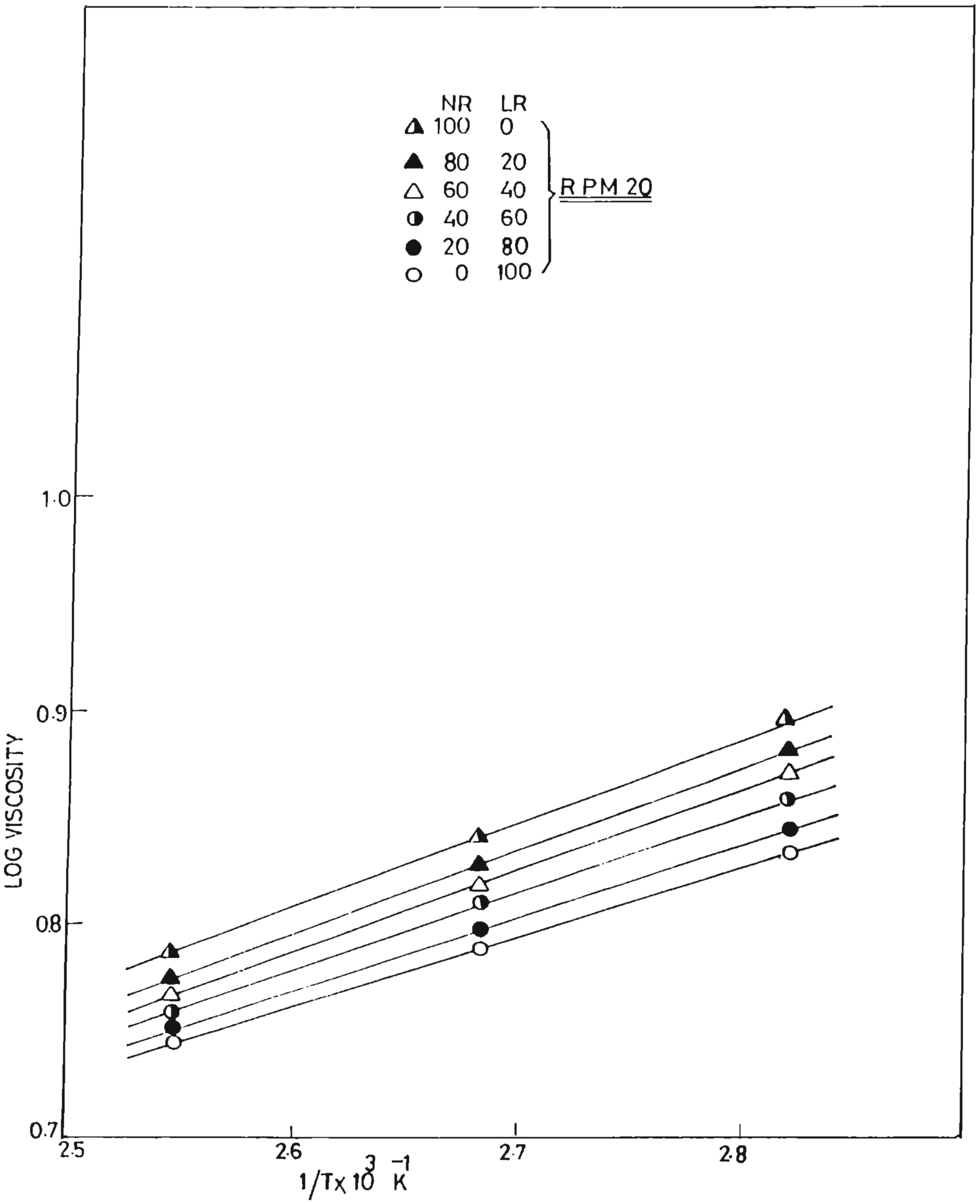

FIG.3.50: Variation in viscosity with temperature of NR/LR blends at 20 rpm

Table 3.10: Flow behaviour index values (n) of NR/LR filled compounds

Blend composition (Percentage of latex reclaim)	Power law index at a temperature of		
	80°C	100°C	120°C
0	0.25	0.23	0.22
20	0.24	0.22	0.21
40	0.23	0.21	0.20
60	0.22	0.20	0.19
80	0.21	0.19	0.18
100	0.19	0.18	0.17

Table 3.11: Activation energy of viscous flow of NR/LR filled compounds

Blend composition (Percentage of latex reclaim)	Activation energy in kJ mol^{-1} at		
	20 rpm	40 rpm	60 rpm
0	3.8	3.6	3.5
20	3.7	3.5	3.3
40	3.5	3.3	3.1
60	3.3	3.0	2.9
80	3.1	2.8	2.7
100	2.8	2.7	2.6

Variation of power law index with temperature is shown in Table 3.10. The value of the power law index decreases with increase in temperature and with the percentage of latex reclaim, which means that the compounds become more pseudoplastic in nature.

The activation energy of viscous flow was calculated from the slope of log (torque/rpm) plotted against the reciprocal of temperature lines[35] (Fig.3.50) and is given in Table 3.11. The natural rubber compound has a slightly higher activation energy compared to latex reclaim compound. However, all the blends have an activation energy intermediate between those of the components.

CONCLUSION

1. The latex reclaim can replace raw rubber upto about 50 percent of its weight in filled natural rubber compounds without any deterioration in mechanical properties.

2. The SEM studies show that the tensile and tear fracture surface and the abraded surface of the NR, latex reclaim and their blends are comparable showing the uniformity in the failure mechanisms.

3. The viscosity of the filled natural rubber compounds decreases with the amount of latex reclaim.

4. The temperature sensitivity of the filled natural rubber compounds marginally decreases with the addition of latex reclaim.

Part IV: RHEOLOGICAL AND EXTRUDATE BEHAVIOUR OF NATURAL RUBBER/LATEX RECLAIM FILLED COMPOUNDS USING A CAPILLARY RHEOMETER

The knowledge of rheological behaviour of rubber compounds is of considerable importance in polymer processing operations such as mixing, extrusion, calendering and moulding. The appropriate classification of raw materials and the prediction of their processibility play an important role in the control of manufacturing processes.[40-45] The addition of the reclaimed rubber to a rubber compound improves its mould flow and reduces its cost.[11,46-48] Further, the incorporation of reclaim rubber to a rubber compound offers processing advantages like better surface finish, higher rate of extrusion, better dimensional stability and lower die swell.[7,20,49]

In contrast to dry rubber reclaim, latex reclaim contains rubber hydrocarbon of very high quality which is only lightly crosslinked. The mechanical properties of the natural rubber/latex reclaim (NR/LR) blends of gum as well as filled vulcanizates have been reported in the previous sections. These studies show that latex reclaim can be added to natural rubber in higher amounts than reclaimed rubber without affecting the mechanical properties of natural rubber.[36,50] The processability studies of such NR/LR compounds were carried out using a Brabender Plasticorder. The study shows that the viscosity of the rubber compounds decreases with the addition of latex reclaim.

The present study was undertaken to investigate the rheological behaviour of filled natural rubber/latex reclaim blends using a capillary rheometer.

EXPERIMENTAL

Preparation of Compounds

Natural rubber was masticated on a laboratory mixing mill and the latex reclaim in the form of a sheet was added at different percentages and the blends were prepared as per the formulations given in Table 3.12. 100% natural rubber compound was also prepared according to the formulation given in Table 3.12 for comparison.

Rheological Measurement

Rheological studies were carried out using a capillary rheometer, attached to a Zwick universal testing machine, model 1474. The capillary used had a length to diameter (lc/dc) ratio of 40. Eight gms of the test sample

Table 3.12: Formulations of NR/LR blends

Materials	A	B	C	D
Natural rubber	100	75	50	25
Latex reclaim	0	25	50	75
ZnO	5	5	5	5
Stearic acid	2	2	2	2
MBTS	0.6	0.45	0.30	0.15
TMTD	0.2	0.15	0.10	0.05
Sulphur	2.5	1.875	1.25	0.625
Carbon black	40	40	40	40
Aromatic oil	5	5	5	5
Accinox ZC	1	1	1	1

was put into the barrel of the capillary rheometer and forced down to the capillary by the plunger attached to the moving crosshead. After a warm-up period of 3 minutes, the sample was extruded through the capillary at 10 different speeds. Forces corresponding to specific plunger speeds could be measured by the pressure transducer attached to the plunger and were recorded using a strip chart recorder assembly.

The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall, respectively, using the following equations involving the geometry of the capillary and plunger:

$$\tau_w = \frac{F}{4A_p\ (l_c/d_c)}$$

$$\dot{\gamma}_w = \frac{3n+1}{4n} \times \frac{32Q}{\pi d_c^3}$$

where F is the force applied at a particular shear rate, A_p is the cross sectional area of the plunger, lc is the length of the capillary, dc is the diameter of the capillary, Q is the volume flow rate (calculated from the velocity of the crosshead and the diameter of the plunger) and n is the flow behaviour index, defined as,

$$n = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})}$$

and determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. $\dot{\gamma}_{wa}$ is the apparent wall shear rate, calculated as $\frac{32Q}{\pi d_c^3}$. The shear viscosity, η, was calculated as,

$$\eta = \tau_w / \dot{\gamma}_w$$

Extrudate Swelling

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured at several points after 24 h of extrusion using a binocular stereo-microscope. The average value of five readings was taken as the diameter of the extrudate (d_e). The extrudate swelling was calculated as the ratio of the diameter of extrudate to that of the capillary (d_e/d_c).

Observation of Extrudate Appearance

The extrudate from capillary rheometer has been observed carefully for any surface imperfections.

RESULTS AND DISCUSSION

The variation in shear viscosity of the compounds with shear stress is shown in Fig.3.51. It is found that the viscosity of the natural rubber/latex reclaim blends is lower than that of the natural rubber compound. The viscosity of the compounds decreases with increase in shear stress and behave as pseudoplastic fluids.

Table 3.13 shows the flow behaviour index (n) of the compounds. These figures again reveal the strong pseudoplastic nature of the compounds.

Fig.3.52 shows the variation in viscosity with temperature at three different shear rates, viz., 16.6 S^{-1}, 166.6 S^{-1} and 1666.6 S^{-1}. It can be seen that, the viscosity decreases with temperature in all the three shear rates. But this effect is more pronounced at higher shear rate as seen from the increased slope of the corresponding curves.

The dependence of melt viscosity on temperature was determined by Arrhenius type equation.

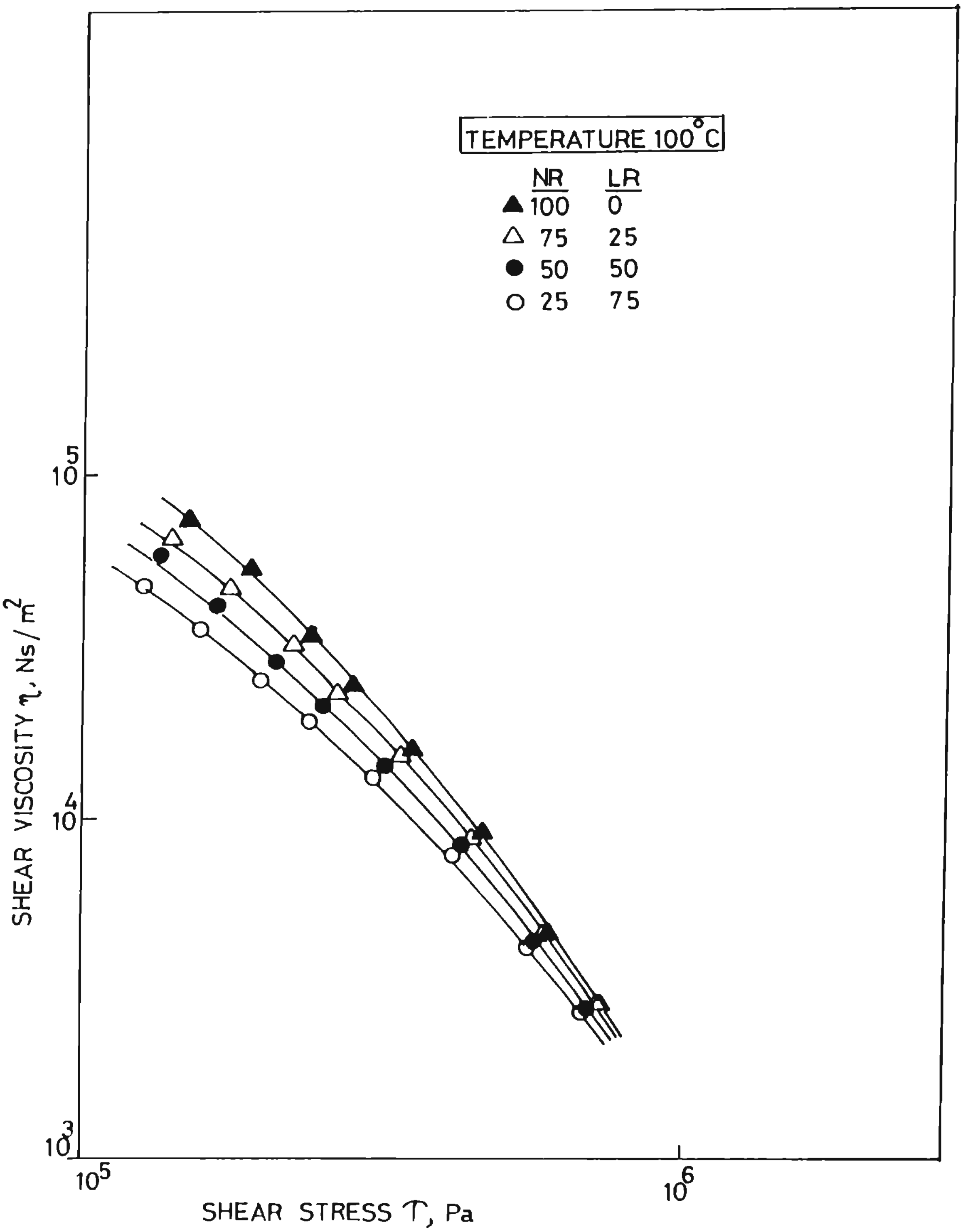

FIG.3.51: Variation in shear viscosity with shear stress of NR/LR blends at 100°C

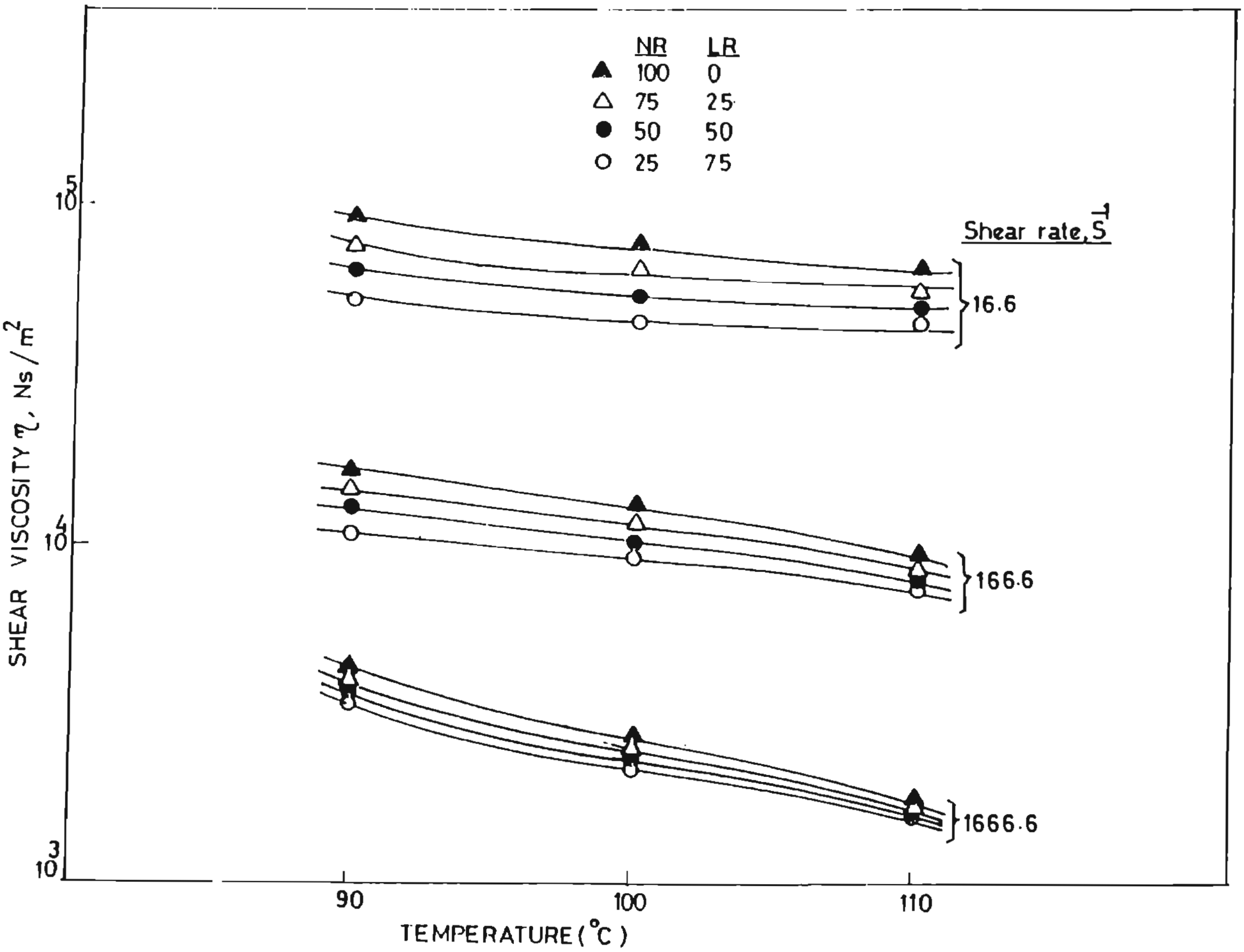

FIG.3.52: Variation in shear viscosity with temperature of NR/LR blends

$$\eta = Ae^{E/RT}$$

where A is a constant, E the activation energy and R the universal gas constant. From the slope of the plots (Fig.3.53) E values were calculated and are given in Table 3.14. The magnitude of the activation energy is a valuable information on the sensitivity of the material towards change in temperature. From the Table 3.14, it is clear that the heat sensitivity of the raw natural rubber is not affected significantly on the addition of latex reclaim.

Table 3.15 gives the die swell ratio d_e/d_c of the raw natural rubber/latex reclaim filled compounds at 90, 100 and 110°C at the two shear rates of 33.32 and 3332.71 S^{-1}. In general, die swell increases with increase in shear rate, which is a common phenomenon exhibited by almost all rubber compounds. Die swell is a relaxation phenomenon since when the molten polymer flows through the capillary, shearing tends to maintain the molecular orientation of polymer chains and when the melt emerges from the die, the molecules tend to recoil, leading to the phenomenon of die swell. The elastic recovery of the polymer chain is influenced by such factors as stress relaxation, crosslinking, presence of fillers, etc. From

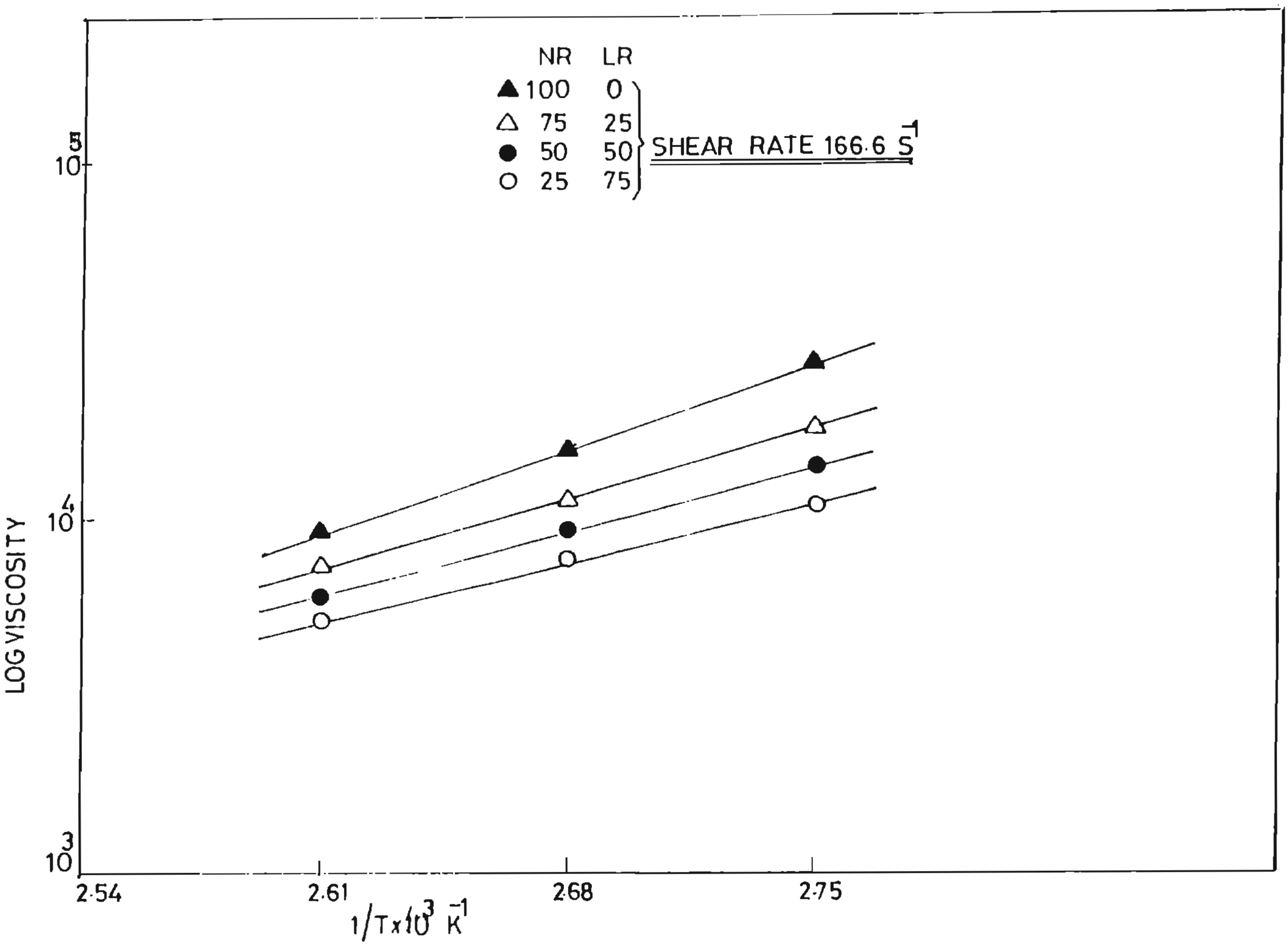

FIG.3.53: Variation in viscosity with temperature of NR/LR blends at a shear rate of 166.6 S^{-1}

Table 3.13: Flow behaviour index (n) of NR/LR blends

Compound (NR/LR)	Temperature (°C)		
	90	100	110
100/0	0.27	0.24	0.23
75/25	0.25	0.23	0.22
50/50	0.24	0.22	0.21
25/75	0.23	0.21	0.20

Table 3.14: Activation energy of flow (kJ mol^{-1}) of NR/LR blends

Compound NR/LR	Shear rate (S^{-1})		
	16.6	166.6	1666.6
100/0	4.0	3.4	2.8
75/25	3.6	3.3	2.7
50/50	3.4	3.1	2.5
25/75	3.2	2.9	2.2

Table 3.15: Die swell ratio (d_e/d_c) at 100°C of NR/LR blends

Compound NR/LR	Shear rate (S^{-1})	
	33.33	3332.71
100/0	1.55	1.89
75/25	1.53	1.87
50/50	1.50	1.84
25/75	1.47	1.81

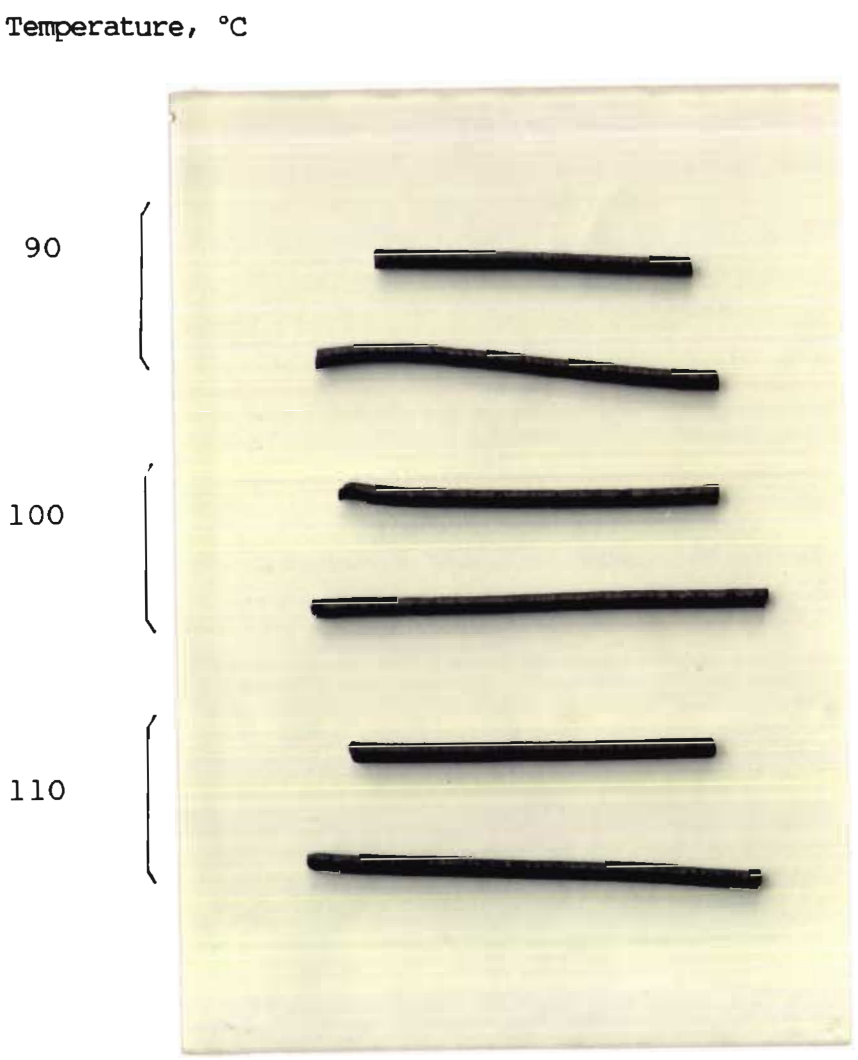

FIG.3.54: NR

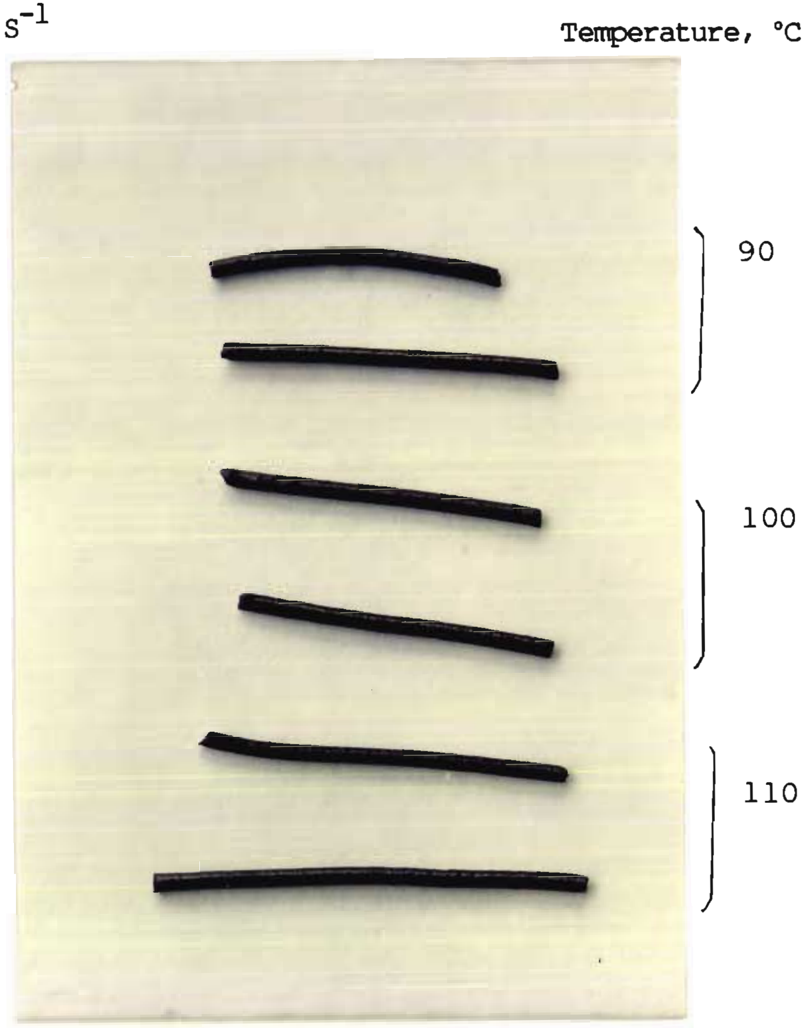

FIG.3.55: NR/LR (75/25)

Photographs of the extrudates of filled NR and NR/LR blend at two shear rates at different temperatures

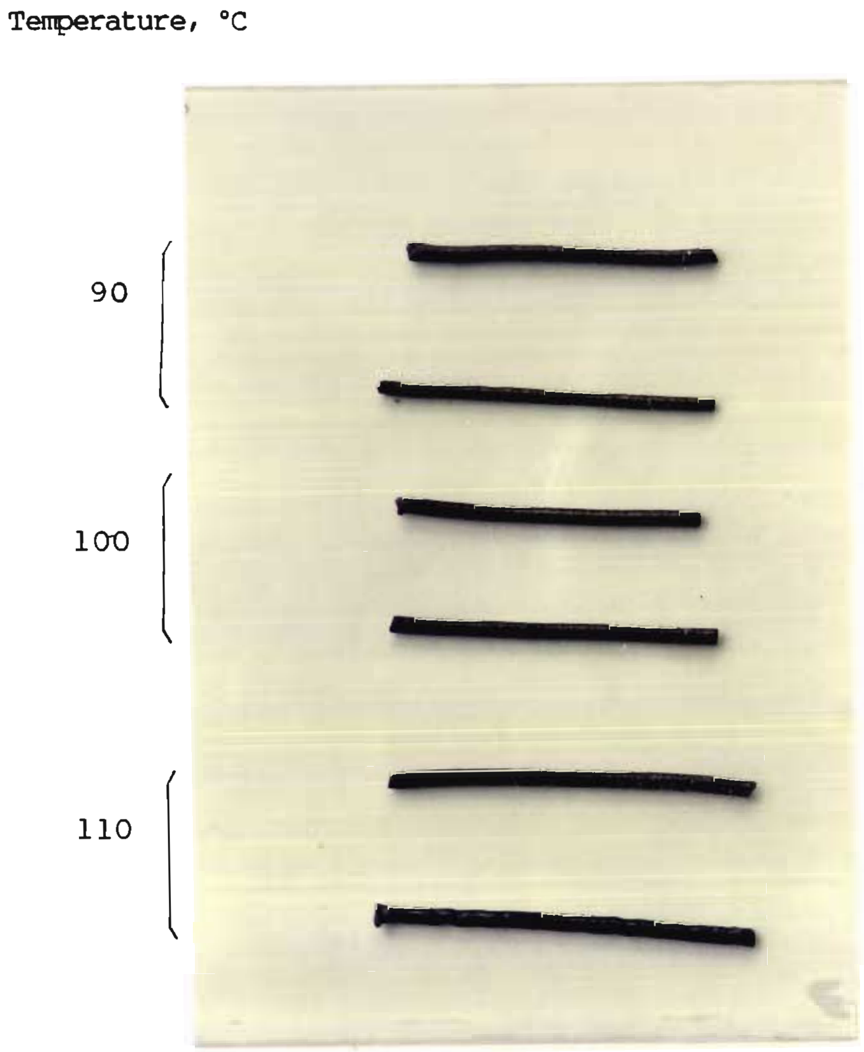

FIG.3.56: NR/LR (50/50)

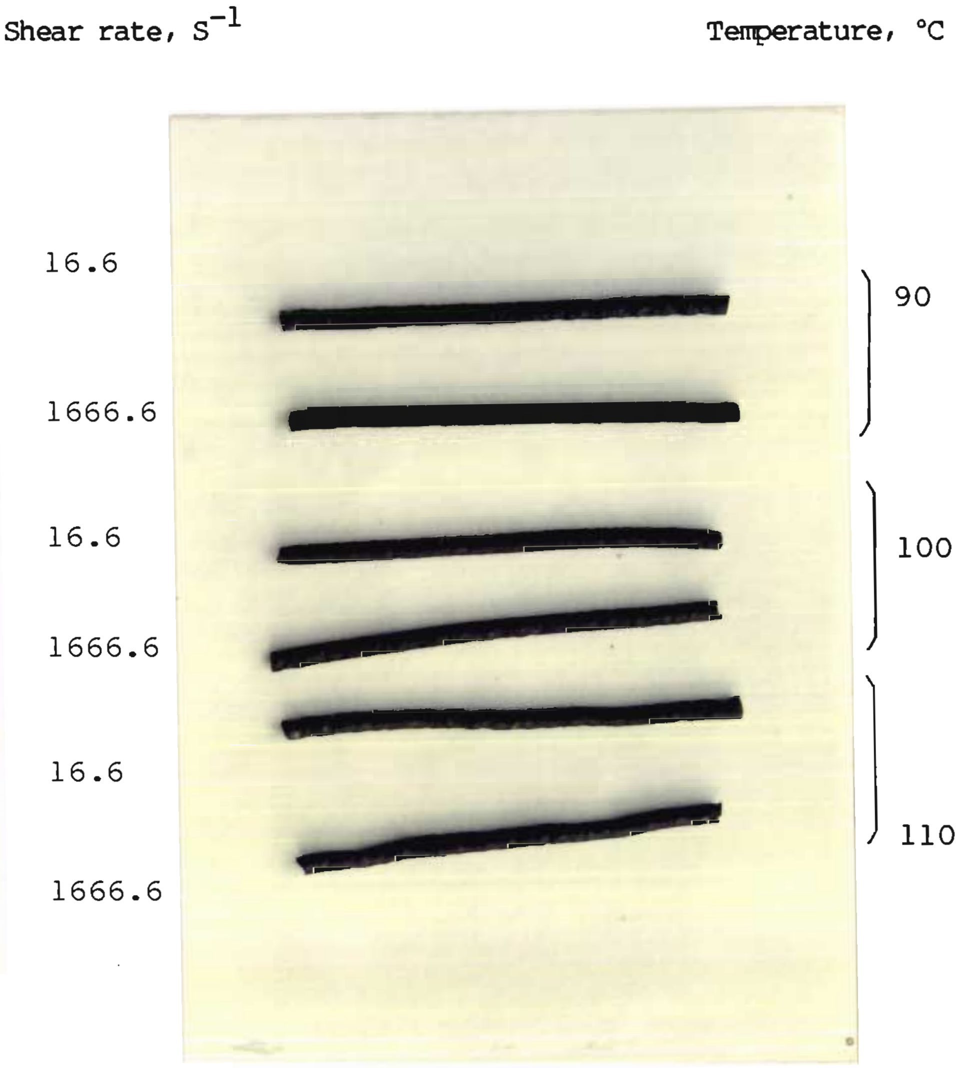

FIG.3.57: NR/LR (25/75)

Photographs of the extrudates of filled NR/LR blends at two shear rates at different temperatures this table, it is also seen that die swell is reduced by the addition of latex reclaim. The same effect has been observed in natural rubber/cryoground rubber compounds.[51]

Figs.3.54-3.57 show the extrudate characteristics of natural rubber and natural rubber/latex reclaim filled compounds at two shear rates and at different temperatures. It is seen that the extrudates are smooth upto about fifty weight percent of latex reclaim in filled natural rubber compounds. This shows that there is good interparticle bonding between the latex reclaim and natural rubber. The compound containing about seventy five weight percent of latex reclaim gives extrudates with rough and screw thread appearances. Turner and Bickley[52], have suggested that a second, low-viscosity phase, which causes a slip, migrates to the surface through the roll mechanism action (radial flow in addition to longitudinal flow) giving the extrudates screw thread appearances.

CONCLUSION

1. The viscosity of raw natural rubber decreases on addition of latex reclaim and the natural rubber/latex reclaim blends are strongly pseudoplastic.

2. The heat sensitivity of raw natural rubber is not changed considerably with the incorporation of latex reclaim.

3. Die swell reduces with the addition of latex reclaim in filled natural rubber compounds.

4. The extrudates of natural rubber/latex reclaim blends are smooth upto about fifty weight percent latex reclaim.

REFERENCES

1. A.A.Harshaft, Environ. Sci. Technol., 6(5), 412 (1972).

2. D.S.Le Beau, Rubber Chem. Technol., 40, 217 (1967).

3. N.R.Braton and J.A.Koutsksky, Chem. Eng. News, 52(6), 21 (1974).

4. G.Grane and E.L.Kay, Rubber Chem. Technol., 48, 50 (1975).

5. N.Kawabata and S.Yamashita, Int. Polym. Sci. Technol., 7(3), T/55 (1980).

6. A.Acetta and J.M.Vergnaud, Rubber Chem. Technol., 55, 961 (1982).

7. R.A.Swor, L.W.Jensen and M.Budzol, Rubber Chem. Technol., 53, 1215 (1980).

8. Y.Saeki and G.Suzuki, Rubber Age, 2, 33 (1976).

9. Y.Aziz, Kautshuk Gummi Kunststoffe, 45, 862 (1992).

10. K.T.Thomas, N.M.Claramma, Baby Kuriakose and E.V.Thomas, Paper presented in the International Conference on Rubber and Rubber-Like Materials, Nov. (6-8), Jamshedpur, India, 511 (1986).

11. A.A.Phadke, S.K.Chakraborty and S.K.De, Rubber Chem. Technol., 57, 19 (1984).

12. R.H.Wolk, Rubber Age **104**, 103 (1972).

13. A.A.Phadke and A.K.Bhowmick, J. Appl. Polym. Sci., 32(4), 4063 (1986).

14. I.Baruta, Int. Polym. Sci. Technol., **18**(4), T/34 (1991).

15. J.N.Lynch and B.D.La Grone, Rubber Chem. Technol., **60**, 202 (1987).

16. P.Elfferding, Int. Polym. Sci. Technol., **9**(10), T/30 (1982).

17. M.D.Burgogne, G.R.Leaker and Z.Krekic, Rubber Chem. Technol., **49**, 375 (1976).

18. J.Stark, Rubber World, **200**(1), 16 (1989).

19. N.P.Chopey, Chem. Eng., **80**, 54 (1973).

20. A.A.Phadke, A.K.Bhattacharya, S.K.Chakraborty and S.K.De, Rubber Chem. Technol., **56**, 726 (1983).

21. G.Adam, A.Sebenik, V.Osredkar, F.Ranogajec and Z.Veksli, Rubber Chem. Technol., **64**, 133 (1991).

22. L.Slusarski and R.Sendlewski, Int. Polym. Sci. Technol., **11**(4), T/6 (1984).

23. K.Fujimoto, T.Nishi and T.Okamoto, Int. Polym. Sci. Technol., **8**(8), 65 (1981).

24. V.F.Drozodovskii, Int. Polym. Sci. Technol., **20**(8), T/64 (1993).

25. R.P.Burford, M.Pittolo, Rubber Chem. Technol., **55**, 1233 (1982).

26. V.N.Kalinichenko, G.A.Blokh, A.Ya Vasker, Sulyaeva, Int. Polym. Sci. Technol., **11**(7), T/87 (1984).

27. B.Ellis, G.N.Welding, Techniques of Polymer Science, Soc. Chem. Ind., London, 46 (1964).

28. P.J.Flory, J.Rehner, J. Chem. Phys., 11, 512 (1943).

29. B.Saville, A.A.Watson, Rubber Chem. Technol., 40, 100 (1967).

30. N.M.Mathew and S.K.De, Polymer, 23, 632 (1982).

31. P.K.Pal, A.K.Bhowmick and S.K.De, Int. J. Polym. Mat., 9, 139 (1982).

32. N.M.Mathew, A.K.Bhowmick, B.K.Dhindaw and S.K.De, J. Mat. Sci., 17, 2594 (1982).

33. L.L.Blyler and J.H.Daane, Polym. Eng. Sci., 7, 178 (1967).

34. G.C.N.Lee and J.R.Purdon, Polym. Eng. Sci., 9, 360 (1969).

35. J.E.Goodrich and R.S.Porter, Polym. Eng. Sci., 7, 45 (1967).

36. Reena Susan George and Rani Joseph, Die Angew. Makromol. Chemie, 215, 25 (1994).

37. A.Kadir and A.G.Thomas, Rubber Chem. Technol., 54, 15 (1981).

38. A.K.Bhowmick, Rubber Chem. Technol., 55, 1055 (1982).

39. A.N.Gent and C.T.R.Pulford, Development in polymer fracture-1, edited by E.H.Andrews, Applied Science, London, 155 (1979).

40. E.L.Ong and C.L.Lim, J. Rubber Res. Inst. Malaysia, 30(2), 91 (1982).

41. G.M.Bristow, NR Technol., 16, 76 (1985).

42. E.L.Ong and C.L.Lim, J. Rubber Res. Inst. Malaysia, 32(1), 63 (1983).

43. B.R.Gupta, Indian J. Nat. Rubber Res., 2(2), 134 (1989).

44. K.Lakdawala and R.Salovey, Polym. Eng. Sci., 27(14), 1035 (1987).

45. B.R.Gupta, Indian J. Nat. Rubber Res.,2(1), 38 (1989).

46. Bing Yang and Jame Lee, Polym. Eng. Sci., 27(14), 1079 (1987).

47. H.Munstedt, Polym. Eng. Sci., 21(5), 259 (1981).

48. Bing Yang and Jame Lee, Polym. Eng. Sci., 27(14), 1089 (1987).

49. A.A.Phadke and Baby Kuriakose, Kautschuk Gummi Kunststoffe, 38(8), 694 (1985).

50. Reena Susan George and Rani Joseph, Paper presented in the 6th Kerala Young Scientists Award Contest, January (27-29), Trivandrum, India, 394 (1994).

51. A.A.Phadke, Plast. Rubber Process. Appln.,6(3), 273 (1986).

52. D.M.Turner and A.C.Bickley, Plast. Rubber Process. Appln., 1(4), 357 (1981).

Chapter 4

Part I THE UTILISATION OF LATEX RECLAIM IN STYRENE-BUTADIENE RUBBER

a) In gum compounds

The study of latex reclaim in gum as well as in filled natural rubber compounds revealed that the latex reclaim can replace raw natural rubber upto about fifty weight percent without seriously affecting their mechanical and rheological properties.[1-3] So in this study the latex reclaim is tried for blending with styrene-butadiene rubber (SBR). SBR and natural rubber (NR) can be usefully blended if the fundamental differences and similarities between them are recognized.[4-12] SBR is more uniform in quality than NR. It retains its plasticity during mastication while the plasticity decreases for NR during processing. SBR compounds tend to be less scorchy than NR compounds and thus allow safer processing. While NR has good tensile strength, SBR requires reinforcing fillers such as carbon black or precipitated silica for developing comparable modulus and tensile strength.[13,14] SBR possesses better abrasion resistance than NR while the resilience is inferior to that of NR. Making use of these characteristics, blends of SBR and NR can be prepared which will give better processing, strength, ageing and resilience properties. These blends are commercially used in tyre treads, beltings, etc.

Blends of reclaimed rubber with SBR are reported to show inferior mechanical properties especially when the reclaimed rubber content is above 30% of the blend.[15] However, as in the case of latex reclaim/natural rubber blends, it may be expected that latex reclaim/SBR blends would result in better mechanical properties. Hence the present study on SBR/latex reclaim blends was undertaken.

In the first part of the study latex reclaim is incorporated in gum SBR compounds.

EXPERIMENTAL

The latex reclaim in the form of a sheet was masticated on a laboratory mixing mill and the SBR was added at different percentages and the blends were compounded as per the formulations given in Table 4.1. 100% SBR was also compounded on a mixing mill as per the formulations given in Table 4.1.

Table 4.1: Formulations and cure characteristics of SBR/LR blends

Materials	A	B	C	D	E
SBR	100	80	60	40	20
LR	0	20	40	60	80
ZnO	4	4	4	4	4
Stearic acid	2	2	2	2	2
MBTS	0.8	0.8	0.8	0.8	0.8
TMTD	0.4	0.4	0.4	0.4	0.4
Sulphur	2.0	2.0	2.0	2.0	2.0
Accinox ZC	1.0	1.0	1.0	1.0	1.0
Cure characteristics					
T_{10} (Scorch time in minutes)	3.9	3.6	2.8	2.5	2.0
T_{90} (Optimum cure time in minutes)	10.1	8.3	5.4	3.8	3.0
Maximum torque (Nm)	0.32	0.39	0.47	0.54	0.62

The optimum cure time of the compounds was determined on a Goettfert Elastograph. The compounds were then vulcanized up to their respective optimum cure times in an electrically heated hydraulic press at 150°C. Test specimens for tensile and tear strength measurements were punched out of these compression moulded sheets along the mill grain direction. The tensile properties and tear resistance of the samples were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/minute.

RESULTS AND DISCUSSION

The cure characteristics of the compounds are shown in Table 4.1. This shows that the optimum cure time and the scorch time decreases as the percentage of latex reclaim in the blend increases. It is also seen that the curing of SBR/latex reclaim blends are faster than SBR/NR blends.[4] This behaviour compares well with that of NR/LR blends and is possibly due to the presence of crosslink precursors and or unreacted curatives in the latex reclaim especially ultra accelerators like ZDC. From this table, it is also seen that the maximum torque increases with the amount of latex reclaim. This is obviously due to the increase in the total crosslink density of the rubber vulcanizates with the addition of latex reclaim as in the case of NR/LR blends.[1,2]

Fig.4.1 shows the tensile and tear strength of SBR and SBR/latex reclaim gum compounds. It shows that both these properties improve with the addition of latex reclaim as expected due to the higher tensile and tear strength of latex reclaim. Further, the linear increase in these properties may be attributed to strong interparticle bonding between latex reclaim and SBR. The increase in these properties also results from the increased crosslink density of the compounds on the addition of latex reclaim.

Fig.4.2 shows the variation in modulus and elongation at break of the rubber compounds with the addition of latex reclaim. There is a gradual increase in modulus on the addition of latex reclaim. This further confirms the increased crosslink density of the blends. It is also seen that the elongation at break decreases with the addition of latex reclaim. When the latex reclaim content is above 60 percent there is a sharp decrease in elongation at break. This may be the region in which the latex reclaim becomes the continuous phase in the blend.[1]

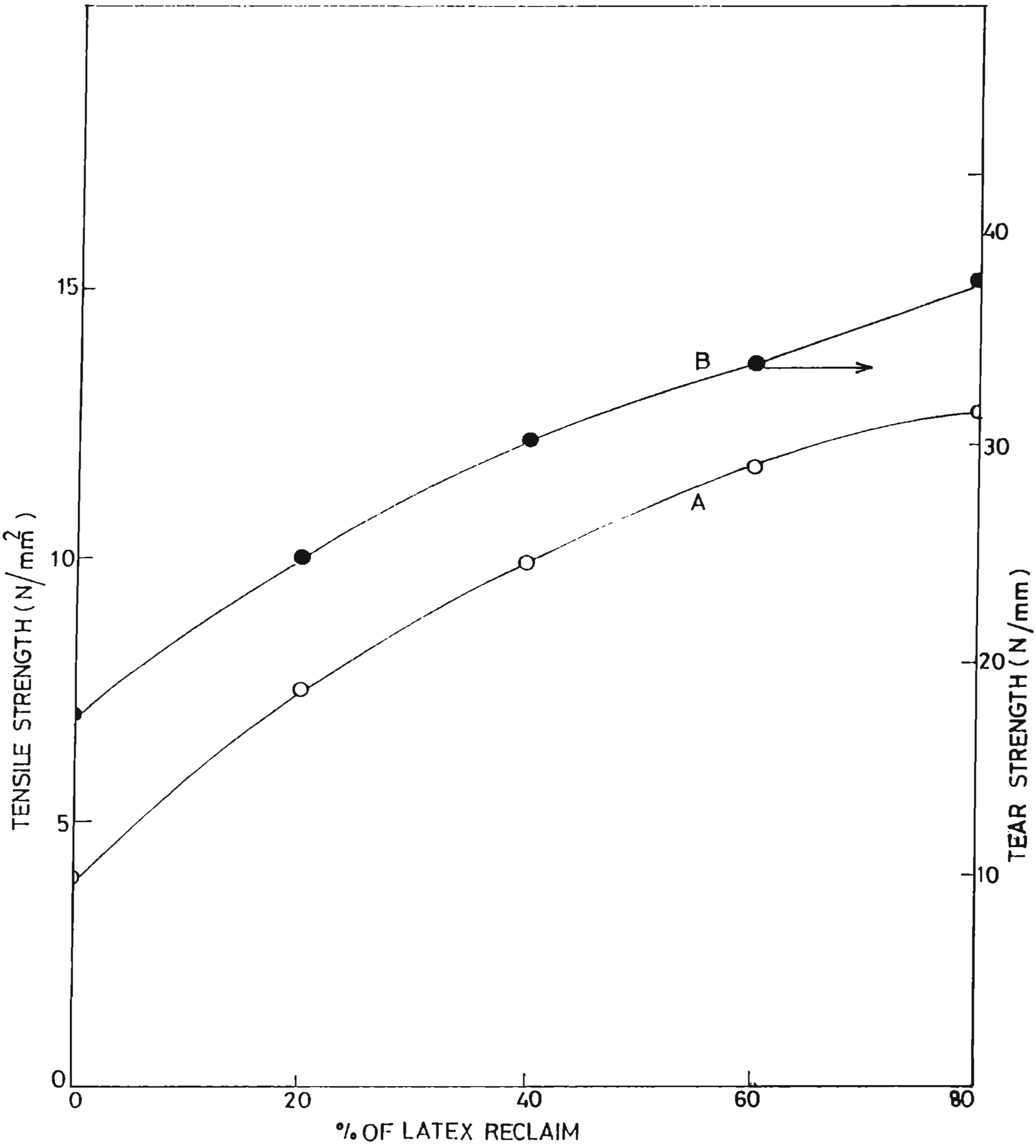

FIG.4.1: Variation in tensile strength and tear strength with latex reclaim of SBR/LR blends

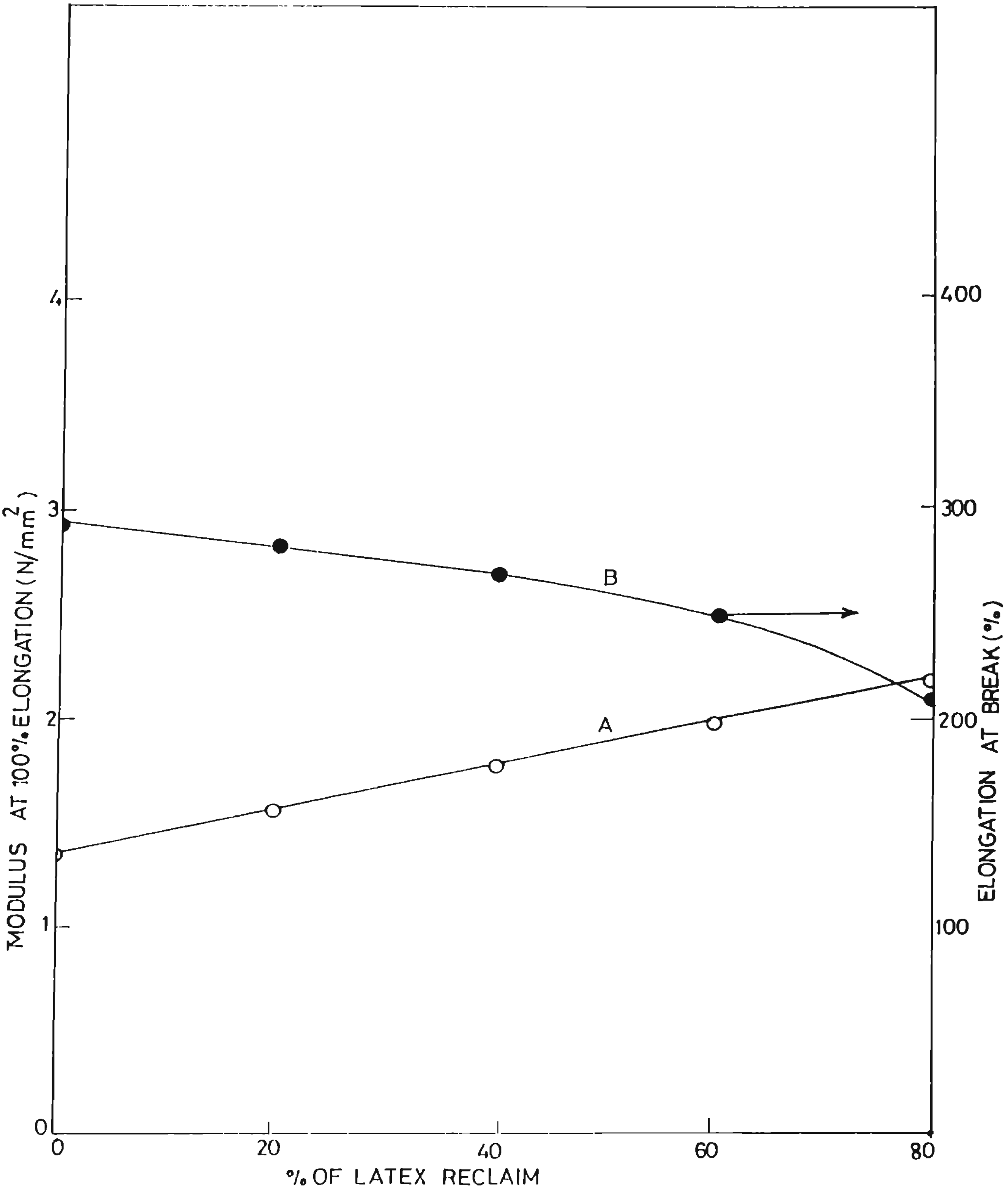

FIG.4.2: Variation in modulus and elongation at break with latex reclaim of SBR/LR blends

CONCLUSION

The study shows that the mechanical properties of styrene-butadiene rubber gum compounds can be improved with the addition of latex reclaim.

b) In filled compounds

In the second part of the study, the effect of adding latex reclaim in styrene-butadiene rubber filled compounds at various percentages was investigated.

EXPERIMENTAL

The latex reclaim in the form of a sheet was masticated on a laboratory mixing mill and the styrene-butadiene rubber was added at different percentages and the blends were compounded as per the formulations given in Table 4.2. 100% styrene-butadiene rubber and 100% latex reclaim were also compounded as per the formulations given in Table 4.2.

The optimum cure time of the compounds was determined on a Goettfert Elastograph. The compounds were then vulcanized up to their respective optimum cure times in an electrically heated hydraulic press at 150°C. Test

Table 4.2: Formulations of SBR/LR blends

Materials	A	B	C	D	E	F
SBR	100	80	60	40	20	0
LR	0	20	40	60	80	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
Carbon black	40	40	40	40	40	40
Aromatic oil	5	5	6	7	8	10
MBTS	0.8	0.8	0.8	0.8	0.8	0.8
TMTD	0.4	0.4	0.4	0.4	0.4	0.4
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0
Accinox ZC	1.0	1.0	1.0	1.0	1.0	1.0

specimens for tensile and tear strength measurements were punched out of these compression moulded sheets along the mill grain direction. The tensile properties and tear resistance of the samples were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/min. Samples for compression set, hardness, abrasion resistance, heat build up and resilience were moulded and tested as per relevant ASTM standards. The ageing resistance of the vulcanizates was studied after ageing the samples at 100°C for 24 and 48 hours in a laboratory air oven.

RESULTS AND DISCUSSION

Fig.4.3 shows the cure characteristics of the compounds. The optimum cure time and scorch time are shown in Table 4.3. This shows that both the cure time and scorch time decrease with the percentage of latex reclaim in the blends as in the case of the gum compounds. The maximum torque also increases with the addition of latex reclaim.

Fig.4.4 shows the variation in tensile strength with the amount of latex reclaim in the blends. The

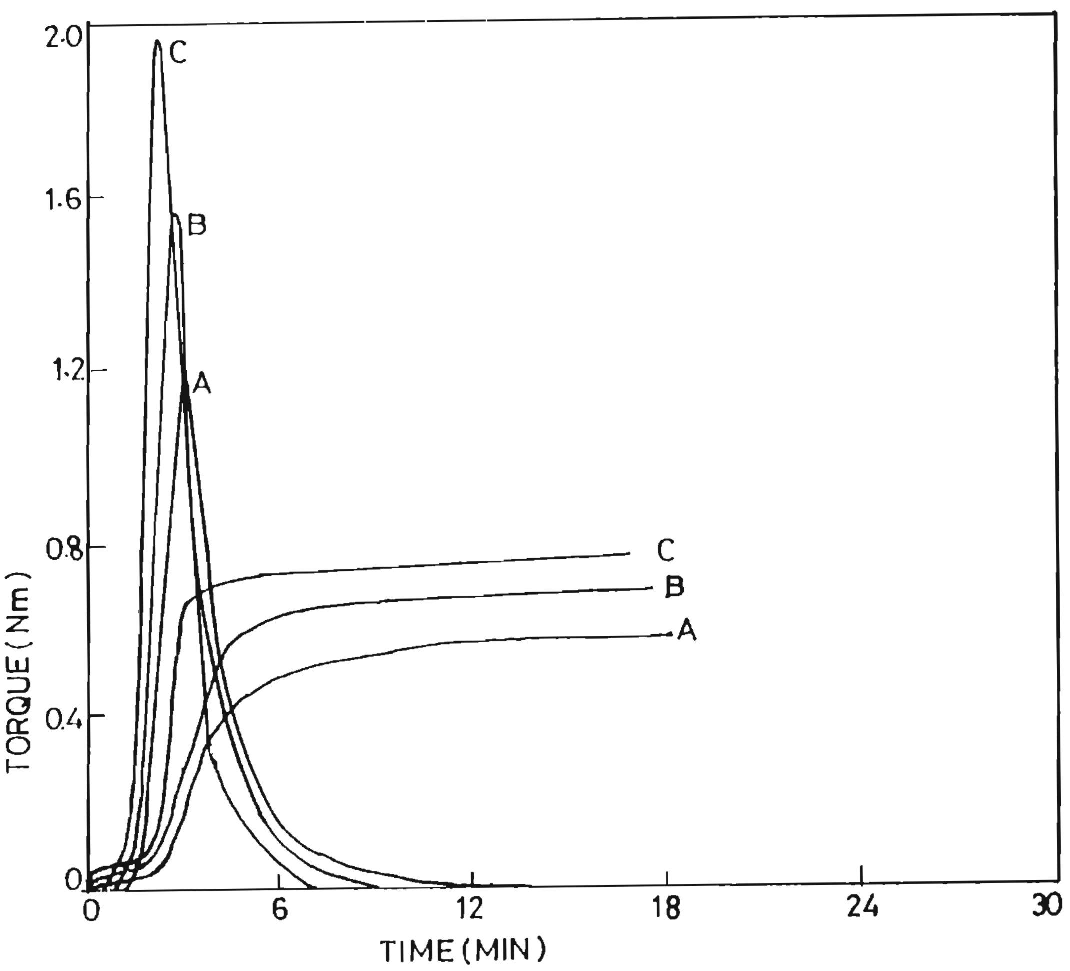

FIG.4.3: Cure curves of filled compounds

A. SBR; B. SBR/LR (50/50); C. LR

Table 4.3: Cure characteristics and vulcanizate properties of SBR/LR blends

	A	B	C	D	E	F
<u>Cure characteristics</u>						
T_{10} (Scorch time in minutes)	2.8	2.6	2.3	1.8	1.4	1.2
T_{90} (Optimum cure time in minutes)	11.1	7.8	4.8	3.9	3.4	2.6
Maximum torque (Nm)	0.56	0.59	0.64	0.69	0.73	0.76
<u>Vulcanizate properties</u>						
Compression set (%)	22.86	22.06	21.36	20.86	20.48	20.21
Hardness (Shore A)	55	57	59	61	63	65
Abrasion resistance (cc/h)	4.2	4.7	5.3	5.9	6.6	7.1
Heat build up (°C)	35	34	33.08	32.67	32.16	31.24
Resilience (%)	44.86	45.61	45.82	46.11	46.56	46.92

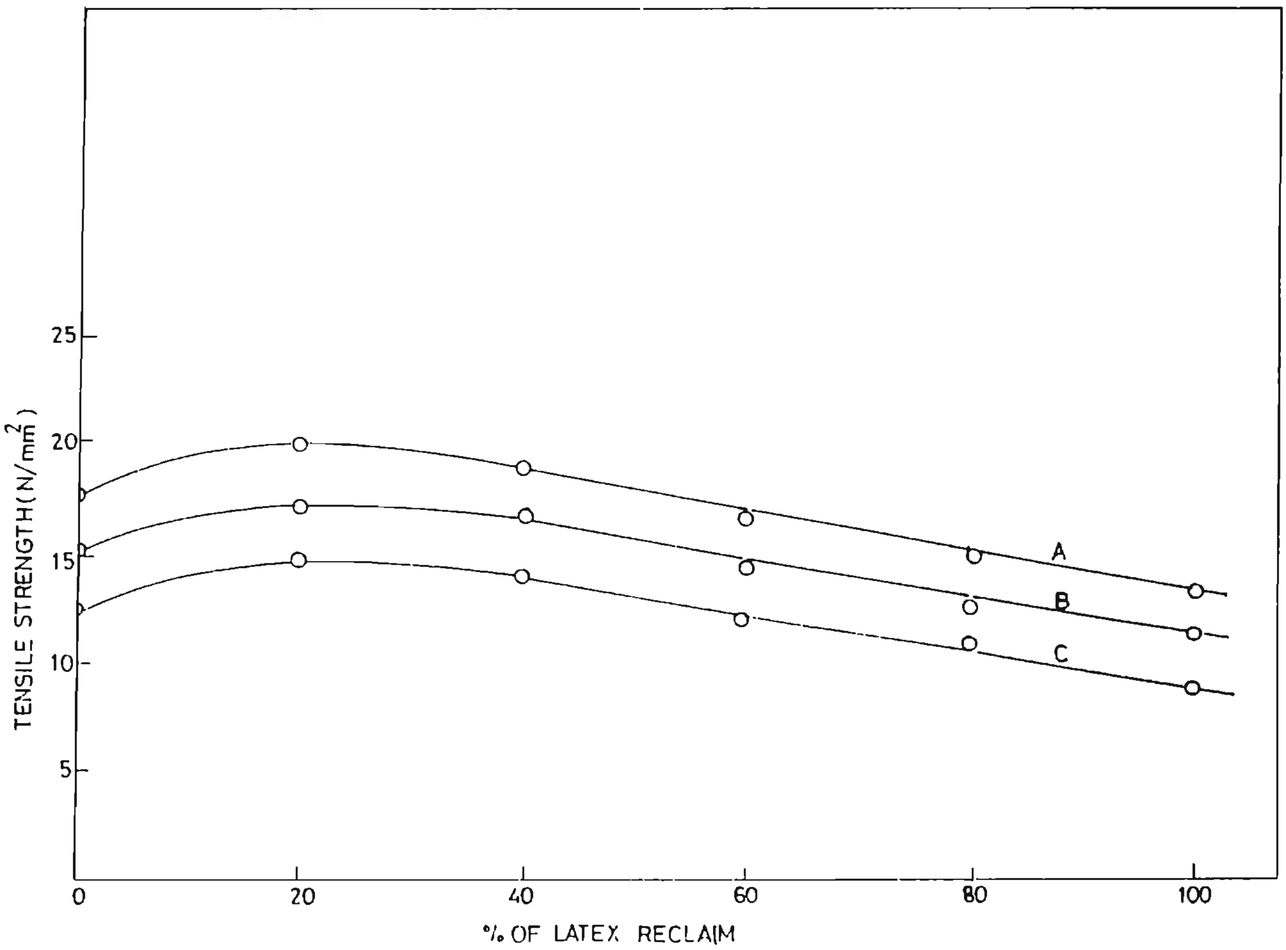

FIG.4.4: Variation in tensile strength with latex reclaim of SBR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

tensile strength first increases as in the case of styrene-butadiene rubber/latex reclaim gum vulcanizate. The tensile strength then decreases when the percentage of latex reclaim in the blend is above sixty percent. This may be the region where the latex reclaim forms a continuous phase.[1] The ageing resistance of the blends also follows a similar pattern.

The variation in tear strength with the addition of latex reclaim is shown in Fig.4.5. There is a gradual increase in tear strength initially and then it slightly decreases with the addition of latex reclaim as in the case of the tensile strength. The retention in tear strength of the samples containing latex reclaim is similar to the retention in tensile strength. It again confirms the strong interparticle bonding between the latex reclaim and styrene-butadiene rubber in the original as well as in the aged samples.

Fig.4.6 shows the variation in modulus with the amount of latex reclaim and the retention in modulus with ageing. There is a gradual increase in modulus with the addition of latex reclaim. This may be attributed to the

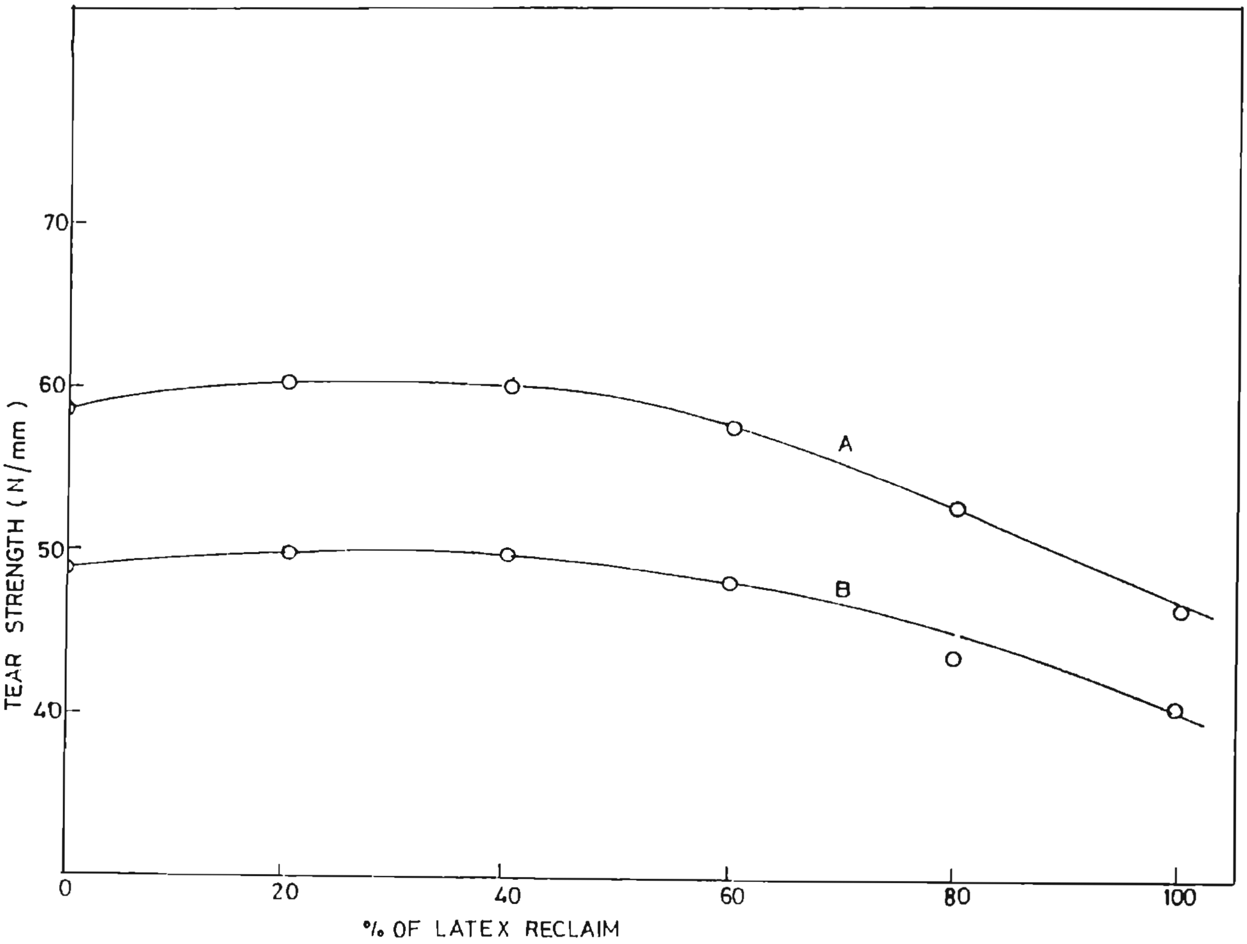

FIG.4.5: Variation in tear strength with latex reclaim of SBR/LR blends

A. Original; B. Aged 24 h, 100°C

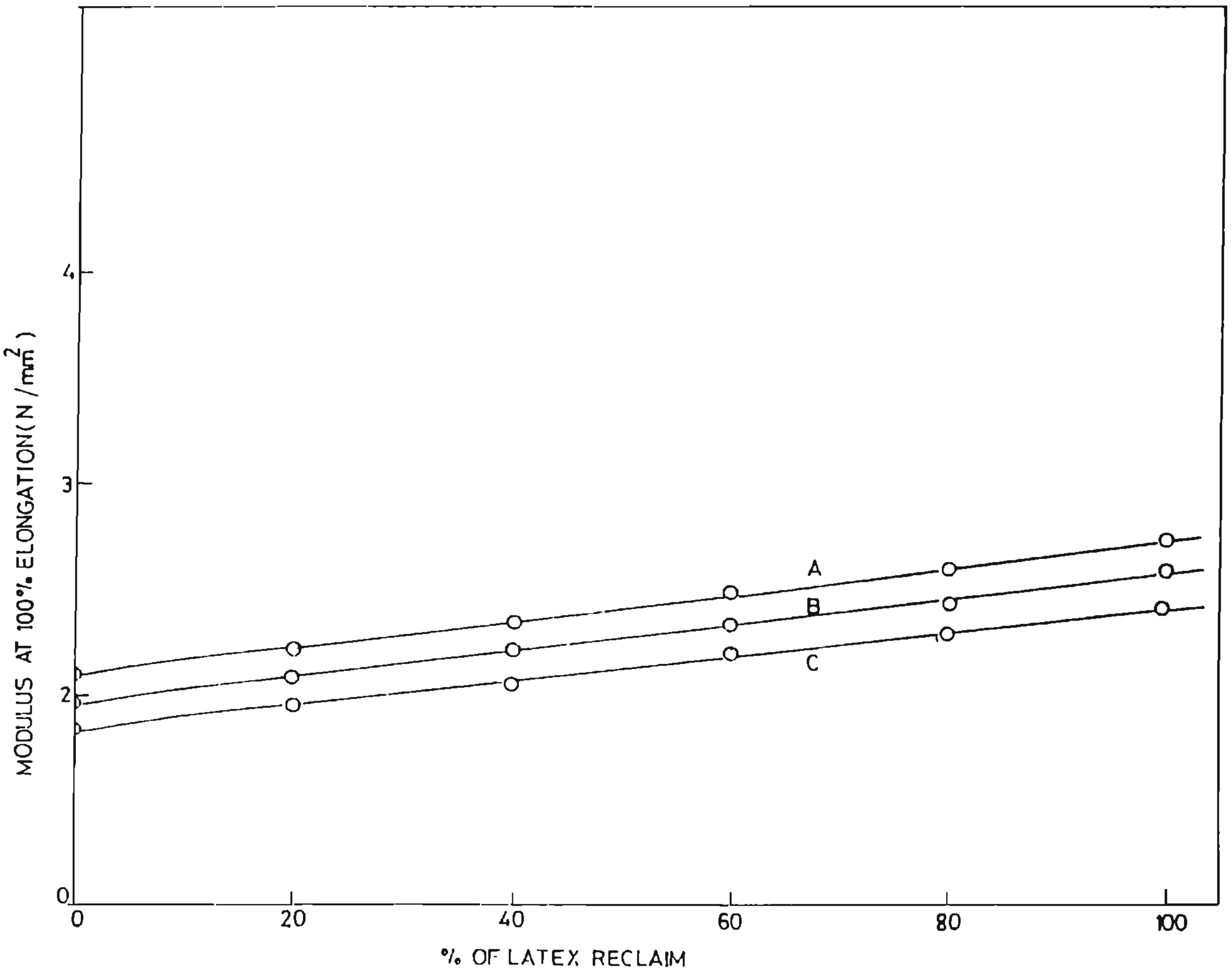

FIG.4.6: Variation in modulus with latex reclaim of SBR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

increased amount of crosslink density in the blends.

The variation in elongation at break with the addition of latex reclaim and its retention after ageing is shown in Fig.4.7. The reduction in elongation at break at higher percentages of latex reclaim may also be due to the higher crosslink density in the blends.

Hardness increases with increase in the amount of latex reclaim as expected (Table 4.3). The compression set decreases with the addition of latex reclaim (Table 4.3) which further confirms the increased crosslink density in the blends.

The resilience (Table 4.3) slightly increases with increasing amount of latex reclaim as in the case of SBR/NR blends.[16]

The abrasion resistance registers only marginal changes initially and decreases at higher concentrations of latex reclaim (Table 4.3). The variation in heat build up is inversely proportional to that of resilience as expected.

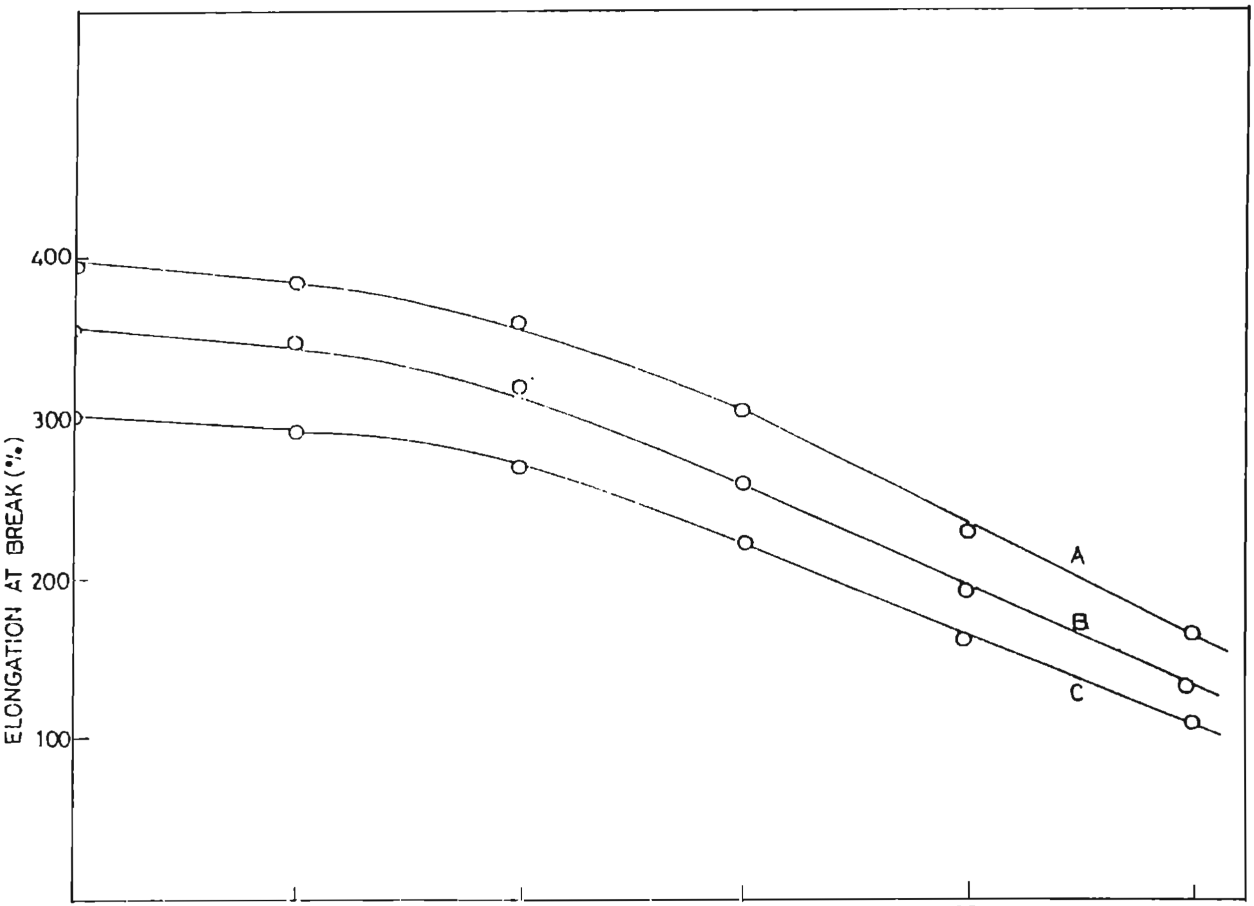

FIG.4.7: Variation in elongation at break with latex reclaim in SBR/LR blends

A. Original; B. Aged 24 h, 100°C; C. Aged 48 h, 100°C

CONCLUSION

The study shows that latex reclaim can be advantageously employed for developing styrene-butadiene rubber/natural rubber blends economically. Mechanical properties of styrene-butadiene rubber/latex reclaim are superior to those of styrene-butadiene rubber/rubber reclaim blends. The properties of styrene-butadiene rubber improve upto about 60% of latex reclaim in the blend.

Part II INVESTIGATION OF THE PROCESSABILITY OF STYRENE BUTADIENE RUBBER/LATEX RECLAIM BLENDS USING A TORQUE RHEOMETER

Melt flow behaviour of polymers is of great importance in optimising the processing parameters. The concept of 'processability' of a rubber mix is closely related to its plasticity or its elastic recovery during shaping. A lot of literature is available on the melt flow behaviour of elastomers and their blends.[17-27]

The rubber industry operates with devices imparting shear stresses and shear rates over a wide range. Therefore the viscosity of a polymer as a function of shear rate and temperature is very important. To be able to investigate the processability of a material, laboratory conditions must simulate operating conditions as closely as possible. Among the testing devices developed, Brabender plasticorder is commonly used for determining the processability of a material.[28-31] In this study the processing characteristics of latex reclaim, styrene-butadiene rubber and their blends are evaluated using a Brabender plasticorder.

EXPERIMENTAL

The styrene-butadiene rubber, latex reclaim and their blend compounds were mixed on a two roll mixing mill as per the formulations given in Table 4.2. Processability studies of the above compounds were done on a Brabender plasticorder at different temperatures (80, 100 and 120°C) and at different shear rates (20, 40 and 60 rpms).

RESULTS AND DISCUSSION

Fig.4.8 illustrates the effect of viscosity (torque/rpm) of the compounds with shear rate at a temperature of 80°C. It shows that the viscosity of styrene-butadiene rubber compounds decreases with the addition of latex reclaim and also with the shear rates. It may also be observed that the addition of latex reclaim up to 20% does not change the viscosity of styrene-butadiene rubber significantly.

Fig.4.9 shows the variation of torque with rpm. The power law index was calculated as the slopes of the log (torque) vs. log (rpm) lines. Variation of power law index with temperature (80, 100 and 120°C) for the rubber compounds is shown in Table 4.4. The value of the power

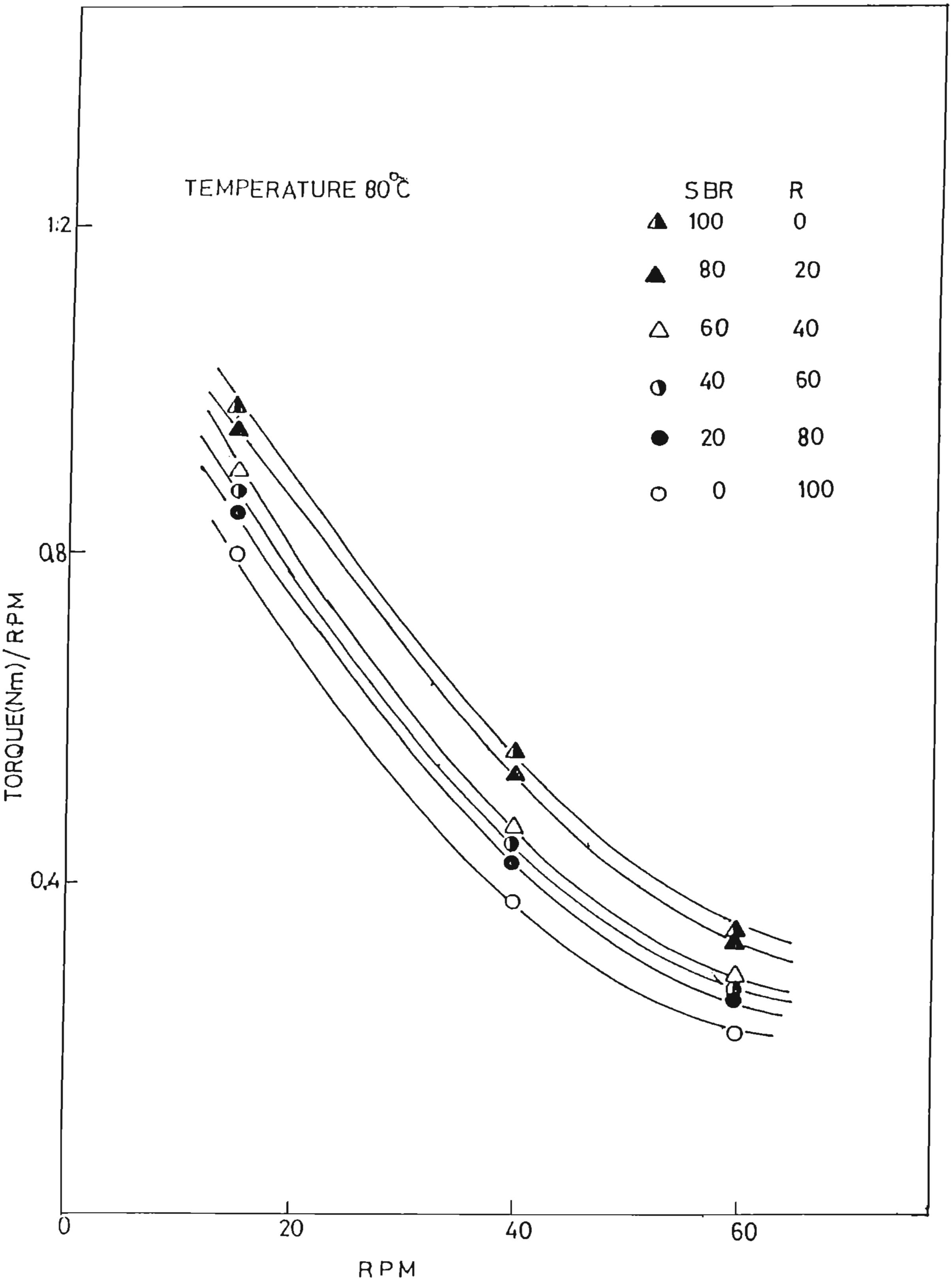

FIG.4.8: Variation in viscosity with shear rate of SBR/LR blends at 80°C

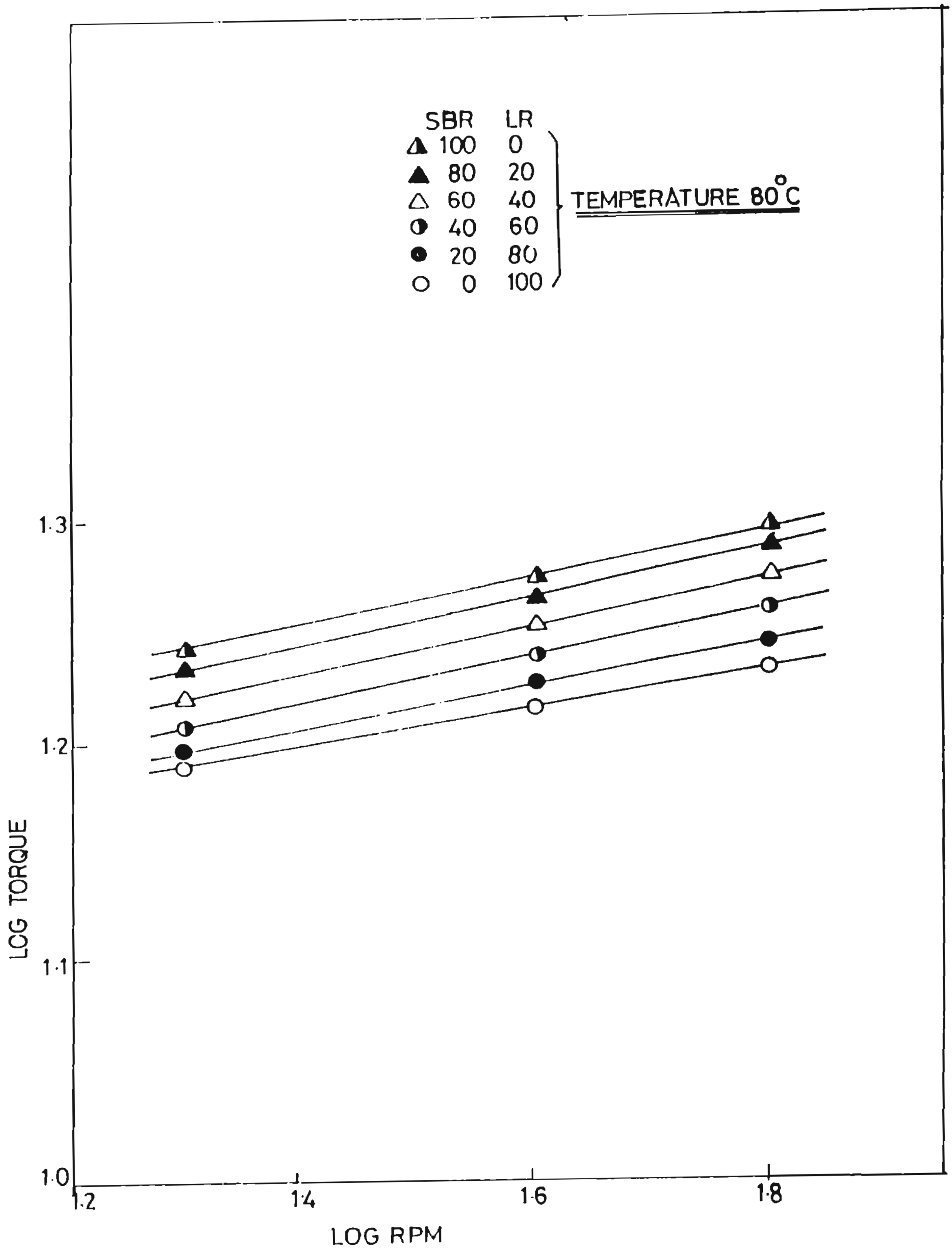

FIG.4.9: Variation in torque with shear rate of SBR/LR blends at 80°C

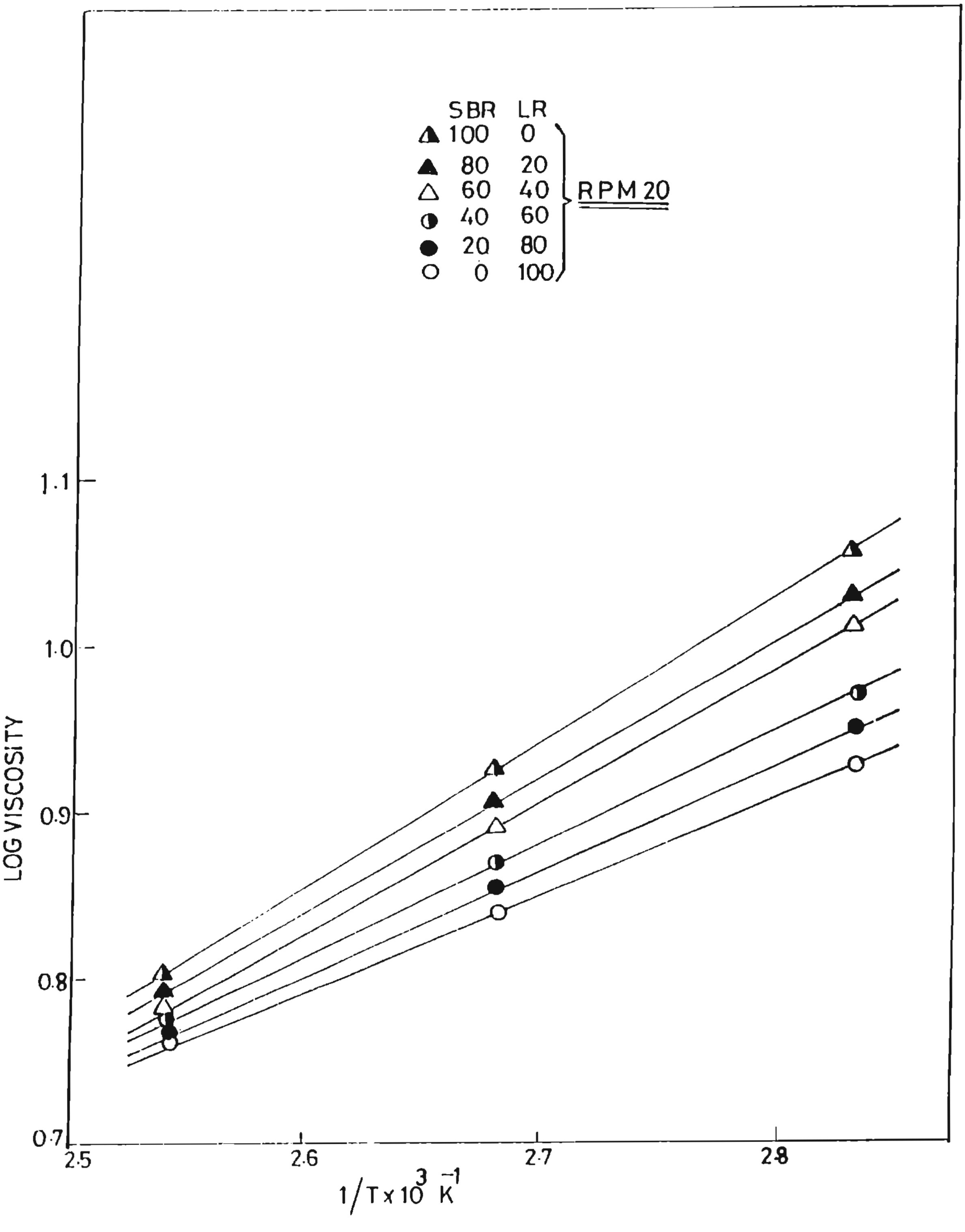

FIG.4.10: Variation in viscosity with temperature of SBR/LR blends at 20 rpm

Table 4.4: Power law index values (n) of SBR/LR blends

Blend composition (Percentage of latex reclaim)	Power law index values at a temperature of		
	80°C	100°C	120°C
0	0.32	0.28	0.27
20	0.30	0.27	0.26
40	0.28	0.26	0.25
60	0.25	0.24	0.23
80	0.22	0.21	0.20
100	0.19	0.18	0.17

Table 4.5: Activation energy of viscous flow (E) of SBR/LR blends

Blend composition (Percentage of latex reclaim)	Activation energy (kJ mol^{-1}) at various rpms		
	20	40	60
0	6.67	5.99	5.44
20	6.23	5.56	5.26
40	5.86	5.34	5.18
60	4.43	4.19	4.11
80	3.24	3.07	3.04
100	3.08	2.97	2.95

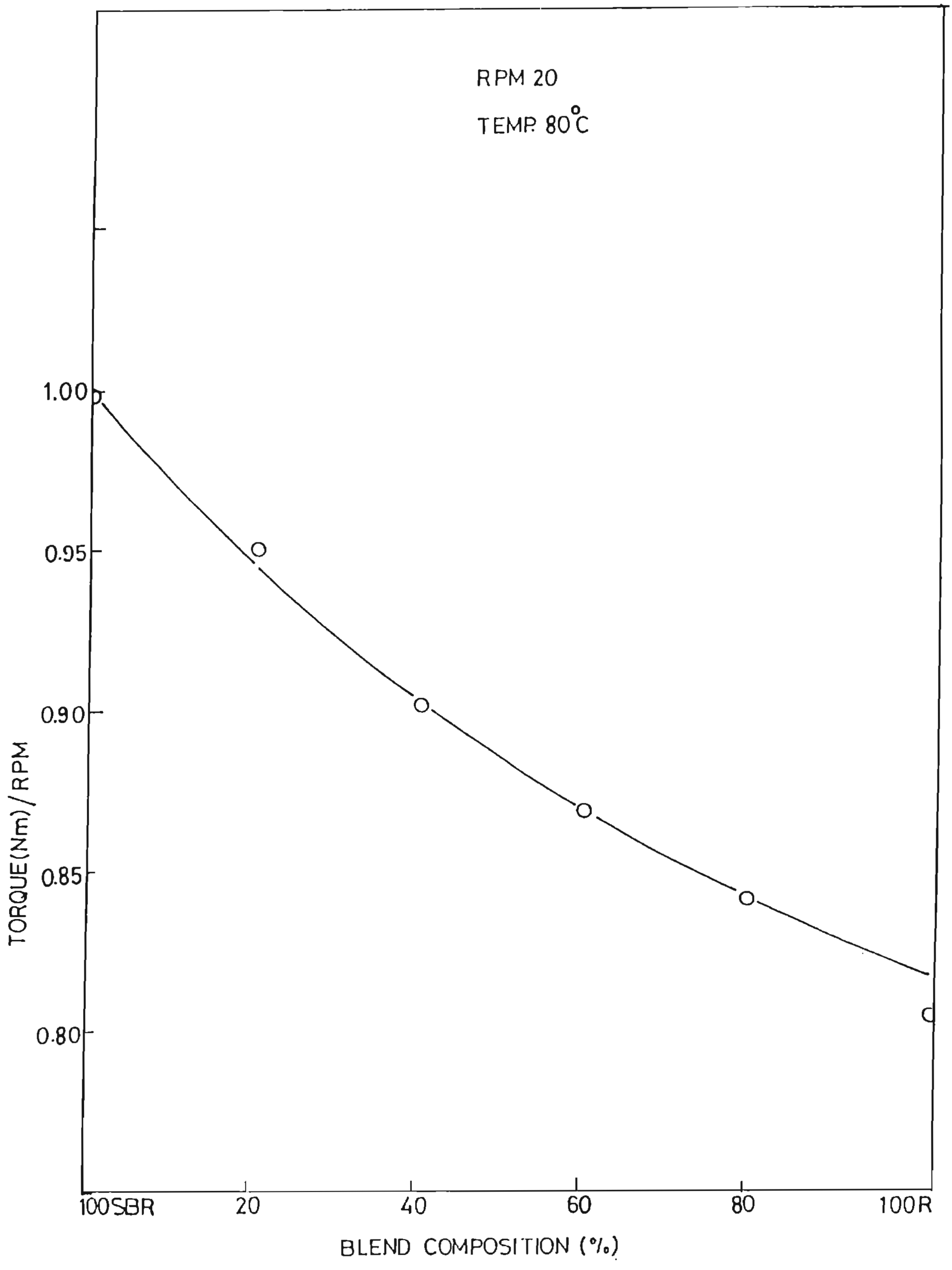

FIG.4.11: Variation in viscosity with latex reclaim of SBR/LR blends

law index decreases with increase in temperature and with the percentage of latex reclaim, which means that the blends become more pseudoplastic as expected.

Fig.4.10 permits the calculation of activation energies of viscous flow of the rubber compounds. In this figure, logarithm of torque/rpm is plotted as a function of reciprocal temperature. The activation energy (E) of flow, calculated from the slope of these lines is given in Table 4.5. It shows that styrene-butadiene rubber has a higher activation energy compared to latex reclaim. Consequently, styrene-butadiene rubber rich blends show slightly higher activation energies. However, all the blends have an activation energy intermediate between those of the components.

Fig.4.11 shows the variation in viscosity of the blends with the percentage of latex reclaim. The viscosity decreases with the amount of latex reclaim as expected in the case of SBR/NR blends.

CONCLUSION

1. The viscosity of styrene-butadiene rubber filled compounds decreases with the addition of latex reclaim.

2. The styrene-butadiene rubber/latex reclaim blends are more pseudoplastic in nature compared to pure styrene-butadiene rubber compound.

REFERENCES

1. Reena Susan George and Rani Joseph, Die Angew.Makromol. Chemie, 215, 25 (1994).

2. Reena Susan George and Rani Joseph, Paper presented in the 6th Kerala Science Congress, Jan. (27-29), 394 (1994).

3. Reena Susan George, Rani Joseph, K.E.George and D.Joseph Francis, J. Elast. Plast.,(In press).

4. F.Gharavi and A.A.Katbab, Prog. Rubber Plast. Technol., 6(2), 129 (1990).

5. M.Shundo, M.Imoto and Y.Minoura, J. Appl. Polym. Sci., 10, 930 (1966).

6. J.B.Gardiner, Rubber Chem. Technol., 43, 370 (1970).

7. Bruce C.Copley, Rubber Chem. Technol., 55, 416 (1982).

8. P.Thavamani and Anil K.Bhowmick, Plast. Rubber Comp. Process. Appln., 20(4), 239 (1993).

9. N.P.Shuydkaya, L.A.Shumanov and A.S.Lykin, Int. Polym. Sci. Technol., 9(9), T/14 (1982).

10. M.Nasir and C.H.Choo, Eur. Polym. J., 25(4), 355 (1989).

11. T.A.Chavchich, L.B.Nikitina, V.V.Senik and N.Borodushkina, Int. Polym. Sci. Technol., 10(9), T/29 (1983).

12. Yu F.Shutilin, A.P.Bobrov and A.P.Zvonkova, Int. Polym. Sci. Technol., 14(4), T/97 (1987).

13. M.Porter, Rubber Chem. Technol., 40, 866 (1967).

14. A.K.Bhowmick and S.K.De, Rubber Chem. Technol., 53, 1015 (1980).

15. R.A.Swor, L.W.Jensen and M.Budzol, Rubber Chem. Technol., 53, 1215 (1980).

16. R.J.Brown, R.B.Knill, J.F.Kersher and R.V.Todd, Rubber Chem. Technol., 35, 546 (1962).

17. A.V.Baranov, L.N.Prokhorova, V.I.Skok and M.E.Vikulenkova, Int. Polym. Sci. Technol., **20**(8), T/27 (1993).

18. R.H.Norman and P.S.Johnson, Rubber Chem. Technol., **54**, 493 (1981).

19. R.Brezik, Int. Polym. Sci. Technol., **11**(12), T/76 (1984).

20. G.S.Kongarov and G.M.Bartnev, Rubber Chem. Technol., **46**, 1188 (1973).

21. D.Sinha, S.Bandhyopadhyay, S.Kole and C.K.Das, Plast. Rubber Process. Appln.,**5**(3), 203 (1985).

22. V.L.Folt and R.W.Smith, Rubber Chem. Technol., **46**, 1193 (1973).

23. S.V.Usachev, N.D.Zakharov, V.N.Kuleznev and A.B.Vetoshkin, Int. Polym. Sci. Technol., 7, T/48 (1978).

24. G.N.Avgeropoulos, F.C.Weissert, P.H.Biddison and G.G.A.Bohm, Rubber Chem. Technol., **49**, 93 (1976).

25. L.F.Ramos-Devalle, Rubber Chem. Technol., 55, 1311 (1982).

26. Yu F.Shutilin, A.I.Dmitrenkov, M.P.Parinova and V.S.Shein, Int. Polym. Sci. Technol., 15(9), T/24 (1988).

27. J.L.White, Rubber Chem. Technol., 50, 163 (1977).

28. I.Mathew, K.E.George and D.J.Francis, Kautschuk Gummi Kunststoffe, 44(5), 450 (1991).

29. J.E.Goodrich and R.S.Porter, Polym. Eng. Sci., 7, 45 (1967).

30. L.L.Blyler and J.H.Daane, Polym. Eng. Sci., 7, 178 (1967).

31. Z.Bartha, P.Erdos and J.Matis, Int. Polym. Sci. Technol., 10(6), T/50 (1983).

Chapter 5

Part 1: STUDIES ON POLYPROPYLENE/LATEX RECLAIM BLENDS

The polyolefin/elastomer blends can be prepared by physical blending in an internal mixer at a temperature above the melting point of the thermoplastic. These blends have gained considerable attention due to the easiness of preparation and the versatility of attaining the required technical properties. The desired properties can be achieved by proper selection of elastomer and thermoplastic component and their ratios in the blend. In polyolefin/ elastomer blends, the effect of characteristics of the components, blend ratios and dynamic crosslinking of the elastomer phase on the technical properties, processing characteristics and failure mechanisms of the resulting blends have already been reported.[1-9] It has been further shown that the addition of a small quantity of crosslinking agent during melt mixing of the polyolefin and the elastomer improves the elastomeric properties of the blend.[10-15] In earlier investigations, it has also been reported that latex reclaim in elastomer blends increases the crosslink density of the blends.[16-18]

The present study was undertaken to understand the effect of adding latex reclaim to polypropylene because of the commercial importance of polypropylene/natural rubber blends. The mechanical properties of the polypropylene/latex reclaim blends were compared with those of polypropylene/natural rubber blend.

EXPERIMENTAL

The blends were prepared on a Brabender Plasticorder model PL3S equipped with roller mixing heads as per formulations given in Table 5.1. The elastomer phase was added upto 60 phr of the blend. Mixing was done at 190°C and 40 rpm. Polypropylene was melted in the mixer for 1 minute and then natural rubber/latex reclaim containing the additives was added and the mixing was continued for 5 minutes. For blends containing dicumyl peroxide curative system, DCP was added after 4 minutes blending of polypropylene and natural rubber/latex reclaim containing other additives and then the mixing was continued for 1 minute. The mix was then taken out and sheeted on a laboratory mixing mill at 2.0 mm nip setting. The sheeted material was cut into small pieces and again mixed in the plasticorder at 190°C for 1 minute so as to

Table 5.1: Formulations of polypropylene/elastomer blends

Materials	A	B	C	D	E	F	G
PP	100	90	80	70	60	50	40
NR or LR	0	10	20	30	40	50	60
Additives	a,b,c,e	a,b,c,d,e	a,b,c,d,e	a,b,c,d,e	a,b,c,d,e	a,b,c,d,e	a,b,c,d,e

a- Blends containing 1.0 phr Accinox ZC for the rubber phase.

b- Blends containing 5.0 phr zinc oxide, 2.0 phr stearic acid and 1.0 phr Accinox ZC for the rubber phase.

c- Blends containing 2.0 phr stearic acid, 1.0 phr Accinox ZC for the rubber phase and 2.0 phr dicumyl peroxide for the plastic phase.

d- Blends containing 5.0 phr zinc oxide, 2.0 phr stearic acid, 0.6 phr MBTS, 0.2 phr TMTD, 2.5 phr sulphur and 1.0 phr Accinox ZC for the rubber phase.

e- Blends containing 5.0 phr zinc oxide, 2.0 phr stearic acid, 0.6 phr MBTS, 0.2 phr TMTD, 2.5 phr sulphur 1.0 phr Accinox ZC for the rubber phase and 1 phr dicumyl peroxide for the plastic phase.

Note: Indices 1, 2 denote the blends containing NR, LR respectively [eg. a_1 denotes the blend containing NR with 'a' type additives and a_2 denotes the blend containing LR with 'a' type additives].

get uniform dispersion of the ingredients. After mixing, it was compression moulded in an electrically heated hydraulic press at 190°C for 3 minutes. The mould used was provided with bolts and nuts so that the material inside could be held under pressure even after taking out the mould from the press. At the end of the moulding time, the sample, still under compression, was immediately cooled by plunging the mould into cold water. Aluminium foils were used between the mould surfaces to reduce shrink marks on the sheets.

Tensile testing of the samples was done as per ASTM D 412-80 test method at a crosshead speed of 50 mm/min. using a Zwick universal testing machine.

Rheological measurements of the uncrosslinked (b) and crosslinked (e) blends were done on the Brabender plasticorder at a temperature of 190°C and 40 rpm rotor speed. The dependence of the viscosity (torque/rpm) of these blends with the percentage of polypropylene was evaluated by taking the torque values of the blends after mixing for 5 minutes.

The scanning electron microscope observations of the tensile failure surface of the uncrosslinked 90/10, 80/20, 70/30, 60/40, 50/50 and 40/60 polypropylene/latex reclaim blends (b) were made using a JEOL JSM 35C SEM.

RESULTS AND DISCUSSION

Fig. 5.1 shows the variation in tensile strength of the uncrosslinked polypropylene/natural rubber blend (a_1 and b_1) and polypropylene/latex reclaim blend (a_2 and b_2) with the amount of polypropylene. The tensile strength of the blends decreases with an increase in the rubber content of the blends as expected.[19] In blends containing a higher proportion of polypropylene, the elastomer phase remains as dispersed particles. Smaller size and uniform dispersion of the dispersed phase improve the tensile properties of the blends.[13] In uncrosslinked blends, the molecular entanglements in the rubber particles alone are unable to prevent rapid flow and fracture in response to an applied stress.[20] This results in lower tensile strength of the uncrosslinked blends. It may be noted that the tensile strength of the blends with latex reclaim is slightly higher than those of the blends with natural rubber. This may be due to the partially crosslinked nature of the latex reclaim.

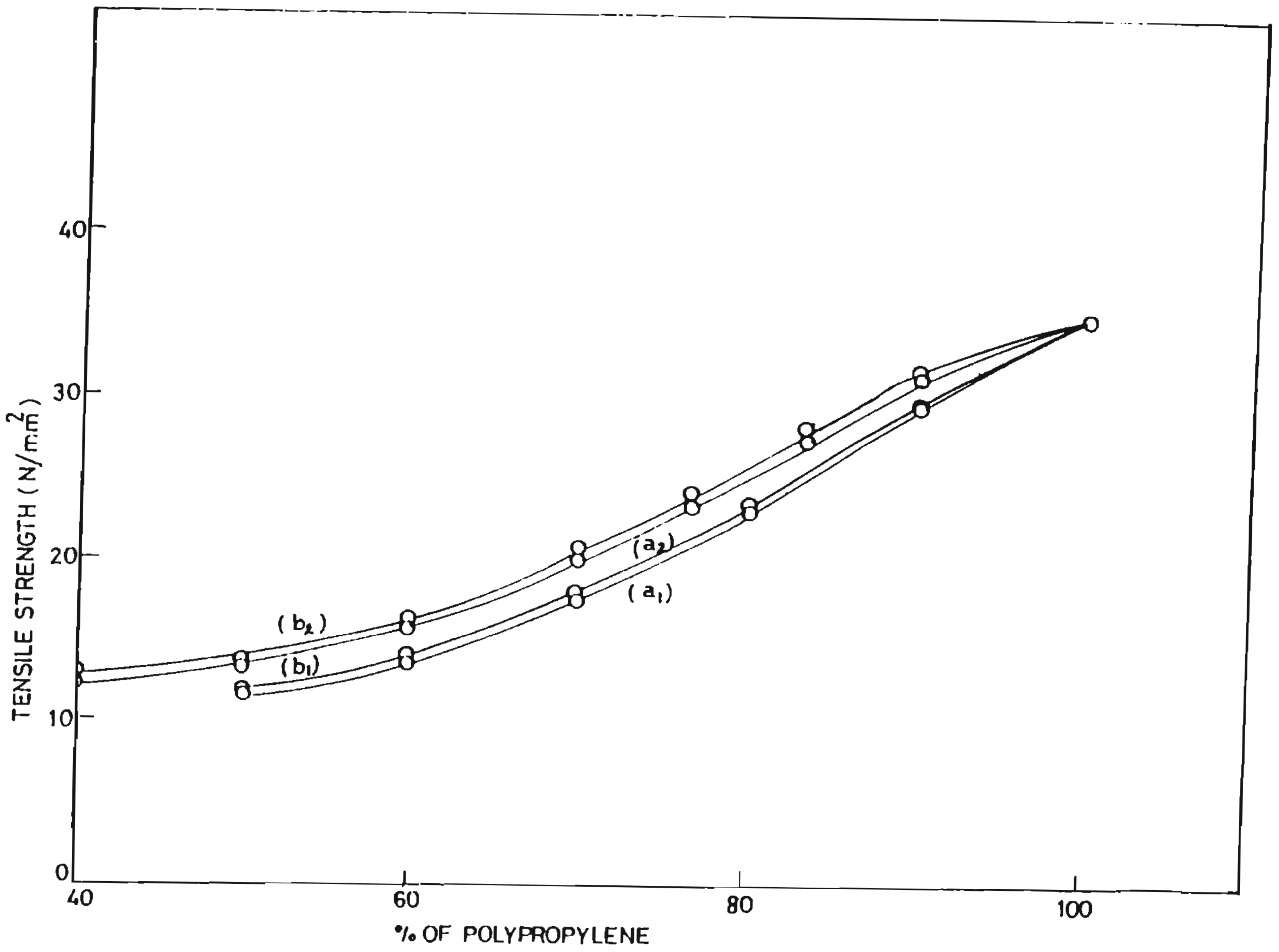

FIG.5.1: Variation in tensile strength with polypropylene of uncrosslinked a_1, b_1 (PP/NR); a_2, b_2 (PP/LR) blends

Fig. 5.2 shows the variation in tensile strength of the crosslinked polypropylene/natural rubber blend (c_1, d_1 and e_1) and polypropylene/latex reclaim blend (c_2, d_2 and e_2) with percentage of polypropylene. The tensile strength of the dynamically crosslinked blends are found to be higher than those of the uncrosslinked blends. Crosslinking of the elastomer phase allows the rubber particles to reach higher strains and at the same time confers mechanical strength to the particles.[20] In the case of dicumyl peroxide cured blends (c), the reduction in tensile strength is probably due to the molecular degradation of polypropylene at the processing temperature in presence of the peroxide.[21] Curing improves tensile strength, the maximum improvement being observed for the thermoplastic elastomer containing 'e' type curatives.

Figs. 5.3 and 5.4 show the variation in elongation at break with polypropylene content of uncrosslinked and dynamically crosslinked blends respectively. The elongation at break was found to be higher for the crosslinked blends and the maximum improvement is observed for the blends crosslinked with dicumyl peroxide and sulphur (e). For both uncrosslinked and dynamically

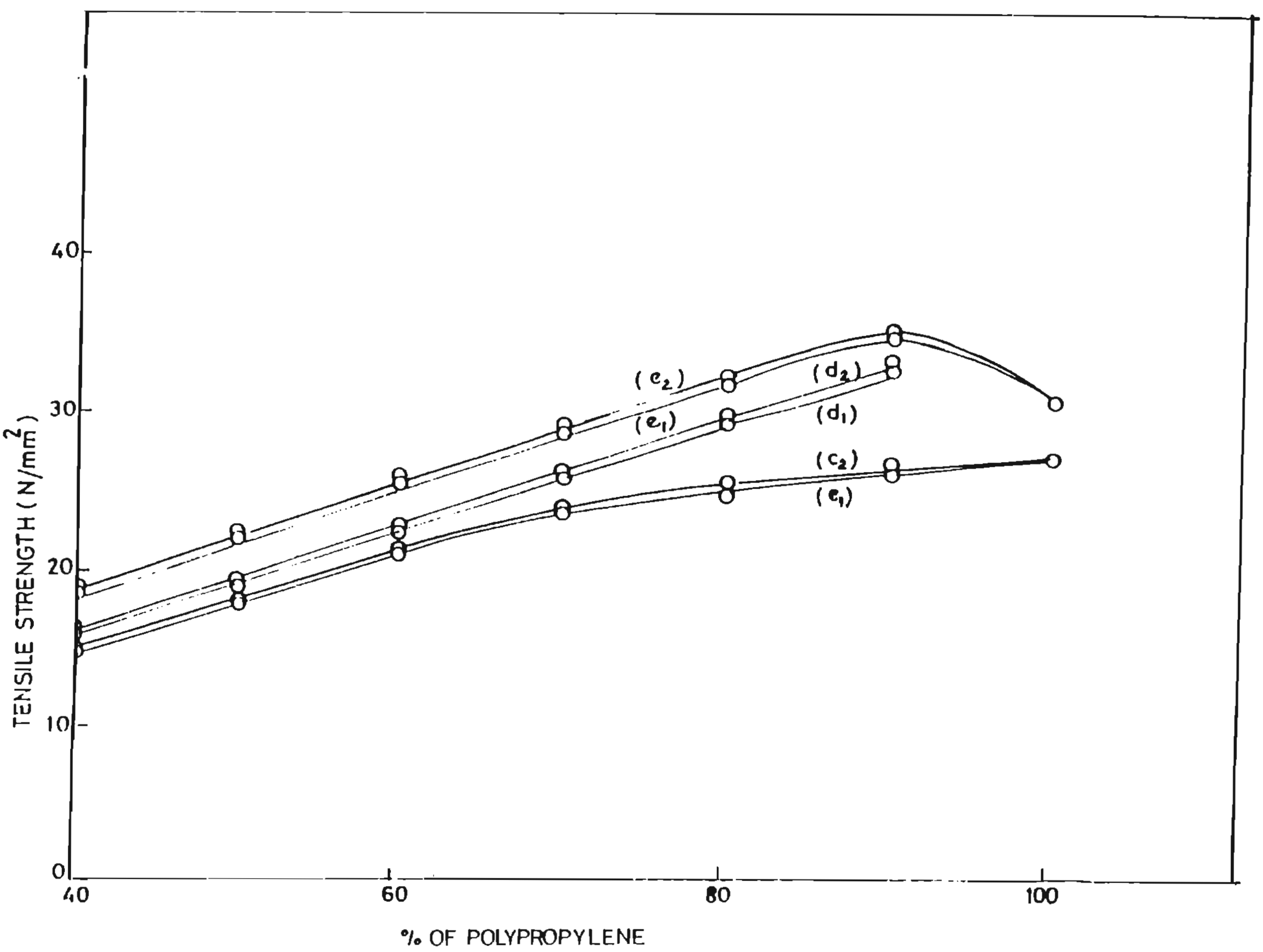

FIG.5.2: Variation in tensile strength with polypropylene of crosslinked c_1, d_1, e_1 (PP/NR); c_2, d_2, e_2 (PP/LR) blends

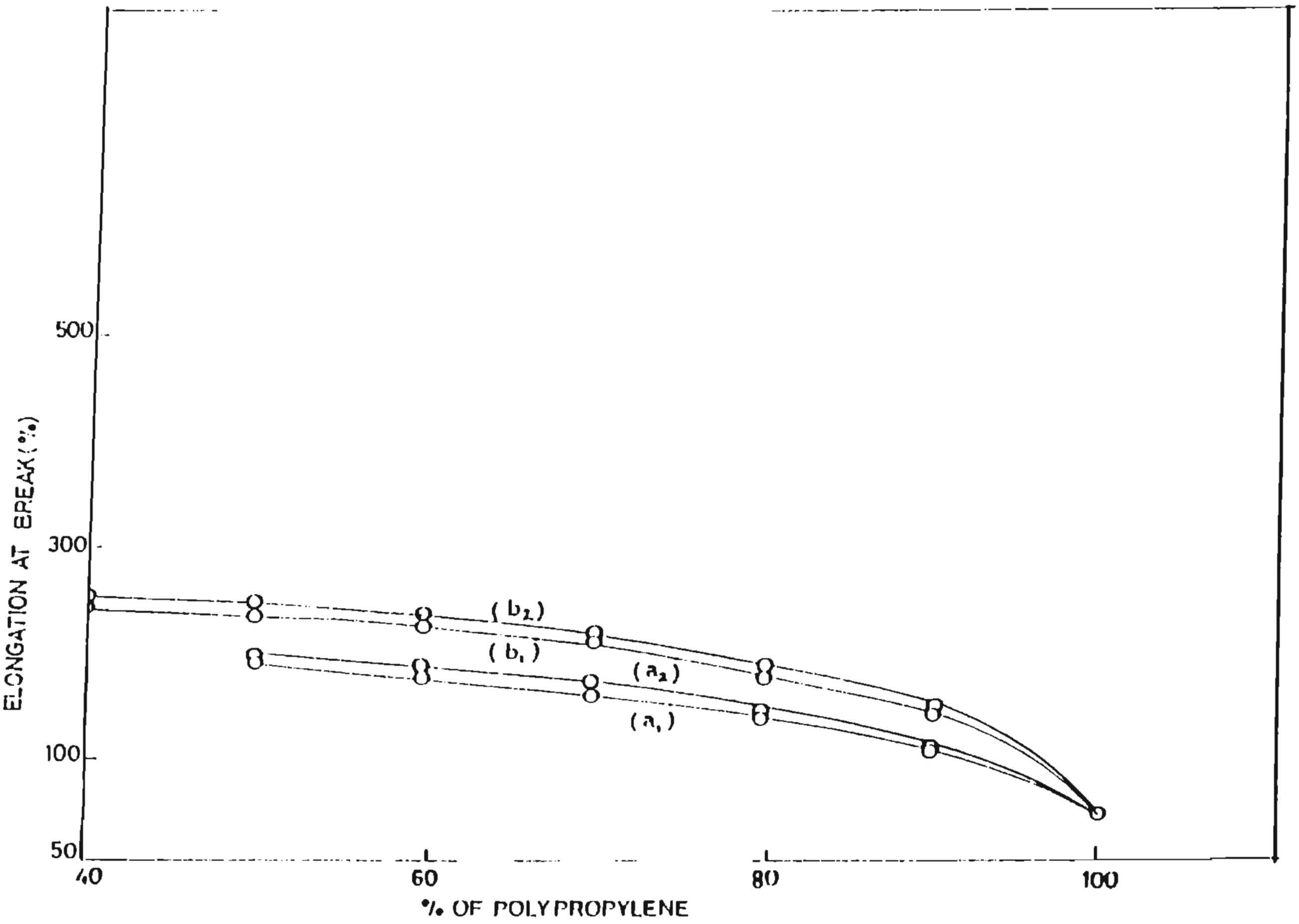

FIG.5.3: Variation in elongation at break with polypropylene of uncrosslinked a_1, b_1 (PP/NR); a_2, b_2 (PP/LR) blends

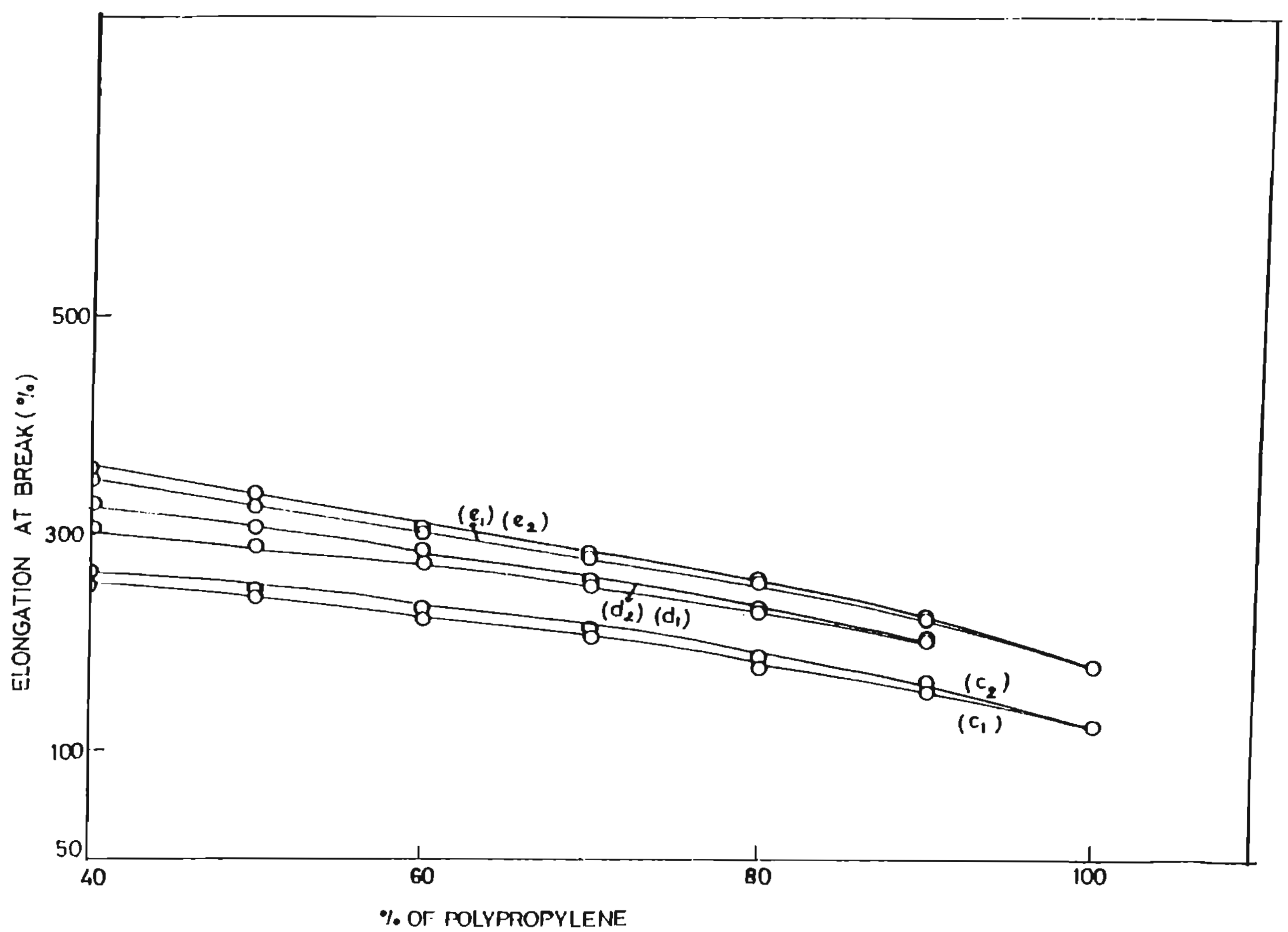

FIG.5.4: Variation in elongation at break with polypropylene of crosslinked c_1, d_1, e_1 (PP/NR): c_2, d_2, e_2 (PP/LR) blends

crosslinked blends, the elongation at break of the polypropylene/latex reclaim blends is found to be higher than those of polypropylene/natural rubber blends. This result may be attributed to the partially crosslinked nature of latex reclaim.

Fig. 5.5 shows the variation of blend viscosity (Torque/rpm) with the percentage of polypropylene of uncrosslinked (b) and crosslinked (e) blends. It shows that the proportion of elastomer phase in the blend and the extent of dynamic crosslinking have a profound influence on the viscosity of the blends. The uncrosslinked blends show lower viscosity compared to that of the crosslinked blends. The viscosity increases with percentage of rubber in the blends. Crosslinking of the elastomer phase increases its viscosity and decreases the deformation of the dispersed particles as indicated by the increase in Brabender mixing torque values. The viscosities of the polypropylene/latex reclaim blends are found to be slightly higher than those of the polypropylene/natural rubber blends as expected.

The morphological studies of the polypropylene/latex reclaim blends were made using the uncross-

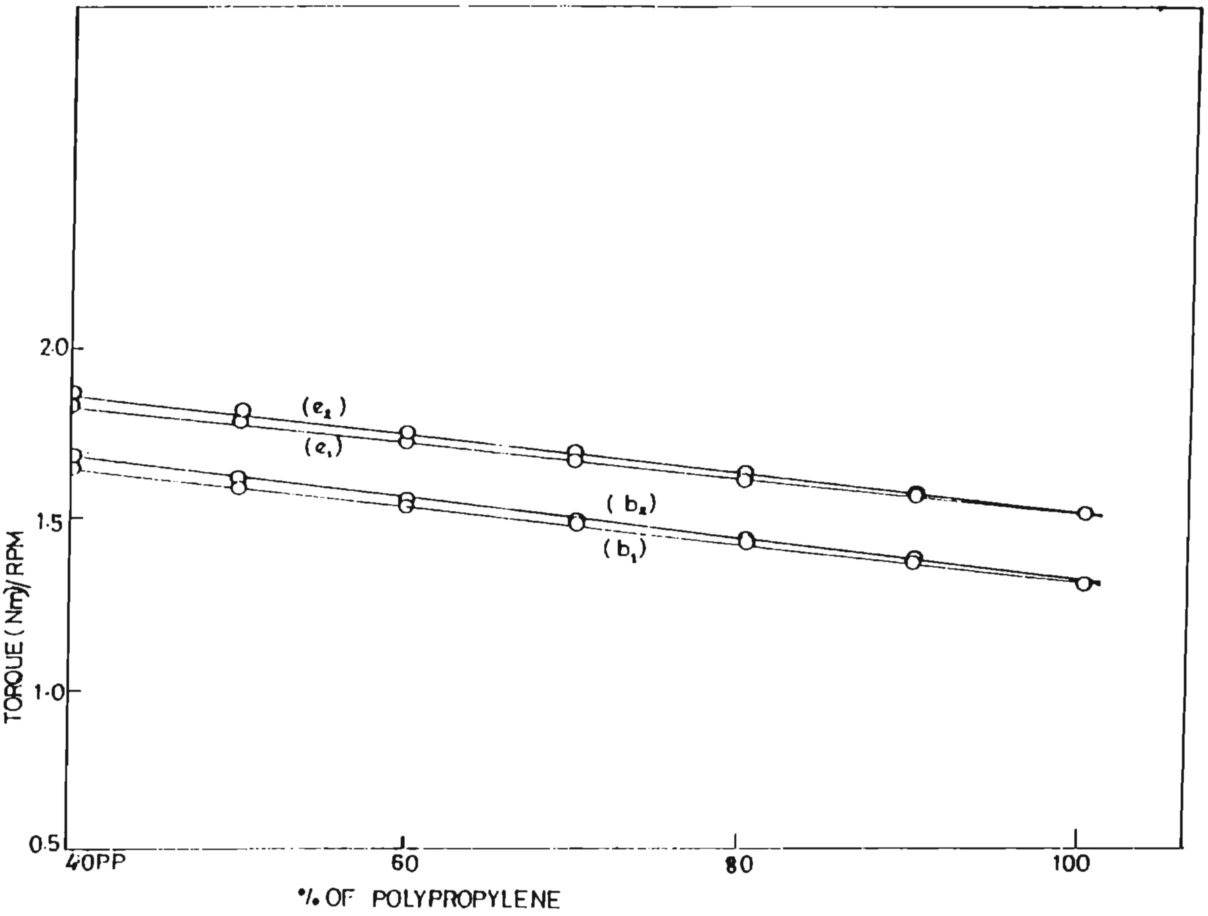

FIG.5.5: Variation in viscosity with polypropylene of uncrosslinked b_1 (PP/NR); b_2 (PP/LR) and crosslinked e_1 (PP/NR); e_2 (PP/LR) blends

linked blends (b). Fig. 5.6 shows the tensile fractograph of 90/10, polypropylene/latex reclaim blend. The failure is of a brittle nature with multidirectional cracks. Fig.5.7 shows the fracture surface of polypropylene/latex reclaim (80/20) blend. It indicates that the initiation of the fracture is propagated concentrically as the shear advances.

Increasing the rubber content in the blend (Figs.5.8-5.10) increases the continuity of the rubber phase and the fracture surface of the (40/60) polypropylene/latex reclaim blend (Fig.5.11) shows a smooth shear path with a rough surface. Due to the partially crosslinked nature of the latex reclaim, it reduces the particle size and improves the dispersion of the rubber phase in the blend. The resistance to high deformation of this crosslinked particles restricts the flow under stress, as shown by the presence of many short curved shear lines on the fracture surface (Figs.5.8-5.10). In the (40/60) polypropylene/latex reclaim blend (Fig.5.11), both the plastic and the rubber phases exist as a continuous interpenetrating two phase system[22] and the crosslinked nature of the latex reclaim reduces the

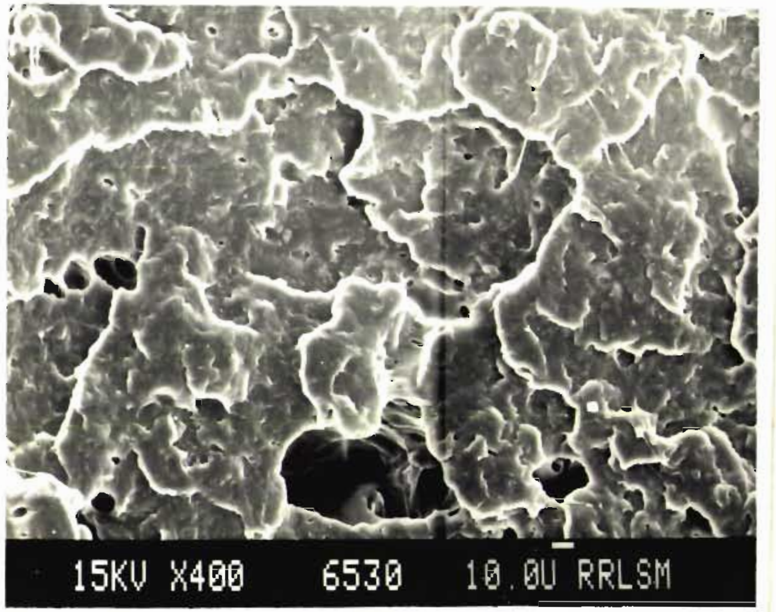

FIG.5.6: PP/LR (90/10)

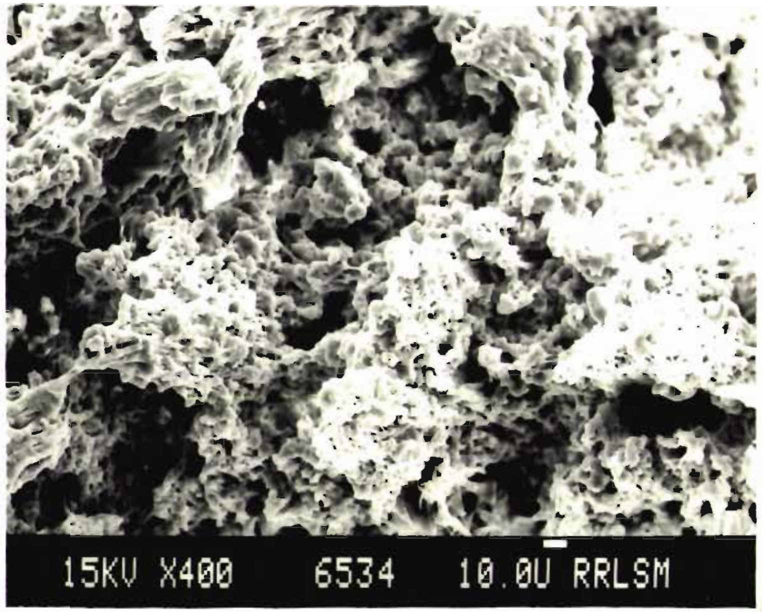

FIG.5.7: PP/LR (80/20)

SEM photographs of the tensile fracture surface of uncrosslinked (b_2) blends

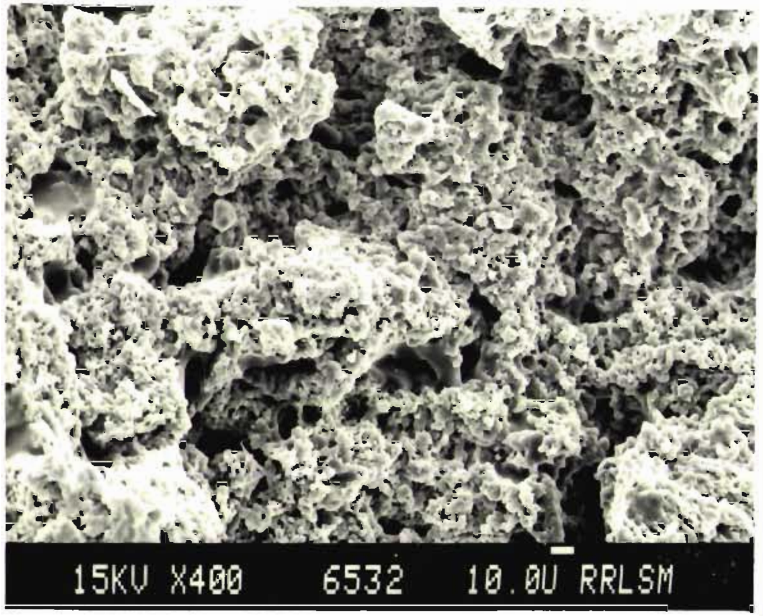

FIG.5.8: PP/LR (70/30)

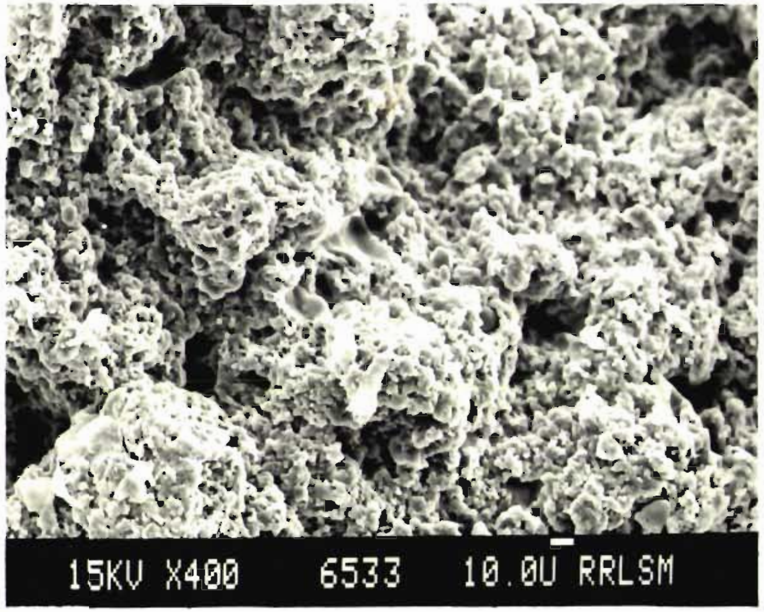

FIG.5.9: PP/LR (60/40)

SEM photographs of the tensile fracture surface of uncrosslinked (b_2) blends

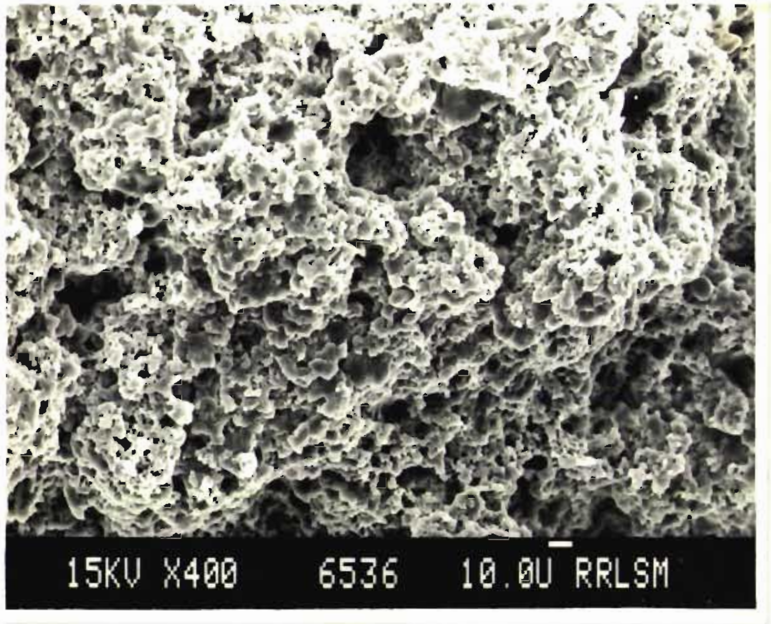

FIG.5.10: PP/LR (50/50)

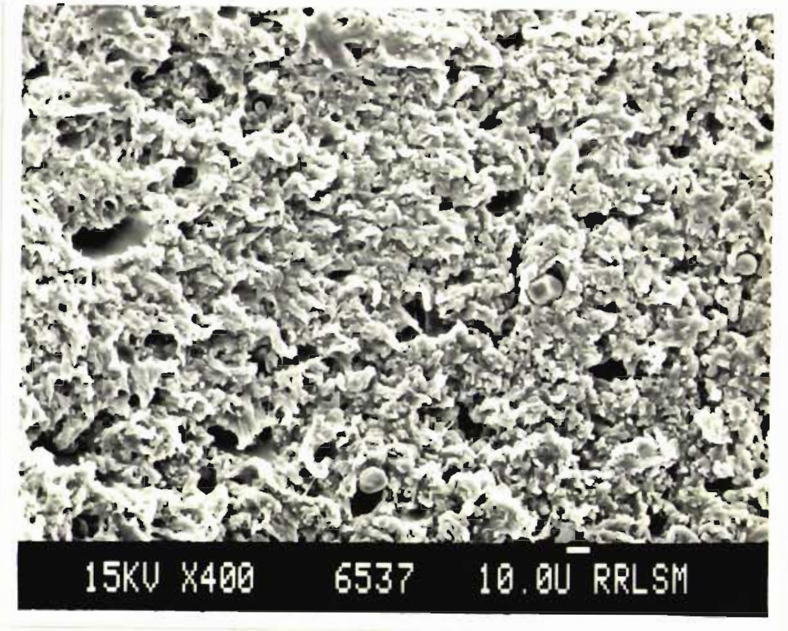

FIG.5.11: PP/LR (40/60)

SEM photographs of the tensile fracture surface of uncrosslinked (b_2) blends

deformation of the rubber phase. Under applied stress, a series of discontinuous cracks are formed on the surface due to the low deformation of the rubber phase.

CONCLUSION

1. The mechanical properties of polypropylene/latex reclaim blends are comparable with those of the blends based on polypropylene and natural rubber.

2. The dynamic crosslinking of the elastomer phase increases the tensile strength of the polypropylene/natural rubber and polypropylene/latex rubber blends.

3. Addition of latex reclaim changes the brittle failure of polypropylene to ductile type as in the case of polypropylene/natural rubber blends.

Part II: RHEOLOGICAL AND EXTRUDATE BEHAVIOUR OF POLYPROPYLENE/LATEX RECLAIM BLENDS USING A CAPILLARY RHEOMETER

The importance of rheological studies in predicting the flow behaviour of polymer systems at high temperature and shear conditions of extrusion and injection moulding processes has been described by several authors.[23-33] Since, thermoplastic/elastomer blends can be injection moulded or extruded, their melt viscosity and extrudate deformation also need to be examined as functions of shear stress, temperature and composition. The mechanical properties of polypropylene and latex reclaim blends are found to be better when compared with those of polypropylene and natural rubber blends.[34] Therefore, the study of the rheological properties of their melts is important and this section reports the rheological and extrudate behaviour of polypropylene and latex reclaim blends. The variation of shear viscosity, die swell, and extrudate deformation with shear rate, temperature and blend ratios were evaluated.

EXPERIMENTAL

Preparation of the blends

Thermoplastic/elastomer blends were prepared on a Brabender plasticorder model PL 3S equipped with roller mixing heads as per formulations given in Table 5.2. Mixing was done at 190°C and 40 rpm. Polypropylene was melted in the mixer for 1 minute and then the latex reclaim containing the additives was added and the mixing was continued for 4 minutes. Then dicumyl peroxide was added and the mixing was again continued for another 1 minute. The mix was then taken out and sheeted on a laboratory mixing mill with 2.0 mm nip setting. The sheeted material was cut into small pieces and again mixed in the plasticorder at 190°C for 1 minute so as to get uniform dispersion of the ingredients and then finally sheeted out in the mill.

Rheological measurements

Rheological studies were carried out using a capillary rheometer, attached to a Zwick universal testing machine, model 1474. The capillary used in this study had a length to diameter (l_c/d_c) ratio of 40. 8 gms of the test sample was put into the barrel of the capillary

Table 5.2: Formulations of PP/LR blends

Materials	A	B	C
PP	90	80	70
Latex reclaim	10	20	30
ZnO	0.5	1.0	1.5
Stearic acid	0.2	0.4	0.6
Accinox ZC	0.1	0.2	0.3

rheometer and forced down through the capillary by the plunger attached to the moving crosshead. After a warm-up period of 3 minutes, the sample was extruded through the capillary at 10 different speeds. Forces corresponding to specific plunger speeds could be measured by the pressure transducer attached to the plunger and were recorded using a strip chart recorder assembly.

The force and crosshead speed were converted into apparent shear stress (T_w) and shear rate ($\dot{\gamma}_w$) at the wall, respectively, using the following equations involving the geometry of the capillary and plunger.

$$\tau_w = \frac{F}{4A_p(l_c/d_c)}$$

$$\dot{\gamma}_w = \frac{(3n+1)}{4n} \times \frac{32\ Q}{\pi d_c^{\ 3}}$$

where F is the force applied at a particular shear rate, A_p is the cross-sectional area of the plunger, l_c the length of the capillary, d_c the diameter of the capillary, Q the volume flow rate (calculated from the velocity of the crosshead and the diameter of the plunger) and n the flow behaviour index, defined as,

$$n = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})}$$

and determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. $\dot{\gamma}_{wa}$ is the apparent wall shear rate, calculated as $\frac{32\,Q}{\pi d_c^3}$. The shear viscosity, η was calculated as,

$$\eta = \tau_w / \dot{\gamma}_w$$

Extrudate swelling

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured at several points after 24 h of extrusion using a binocular stereo microscope. The average value of five readings was taken as the diameter of the extrudate (d_e). The extrudate swelling was calculated as the ratio of the diameter of extrudate to that of the capillary (d_e/d_c).

Observation of extrudate appearance

The extrudate from capillary rheometer has been observed carefully for any surface imperfections.

RESULTS AND DISCUSSION

Fig.5.12 shows the effect of blend ratio and shear stress on viscosity of the polypropylene/latex reclaim

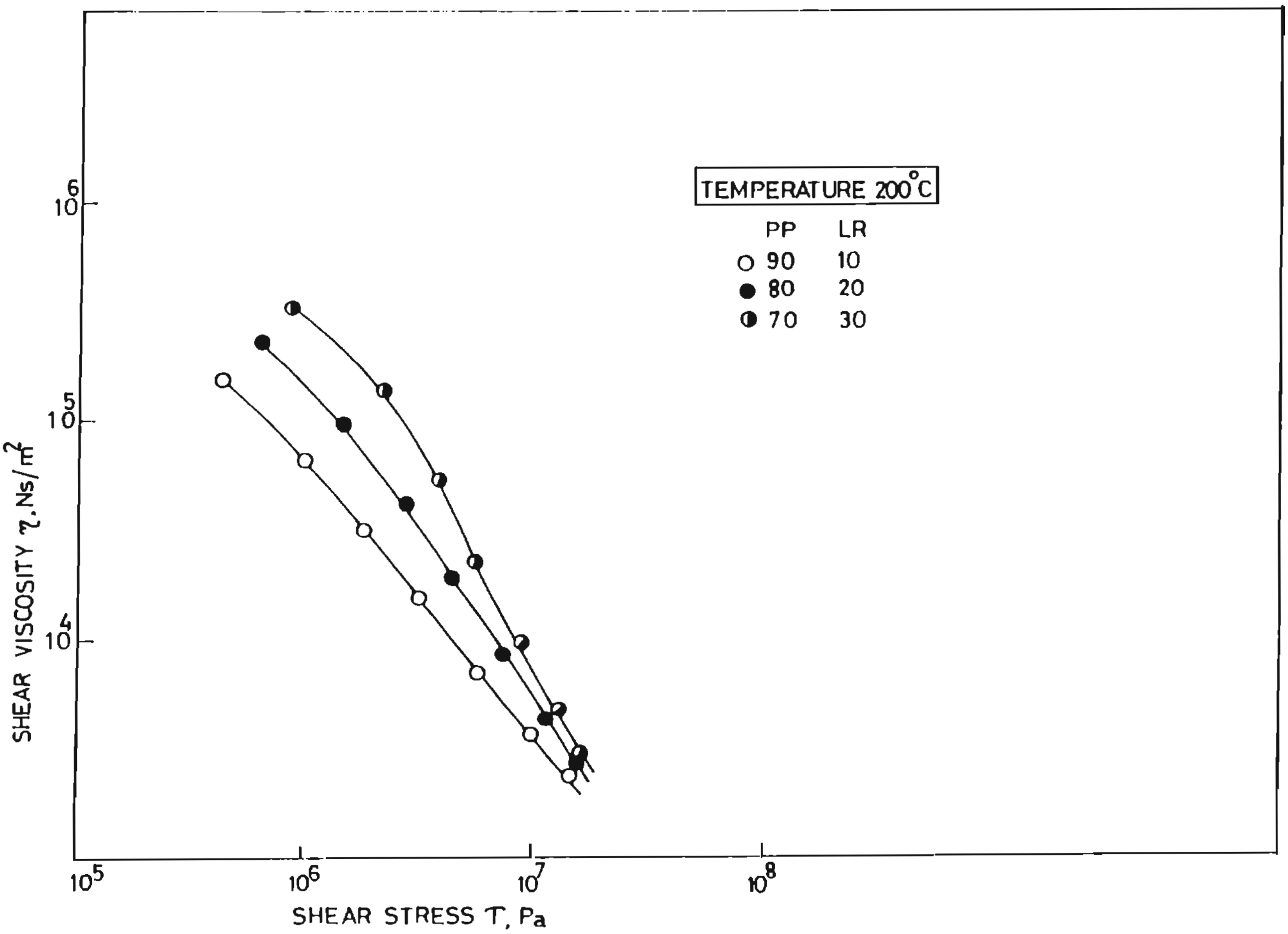

FIG.5.12: Variation in shear viscosity with shear stress of PP/LR blends at 200°C

blends at 200°C. The viscosity of all the blends decreases with increasing shear stress at a particular temperature, showing the pseudoplastic behaviour of the blends. At low shear stresses, the viscosity of the blend increases with increasing proportion of rubber in the blend, but at high shear stresses, the difference in the viscosity is only marginal.

Fig.5.13 shows the dependence of temperature on the shear viscosity of the polypropylene/latex reclaim blends at different shear rates. The viscosity of all the blends drops with increasing temperature irrespective of the blend ratio at all shear rates. It is also seen that the blends having higher rubber content have higher viscosities at low shear rates.

The activation energy of viscous flow was derived from the Arrhenius equation ($\eta = Ae^{E/RT}$) and calculated from Fig.5.14. A plot of log E versus 1/T yields straight lines at different shear rates with a slope equal to E/R and thus the activation energy of flow (E) can be calculated. The E values of polypropylene/latex reclaim blends at different shear rates is given in Table 5.3.

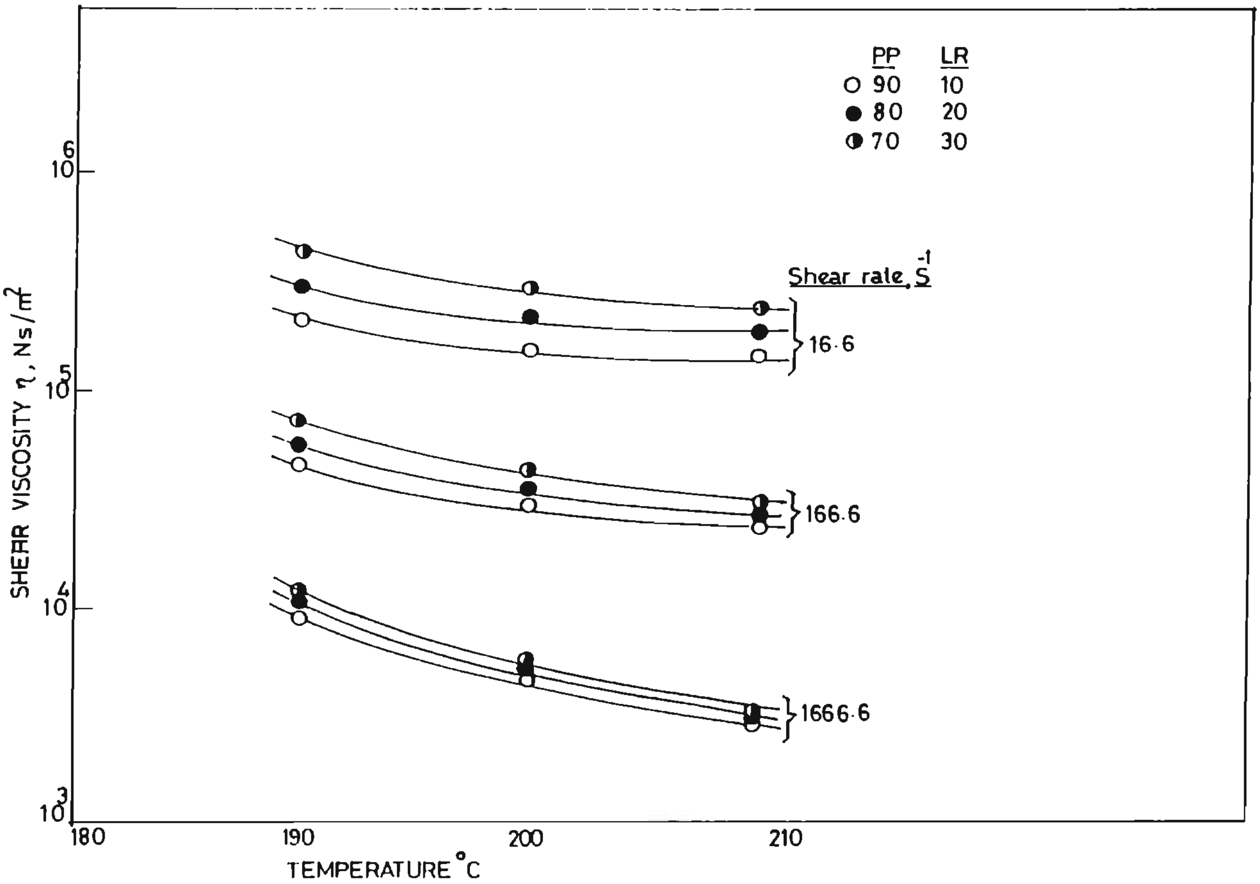

FIG.5.13: Variation in shear viscosity with temperature of PP/LR blends

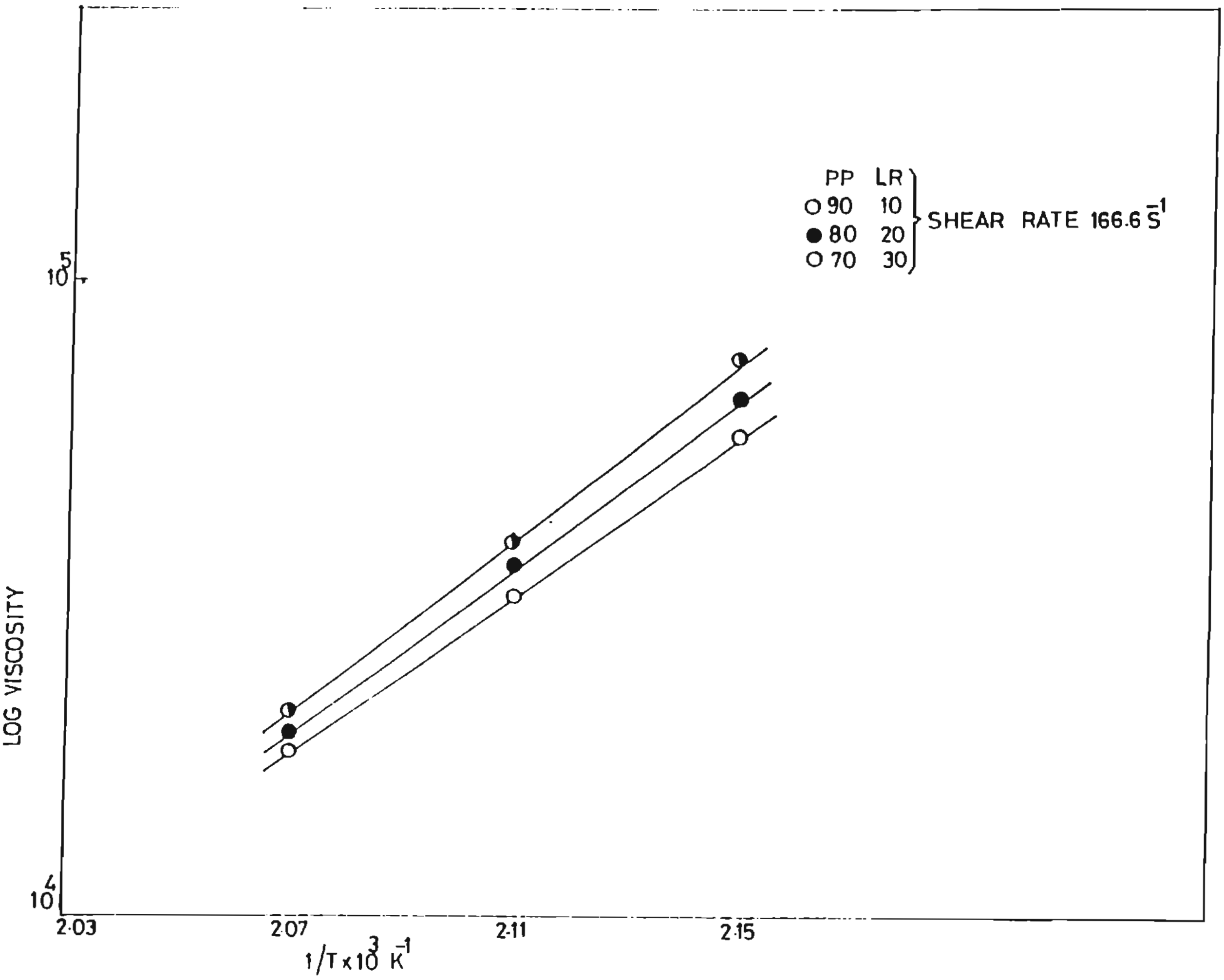

FIG.5.14: Variation in viscosity with temperature of PP/LR blends at a shear rate of 166.6 S^{-1}

From this table, it is clear that the activation energy of viscous flow decreases with increasing shear rate irrespective of the blend ratio and it marginally decreases with increasing latex reclaim content.

Table 5.4 shows the effect of temperature on the flow behaviour index (n) of the blends. The low values of n (< 1) show the strong pseudoplastic nature of the mixes. From this table, it is seen that the values of n decreases with increasing temperature and increases with increasing latex reclaim content in the blend. This may be due to the dispersed inter-connected structure of the latex reclaim which contributes to increase in viscosity of the blends and leads to higher values of n.

The variation in extrudate die swell ratio with the amount of latex reclaim of the polypropylene/latex reclaim blends is given in Table 5.5. The extrudate swell increases with increasing shear rate and this difference is minimum for the blends having higher latex reclaim content. This is due to the low deformation and quick recovery of crosslinked latex reclaim particles, since the elastic recovery of the polymer chain is influenced by several

Table 5.3: Activation energy of viscous flow (kJ mol^{-1}) of PP/LR blends

Sample (PP/LR)	Shear rate (s^{-1})		
	16.6	166.6	1666.6
90/10	15.6	12.5	10.1
80/20	14.1	10.4	9.6
70/30	13.4	9.0	8.4

Table 5.4: Flow behaviour index (n) of PP/LR blends

Sample (PP/LR)	Temperature (°C)		
	190	200	210
90/10	0.28	0.27	0.26
80/20	0.29	0.28	0.27
70/30	0.32	0.30	0.29

Table 5.5: Die swell ratio (d_e/d_c) of PP/LR blends at 200°C

Sample (PP/LR)	Shear rate (s^{-1})	
	16.6	1666.6
90/10	1.42	1.63
80/20	1.40	1.58
70/30	1.37	1.46

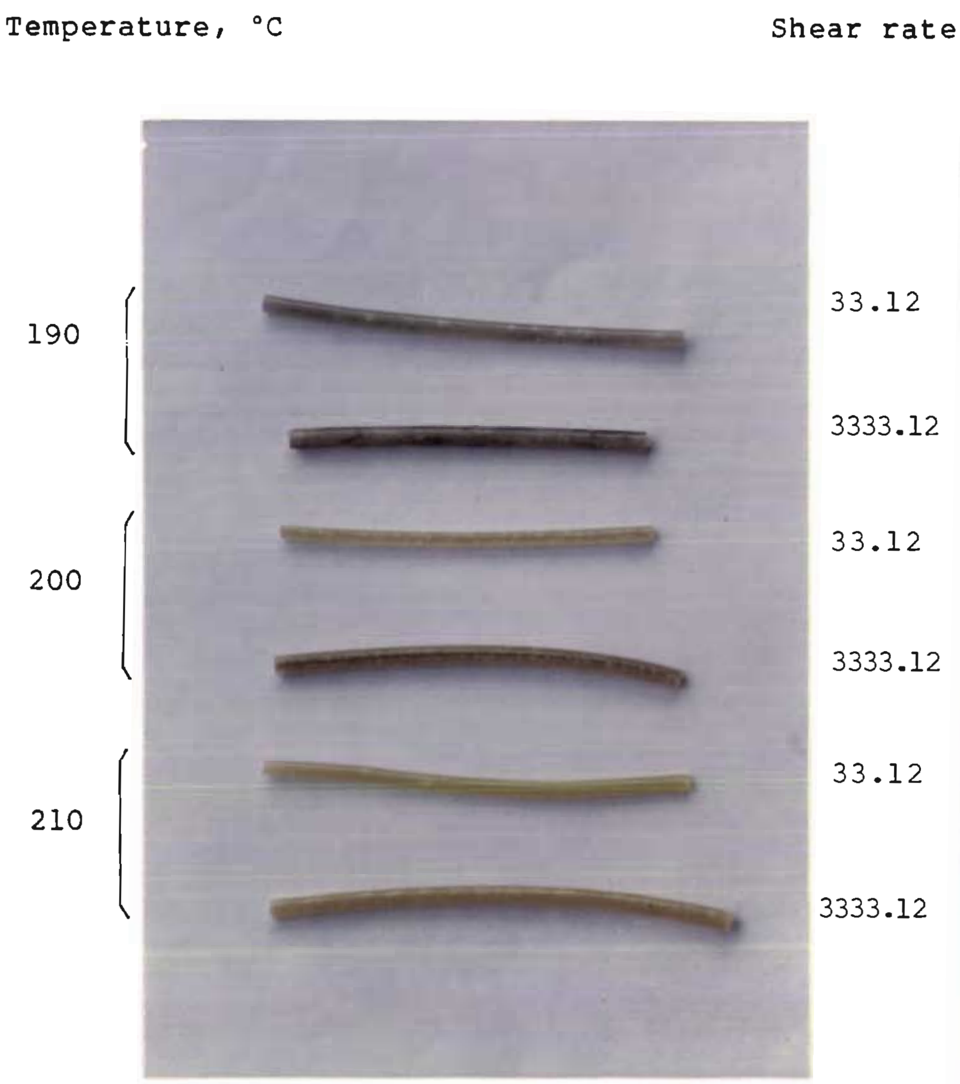

FIG.5.15: PP/LR (90/10)

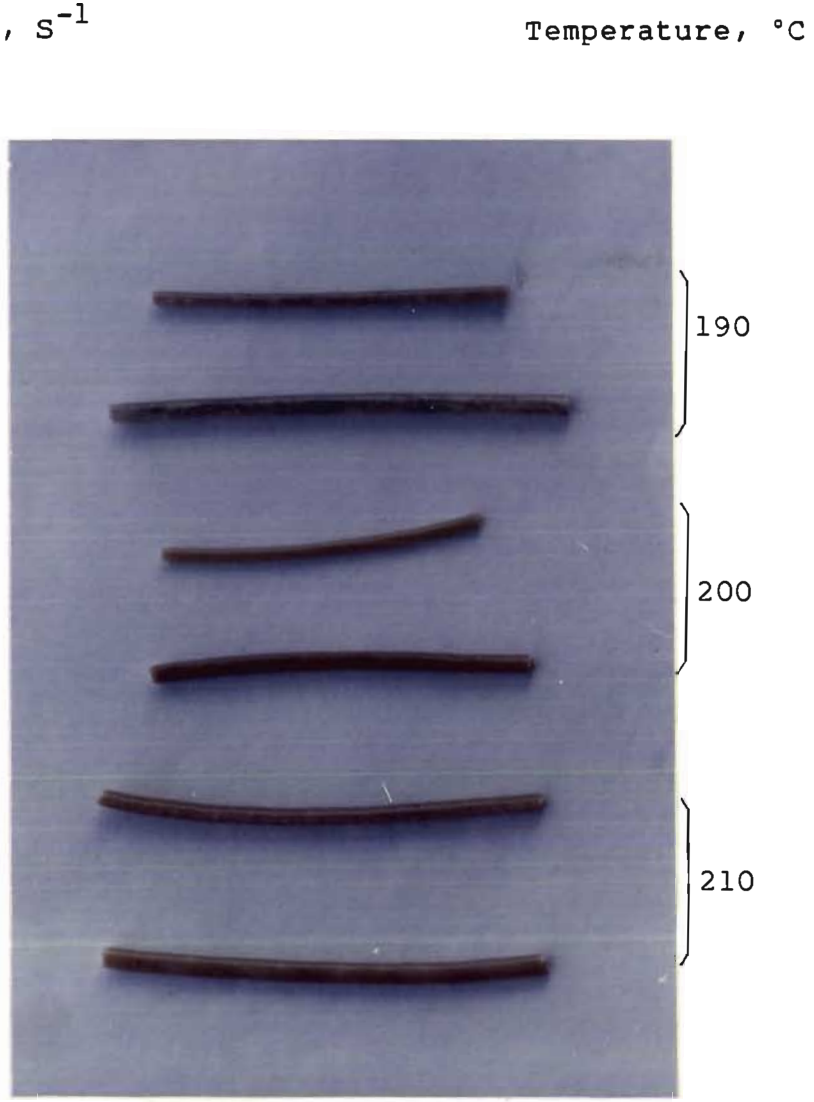

FIG.5.16: PP/LR (80/20)

Photographs of the extrudates of PP/LR blends at two shear rates at different temperatures

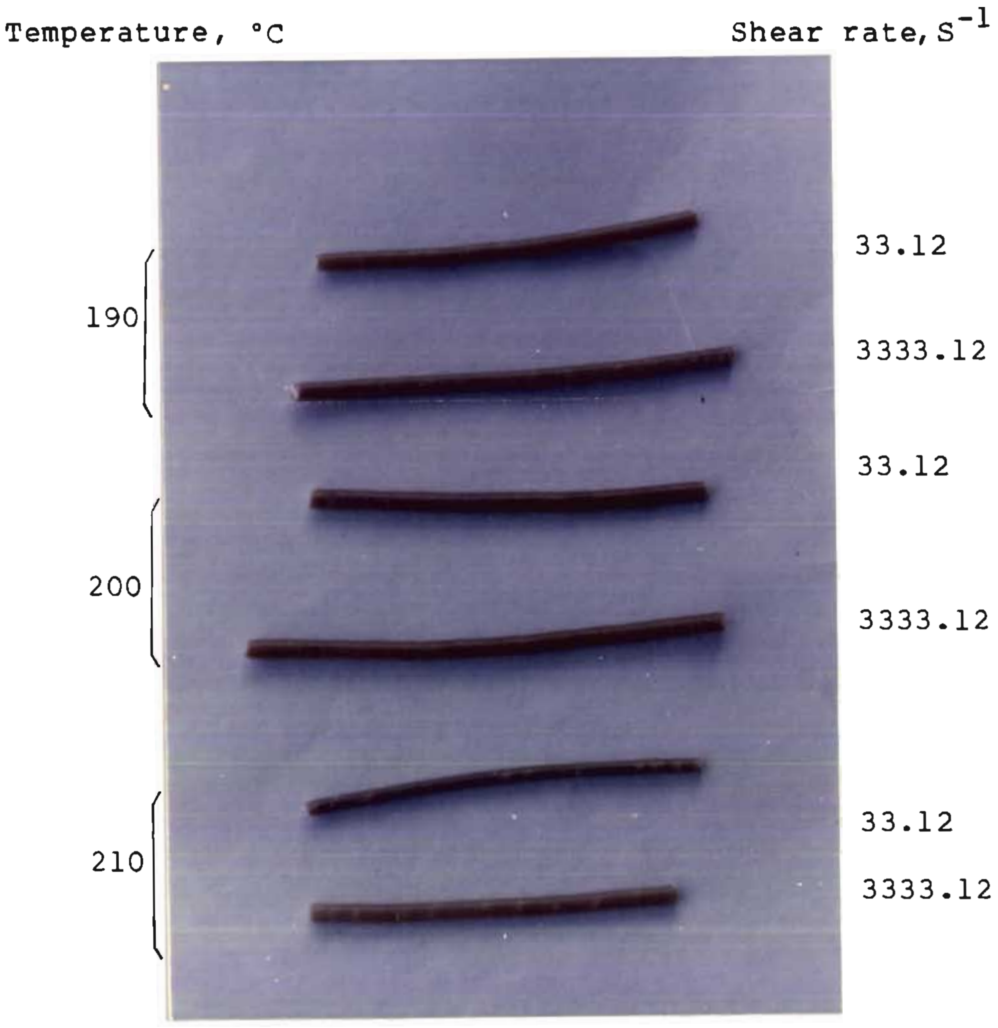

FIG.5.17: Photograph of the extrudates of PP/LR (70/30) blend at two shear rates at different temperatures

factors like stress relaxation, crosslinking, presence of fillers etc.

Figs. 5.15-5.17 show the photographs of the extrudates of polypropylene/latex reclaim blends at different temperatures and at different shear rates. The blends give smooth extrudates at all temperatures (190, 200 and 210°C) studied. It is also seen that, even at high shear rates, the 70/30 (polypropylene/latex reclaim) blend gives smooth extrudates. This may be because of the crosslinked nature of the latex reclaim in the blends which helps to retain their morphology even at high shear stresses.

CONCLUSION

1. In polypropylene/latex reclaim blends, increase in viscosity with increase in rubber content is predominant only at lower shear stresses.

2. The viscosity of the polypropylene/latex reclaim blends decreases with increasing temperature.

3. The activation energy of viscous flow of the polypropylene/latex reclaim blends does not vary

considerably with the addition of about 30 weight percent latex reclaim in the temperature range of 190-210°C.

4. The die swell ratio of the polypropylene/latex reclaim blend marginally decreases with increase in latex reclaim content.

5. The latex reclaim reduces the distortion of the extrudates even at higher shear rates.

REFERENCES

1. J.Karger-Kocsis, L.Kiss and V.N.Kulennev, Int. Polym. Sci. Technol., 8(10), T/21 (1981).

2. J.Karger-Kocsis, Zs Senyei and L.Kiss, Int. Polym. Sci. Technol., 11(2), T/11 (1984).

3. H.Hatsuki, Int. Polym. Sci. Technol., 12(7), T/57 (1985).

4. J.Yamada, Int. Polym. Sci. Technol., 12(4), T/92 (1985).

5. L.F.Ramos-Devalle and R.R.Ramirez, Rubber Chem. Technol., 55, 1328 (1982).

6. J.Karger-Kocsis and V.N.Kuleznev, Polymer, 23(4), 699 (1982).

7. A.J.Tinker, Polymer Commns.,25(11), 325 (1984).

8. Decai Yang, Bailan Zhang, Yongkuan Yang, Zheng Fang, Guifen Sun and Zhiliu Feng, Polym. Eng. Sci., 24(8), 612 (1984).

9. L.A.Goettler, J.R.Richwine and F.J.Wille, Rubber Chem. Technol., 55, 1448 (1982).

10. V.S.Glukhovskoi, G.I.Popova, E.S.Kretinina, T.M.Rogova and M.I.Sokolov, Int. Polym. Sci. Technol., 16(10), T/80 (1989).

11. B.Kuriakose, S.K.De, S.S.Bhagawan, R.Sivaramakrishnan and S.K.Athithan, J. Appl. Polym. Sci., 32(6), 5509 (1986).

12. C.S.Ha, D.J.Ihm and S.C.Kim, J. Appl. Polym. Sci., 32(8), 6281 (1986).

13. A.Y.Coran and R.P.Patel, Rubber Chem. Technol., 53, 141 (1980).

14. A.Y.Coran and R.P.Patel, Rubber Chem. Technol., 53, 781 (1980).

15. A.Y.Coran, R.P.Patel and D.Williams, Rubber Chem. Technol., 55, 116 (1982).

16. Reena Susan George and Rani Joseph, Die Angew.Makromol. Chemie, 215, 25 (1994).

17. Reena Susan George and Rani Joseph, paper presented in the sixth Kerala Science Congress, January (27-29), Trivandrum, India, 394 (1994).

18. Reena Susan George and Rani Joseph, J. Mat. Sci. (In press).

19. B.Kuriakose, S.K.Chakraborty and S.K.De, Mat. Chem. Phys., 12, 157 (1985).

20. B.Kuriakose and S.K.De, J. Mat. Sci. Lett., **4**, 455 (1985).

21. S.A.Malaika and G.Scott, Degradation and stabilization of polyolefins, N.S.Allen, Ed., Applied Science Publishers, London, 247 (1983).

22. E.N.Kresge, Polymer Blends, Vol.2, edited by D.R.Paul and S.Newman, Academic press, London and New York, 293 (1978).

23. J.A.Brydson, Flow properties of polymer melts, George Godwin Ltd., 2nd edition, London (1981).

24. J.L.White, Rubber Chem. Technol., **42**, 257 (1969).

25. J.L.White, Rubber Chem. Technol., **50**, 163 (1977).

26. L.F.Ramos-Devalle, Rubber Chem. Technol., **55**, 1341 (1982).

27. C.K.Das, Plast. Rubber Process. Appln., 8(1), 59 (1987).

28. S.S.Bhagawan and S.K.De, Plast. Rubber Process. Appln., 9(1), 37 (1988).

29. J.Kurian, S.Akhtar, P.P.De and G.B.Nando, Plast. Rubber Process. Appln., 10(1), 53 (1988).

30. Sania Akhtar, B.Kuriakose, Prajna P.De and Sadhan K.De, Plast. Rubber Process. Appln., 7(1), 11 (1987).

31. Baby Kuriakose and S.K.De, Polym. Eng. Sci., 25(10), 630 (1985).

32. S.Danesi and R.S.Porter, Polymer, 19, 448 (1978).

33. A.Akhtar, P.P.De, and S.K.De, Int. Polym. Sci. Technol., 16(6), T/55 (1989).

34. Reena Susan George and Rani Joseph, Kautschuk Gummi Kunststoffe, (In press).

Chapter 6

DEVELOPMENT OF MICROCELLULAR SHEETS WITH LATEX RECLAIM

Cellular rubber products are probably more versatile than any other rubber product. Apart from the technical property variation between compound formulations, the degree of expansion causes significant changes in the properties and these are further varied by the cellular structure, which may be open or closed. Microcellular rubber soles are used in footwear applications due to their high strength to weight ratio, wearing comfort and flexural strength. Natural rubber/high styrene resin (NR/HSR) blends are used in the manufacture of microcellular products due to its high abrasion resistance, fairly constant mooney viscosity and cure characteristics, high resistance to crack initiation and crack growth etc.[1]

For reducing the compound cost and environmental pollution and to conserve raw materials and energy, use of reclaim rubber has been practised widely in rubber industry for making useful rubber products. For example, footwear industry uses microcellular crumb. Further, it is reported that the strength of microcellular sheet can be improved by increasing the crosslink density.[2] From the earlier part of the present study latex reclaim has been found to increase the crosslink density of its blends with elastomers.[3-5] In the present work, the effect of replacing part of natural rubber by latex reclaim in NR/HSR based microcellular sheet was studied. The technical properties of microcellular sheets produced from ternary blends of NR/latex reclaim/HSR (NR/LR/HSR) were evaluated and compared with those prepared from NR/HSR blend.

EXPERIMENTAL

Natural rubber was masticated on a laboratory mixing mill and latex reclaim was added at different percentages. SBR-1958 in the form of a sheet was then added and the blends were compounded according to the formulations given in Table 6.1.

The optimum cure time and scorch time of the compounds were determined using Goettfert Elastograph.

Microcellular sheets were moulded in an electrically heated hydraulic press at 150°C. The mould was loaded with three per cent excess of the compound on

Table 6.1: Formulations of NR/LR/HSR blends

Materials	A	B	C	D
NR	70	60	50	40
LR	0	10	20	30
HSR	30	30	30	30
Clay	50	50	50	50
Precipitated Silica	40	40	40	40
Naphthenic oil	5	5	5	5
Diethylene glycol	1	1	1	1
ZnO	5	5	5	5
Stearic acid	6	6	6	6
DNPT	6	6	6	6
Vulcafor F	1.2	1.2	1.2	1.2
Sulphur	2.5	2.5	2.5	2.5
Wax	1.0	1.0	1.0	1.0
Antioxidant SP	1.0	1.0	1.0	1.0
Titanium dioxide	2.0	2.0	2.0	2.0
Wood rosin	1.5	1.5	1.5	1.5

volume basis. The compounds were precured in the mould to eighty percent of their respective optimum cure times. The expanded precured sheets were then post cured in an oven for 5 hours at 80°C.

The mechanical properties like relative density, hardness, change in hardness after ageing, compression set, split tear strength, heat shrinkage and water absorption were evaluated according to relevant Indian standards. The flexing resistance, in number of cycles (Initial crack development) and cut growth at the end of 1,00,000 cycles was tested using a Ross flexing machine. Abrasion resistance was tested using a DIN abrader.

Cell structure studies were done on a cut portion of the microcellular sheets using a Nikkon trinocular research microscope model Alphaphot-2. Photographs were taken at a magnification of 50.

RESULTS AND DISCUSSION

Table 6.2 shows the cure characteristics of the compounds. The optimum cure time and the scorch time are found to decrease with the addition of latex reclaim. This

Table 6.2: Cure characteristics and vulcanizate properties of NR/LR/HSR blends.

	A	B	C	D
Scorch time (T_{10} in minutes)	2.9	2.4	2.2	2.0
Optimum cure time (T_{90} in minutes)	10.6	9.4	8.2	7.8
Maximum torque, (Nm)	0.27	0.33	0.36	0.38
Relative density	0.38	0.40	0.41	0.42
Hardness, (Shore A)	38	40	42	44
Change in Hardness (after ageing at 100°C, 24 h)	+3	+2	+3	+2
Compression set, (%)	15.63	14.48	14.34	14.19
Split tear strength (kg)	7.2	7.56	8.21	8.67
Expansion ratio* (%)	138	137.5	136.9	136
Abrasion loss, (cc/h)	4.58	4.47	4.39	4.30
Water absorption, (%)	1.06	1.065	1.08	1.09
Heat shrinkage (%), (at 100°C, 1 h)	2.06	2.08	2.1	2.14
Flex resistance, number of cycles				
a) Initial crack	$>$60000	$>$60000	$>$60000	$>$60000
b) Cut growth at the end of 1,00,000 cycles (%)	$<$600	$<$600	$<$600	$<$600

$$* \text{ Expansion ratio} = \frac{\text{Area of the microcellular sheet}}{\text{Area of the mould}} \times 100$$

is possibly due to the presence of crosslink precursors and/or unreacted curatives in latex reclaim. In latex products manufacture, usually ultra-accelerators such as ZDC, ZMBT, TMTD etc. are used and these accelerators even at very low dosages can accelerate the curing reaction at 150°C. It is also noticed that the maximum torque increases with the addition of latex reclaim as observed in natural rubber/latex reclaim compounds.[2,3]

Relative density of the microcellular sheets increases marginally with the addition of latex reclaim while the expansion ratio decreases marginally (Table 6.2). This behaviour is in conformity with our earlier observation that the modulus and crosslink density of NR/LR blends increases with the addition of latex reclaim.

Table 6.2 shows the variation in compression set with the addition of latex reclaim. Compression set decreases with increase in latex reclaim content. This may be again due to the increased crosslink density of the microcellular sheets prepared from the latex reclaim blends.

Heat shrinkage is found to be almost constant irrespective of the polymer variation and the water absorption marginally increases with the addition of latex reclaim as shown in Table 6.2.

Abrasion loss of the microcellular sheets decreases with the amount of latex reclaim as shown in Table 6.2. This may be attributed to the higher modulus of the latex reclaim containing blends.

The variation of split tear strength with the addition of latex reclaim is shown in Table 6.2. Latex reclaim based microcellular sheets show higher split tear strength compared to NR/HSR based microcellular sheets. The tear strength of natural rubber/latex reclaim blends slightly increases with the addition of latex reclaim upto about 30 percent.[1] This may be due to the faster cure rate and higher degree of crosslinking of latex reclaim containing blends.

Table 6.2 shows the variation of the flex resistance of the blends with the amount of latex reclaim. The flex resistance of all the samples is found to be in the specification limit given in Indian standard (IS: 3400 (part 16) 1974).

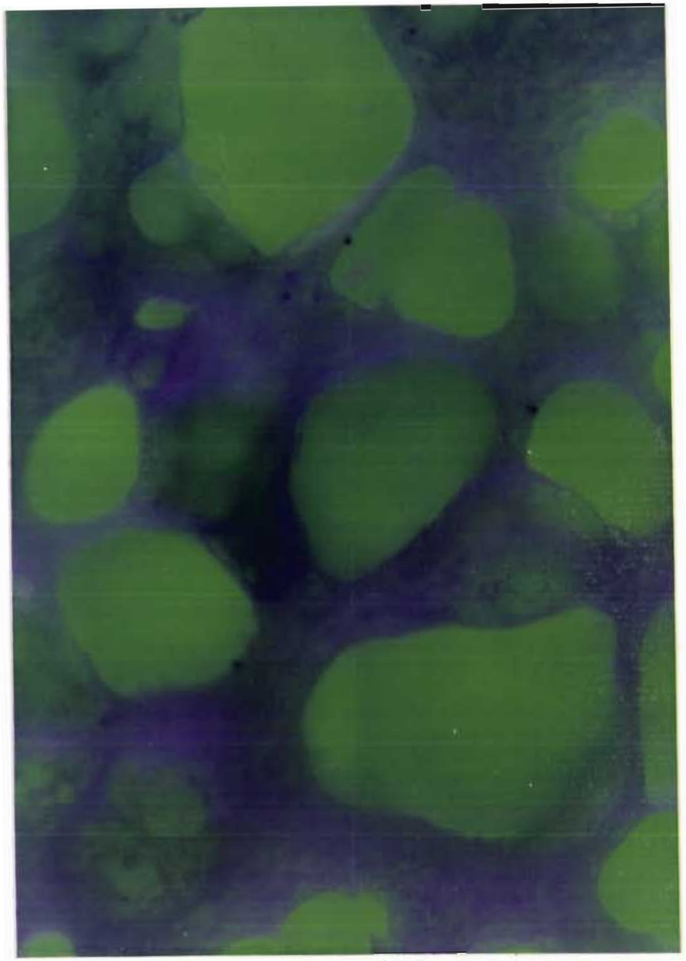

FIG.6.1: NR/HSR (70/30)

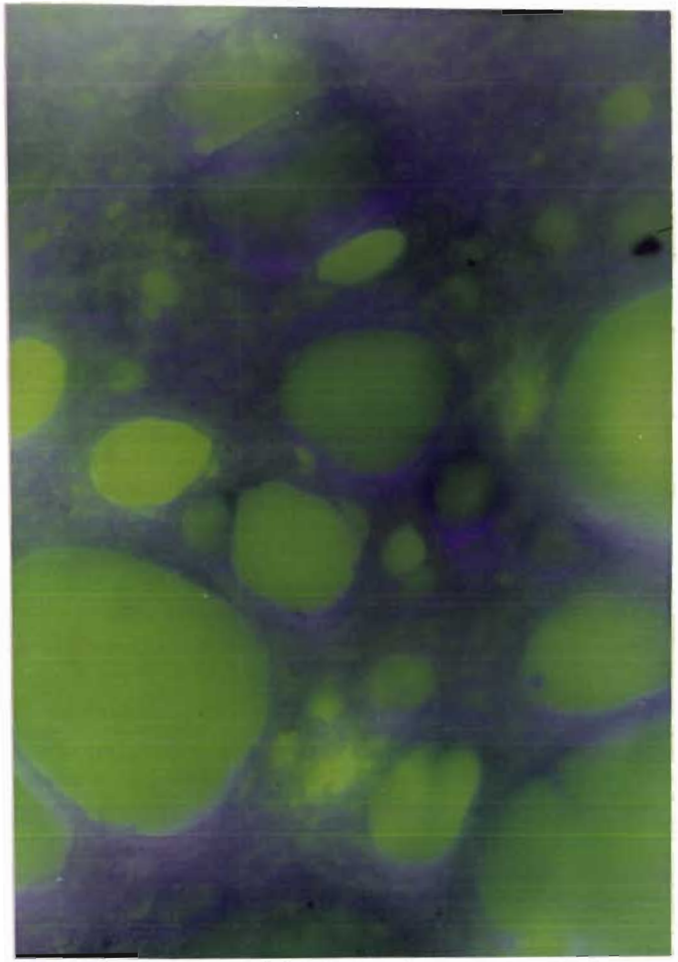

FIG.6.2: NR/LR/HSR (60/10/30)

Optical photographs of microcellular sheet

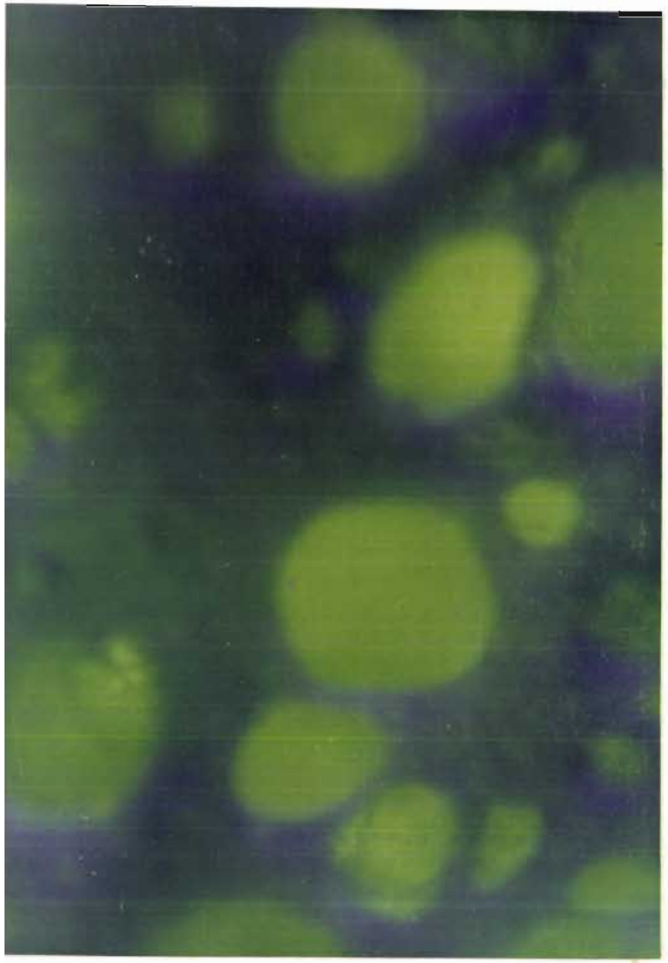

FIG.6.3: NR/LR/HSR (50/20/30)

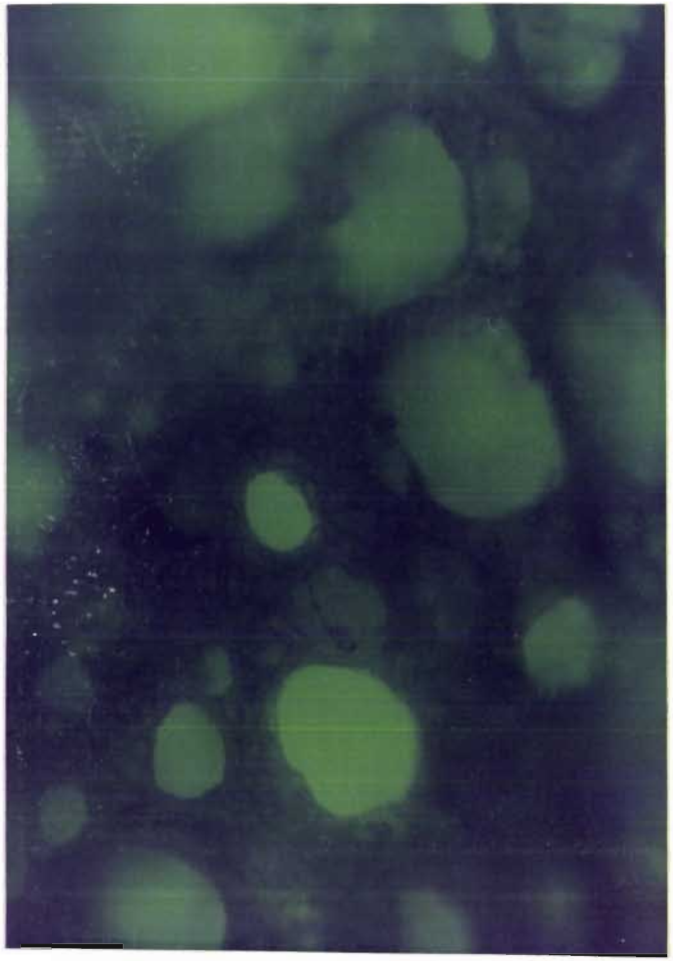

FIG.6.4: NR/LR/HSR (40/30/30)

Optical photographs of microcellular sheet

Figs.6.1-6.4 show the optical photographs of NR/HSR (70/30), NR/LR/HSR (60/10/30), NR/LR/HSR (50/20/30) and NR/LR/HSR (40/30/30) microcellular sheets. Compared to the cell structure of NR/HSR microcellular sheets, the average size of cells are smaller and the number of cells are more in the NR/LR/HSR based microcellular sheets. This may be due to the uniform distribution of latex reclaim in the compounds and the higher crosslink density of the compound containing latex reclaim.[6]

CONCLUSION

1. The curing of NR/LR/HSR based microcellular sheets are faster compared to NR/HSR based microcellular sheet.

2. The technical properties like hardness, compression set, split tear strength and abrasion resistance are superior for the latex reclaim based microcellular sheets.

3. There is only a marginal increase in heat shrinkage, water absorption and relative density on the addition of latex reclaim in microcellular sheets.

4. The latex reclaim can replace natural rubber up to about 30 weight percent in NR/HSR based microcellular products without affecting their technical properties.

REFERENCES

1. Jacob K.Varkey, N.M.Mathew and P.P.De, Indian J. Nat. Rubber Res.,2(1), 13 (1989).

2. Vipin Kumar, Prog. Rubber Plast. Technol., 9(1), 54 (1993).

3. Reena Susan George and Rani Joseph, Die Angew.Makromol. Chemie, 215, 25 (1994).

4. Reena Susan George and Rani Joseph, paper presented in the 6th Kerala Science Congress, January (27-29), Trivandrum, India, 394 (1994).

5. Reena Susan George and Rani Joseph, J. Mat. Sci., (In press).

6. J.G.Webster and R.R.Heathfield, Rubber Technology and Manufacture, edited by C.M.Blow and C.Hepburn, 2nd edition, Butterworths, 474 (1982).

Chapter 7

SUMMARY AND CONCLUSIONS

The overall objective of the present study was to develop a novel and economic reclaiming process that does not adversely affect the quality of rubber and to investigate methods of utilising the reclaim. Since waste latex products represent a potential source of high quality rubber hydrocarbon, it was decided to develop a process based on such latex wastes.

After several trials, a promising process was developed for generating good quality rubber from the latex products (latex reclaim). The latex reclaim thus developed had properties such as mooney viscosity, initial plasticity, plasticity retention index, acetone extract, volatile matter etc. comparable to those of raw natural rubber. The rubber hydrocarbon content was slightly lower while the ash content was slightly higher for the latex reclaim. The details of the reclaiming process are outlined in Part I of Chapter 3.

Since rubber reclaim is normally used to replace a part of raw natural rubber, in the second part of the study, latex reclaim was utilised for developing blends with raw natural rubber. The study revealed that latex reclaim could replace raw natural rubber upto about 50 per cent of its weight without any serious deterioration in mechanical properties. Further, morphology studies showed that the latex reclaim distributed uniformly in natural rubber compounds and there was good bonding between the two. The scanning electron microscope studies showed that the failure mechanism of the blends in tension and tear was similar to those of pure natural rubber. The processing of the blends also did not call for higher energy consumption, since the viscosity of the blends was found to decrease marginally with the addition of latex reclaim. These studies on the blends of latex reclaim with natural rubber in gum compounds are outlined in Part II of Chapter 3.

Part III of Chapter 3 describes the utilisation of latex reclaim in filled natural rubber compounds. It was found that the latex reclaim could replace raw natural rubber upto about fifty weight per cent in filled compounds too without any appreciable deterioration in mechanical properties. The scanning electron microscope studies showed that the failure mechanism of the blends in tension, tear and abrasion was essentially similar to that of filled natural rubber vulcanizate. The rheological studies of the blends in a torque rheometer showed marginal decrease in viscosity with the addition of latex reclaim as in the case of the gum compounds.

The rheological behaviour of filled natural rubber/latex reclaim blends was further studied in a capillary rheometer. The reduction in viscosity of raw natural rubber with the addition of latex reclaim was confirmed. The blends were found to be more pseudoplastic than raw natural rubber. It shows that the melt viscosity of the blends under high shear operations such as injection moulding would be lower than that of raw natural rubber. Further, the elasticity of the blends was marginally lower. It gave smoother extrudates with lower die swell. The details of the rheological behaviour of the blends are outlined in Part IV of Chapter 3.

Because of the commercial importance of blends of different elastomers, the next part of the study was done on the blends of latex reclaim with styrene-butadiene rubber. Almost a linear increase in tensile strength, tear strength and modulus was observed when latex reclaim was added to styrene- butadiene rubber in gum compounds. In filled styrene-butadiene rubber/latex reclaim blends,up to about 60 percent of latex reclaim, there was not any appreciable reduction in mechanical properties. The study showed that the latex reclaim could be advantageously employed for developing styrene-butadiene rubber/natural rubber blends economically. The viscosity of styrene-butadiene rubber filled compounds was found to decrease with the addition of latex reclaim as in the case of natural rubber/latex reclaim blends. The details of the study on styrene-butadiene rubber/latex reclaim blends are given in Chapter 4.

Since a low amount of crosslinking in the rubber phase is beneficial for developing thermoplastic elastomers from blends of plastics and elastomers, the next part of the study was aimed at utilising the residual crosslinking in latex reclaim for developing polypropylene/natural rubber blends. As expected, the mechanical properties of polypropylene/latex reclaim blends were superior to those of polypropylene/natural rubber blends. It was also observed that the dynamic crosslinking of the elastomer phase could further improve the mechanical properties of polypropylene/latex reclaim blends. In the case of polypropylene rich blends the latex reclaim was efficient in transforming the brittle failure of polypropylene to that of a ductile one. The viscosity of polypropylene was marginally increased with the addition of latex reclaim. However, this phenomenon was mainly limited to low shear region. The details of the study on polypropylene/latex reclaim blends are given in Chapter 5.

In Chapter 6, utilisation of latex reclaim in the manufacture of microcellular sheets is described. It is attempted to replace part of natural rubber in natural rubber/high styrene resin blends by latex reclaim for economic and other reasons. Technical properties such as hardness, compression set, split tear strength and abrasion resistance were found to be superior in latex reclaim based microcellular sheets compared to conventional microcellular sheets. It was found that about 30 per cent of natural rubber in natural rubber/high styrene resin based microcellular product could be replaced by latex reclaim without affecting their technical properties.

LIST OF PUBLICATIONS

1. The utilisation of latex reclaim in natural rubber compounds, Die Angewandte Makromolekulare Chemie. **215**, 25 (1994).
2. Studies on the use of reclaimed rubber from waste latex products. This was won the Best Paper Award in Students Technical Paper Competition held by Anna University, Madras.
3. The utilisation of latex reclaim in filled natural rubber compounds, 6th Kerala Science Congress - Young Scientist Award Contest Proceedings, Jan. 27-29, 1994, p.394.
   This has been communicated to the Journal of Polymer Recovery.
4. The utilisation of waste latex products in styrene-butadiene rubber, Journal of Materials Science (In press).
5. Thermoplastic elastomers from latex products, Kautschuk Gummi Kunststoffe (In press).
6. Rheological and extrudate behaviour of natural rubber/latex reclaim blends, Journal of Elastomers and Plastics (In press).
7. Studies on the cell structure and mechanical properties of NR/latex reclaim/HSR based microcellular sheets, Journal of Polymer - Plastics Technology and Engineering (Communicated).