STUDIES ON POLYMER BLENDS

WITH SPECIAL REFERENCE TO

NBR/PVC AND CR/PVC BLENDS

A thesis submitted by

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DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the supervision of Dr. D.Joseph Francis, Professor and Head, Department of Polymer Scienc & Rubber Technology, Cochin University of Science & Technology, Cochin 682 022, in the Dept. of Polymer Science & Rubber Technology. No part of this thesis has been presented for any other degree from any other institution.

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CERTIFICATE

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

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CONTENTS

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LIST OF ABBREVIATIONS USED IN THIS THESIS

PVC - Poly(vinyl chloride)
UPVC - Unplasticized poly(vinyl chloride)
NBR - Butadiene-acrylonitrile rubber
CR - Chloroprene rubber
NR - Natural rubber
SBR - Styrene-butadiene rubber
BR - Poly butadiene rubber
ABS - Acrylonitrile-butadiene-styrene
MBS - Methacrylate-butadiene-styrene
MBA - Methacrylate-butyl-acrylate
SAN - Styrene-acrylonitrile copolymer
EVA - Ethylene/vinyl acetate copolymer
CPE - Chlorinated polyethylene
PE - Polyethylene
POM - Poly oxymethylene
TBLS - Tribasic lead sulphate
DBLS - Dibasic lead stearate
MBTS - Benzothiazyl disulphide
TMTD - Tetramethyl thiuram disulphide
CBS - N-cyclohexyl-2-benzo thiazyl sulphenamide
DPG - Diphenyl guanidine
NA-22 - Ethylene thiourea
PBN - Phenyl-β-naphthylamine
SEM - Scanning electron microscope
T_g - Glass transition temperature
SRF black - Semi reinforcing furnace black

ML(1+4) at 100°C - Mooney viscosity determined using large rotor after a dwell time of one minute and motor run of 4 minutes at 100°C

IR - Infrared

phr - Parts per hundred rubber/resin

pphm - Parts per hundred million

rpm - Revolutions per minute

ASTM - American Society for Testing and Materials

DIN - Deutsches Institut für Normung

IS - Indian Standards

CHAPTER - 1

INTRODUCTION

INTRODUCTION

The art of combining different materials in order to improve properties constitutes one of the most ancient technologies known to civilization. By the middle of this century, soon after the development of synthetic polymers, this old art had been applied to the preparation of polymer blends. Polymer blends may be defined as intimate mixtures of two kinds of polymers with no covalent bond between them. Blending of polymers is carried out to improve the performance, modify the properties, extend the use of expensive polymers, reuse scrap, generate unique processable materials etc[1]. The largest volume of polymer blends is produced to improve and modify mechanical properties. Indeed, at present, the emphasis of polymer science and technology is tending to move away from wholly new polymers toward modification of existing ones.

There are a number of reasons, why research and development are turning their attention to blend technology[2]. Firstly, it has been possible to show that the technological gaps in the field of polymers can be filled by using appropriate combinations of polymers which are either available or can be manufactured using established processes. Secondly, with the help of blend technology, it is possible in many cases to improve a single critical property for a desired application without the need to accept large reductions in the remaining properties of the original polymers. Another reason for the attractiveness of blends from the point of view of the manufacturer of raw materials is the aspect of development time. Practical experience has shown that the time taken to achieve market maturity from the commencement of research and subsequent development of a project with a specific aim is appreciably shorter for blends than for base polymers.

Methods of preparation of polymer blends

There are three main approaches in the manufacture of polymer blends[2]:

1. Combinations of different granulated thermoplastics which the processor converts into a finished product, mainly by means of an extruder or an injection moulding machine. In this version, therefore the mastication process, the physical combination of the original polymers and the conversion into a finished or semi-finished product is all achieved in a single operation.

2. Particular properties of a single base polymer, e.g., its impact resistance, are modified by the addition of

relatively low proportions of a polymeric additive. This modification could be done using the processing machinery itself or along with the manufacture of the raw materials.

3. In the third variant, higher proportions (at least 10%) of two or more polymers are compounded under specified conditions of temperature and shear ready for processing.

General characteristics of polymer blends

It has been recognized that the properties of blends strongly depend on the morphology, i.e., on the miscibility, size and form of dispersed phase, the character and size of the interphase domains, and the distribution of residual stresses[1,3]. One of the key subjects of study relating to the performance of polymer blends is the degree of miscibility among components[4-6]. This is a thermodynamic criterion of compounds interaction. Unless the blends are thermodynamically compatible, phase separations occur with time and these may be reflected in significant property changes of the materials[7,8].

Miscibility in polymers

Generally, a necessary, although insufficient condition for thermodynamic miscibility is a negative

(Gibbs) free energy of mixing (ΔG_M).

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad (1)$$

where ΔH_M and ΔS_M are respectively the changes in enthalpy and entropy due to mixing at a given temperature, T. For high molecular weight polymers, ΔS_M is a small number and consequently for two polymers to be thermodynamically miscible ΔH_M must be either negative, zero, or atmost a small positive value. For ΔH_M to be negative, specific interactions such as donor-acceptor or hydrogen-bonding between the two polymer components must be possible. Since this is not common, the number of known miscible blends is small[9,10].

The concept of solubility parameter, a measure of the attractive forces between molecules is also used as an aid in comparing the relative compatibility of polymers[4,5]. This is based on the principle that molecules of two different species will be able to coexist if the force of attraction between different molecules is not less than the force of attraction between the two like molecules of either species. The energy of vaporization per unit weight gives a measure of the forces of attraction holding molecules together. The energy of vaporization per molar volume is known as the cohesive energy density and its square root is known as the solubility parameter, δ.

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}} = \left(\frac{H - RT}{M/D}\right)^{\frac{1}{2}} \qquad (2)$$

where

ΔE = energy of vaporization

V = molar volume

R = gas constant

T = temperature

M = molecular weight and

D = density.

Solubility parameter of a polymer is taken to be the same as that of a solvent in which the polymer will mix in all proportions and is determined by immersing samples in a range of solvent of known δ. Solubility parameter could also be calculated from a list of molar attraction constant, G, for the various parts of a molecule[11], which on addition gives δ from the relation,

$$\delta = \frac{D\Sigma G}{M} \qquad (3)$$

where D = density, and

M = molecular weight.

The solubility parameter values calculated this way are found to be more useful in predicting the compatibility. Single phase polymer blends with only one glass transition temperature (T_g) generally occurs when the solubility parameters of the constituent polymers do not differ more than[12] 0.7 $(cal/cm^3)^{1/2}$. However, it has been demonstrated that the solubility parameter approach to miscibility has limitations[5] and that specific interactions between unlike polymers differing in their solubility parameters can result in negative value of ΔH_M that can make ΔG_M favourable to mixing. Specifically it has been shown that such interactions like hydrogen bonding or more generalized electron donor-electron acceptor (Lewis acid-base) interactions dominate in the mixing of two polar species and that dipole-dipole interactions typically are negligible[13]. Interaction due to dispersion forces exist, but is not usually strong. Poly(vinyl chloride) (PVC) generally behaves as an electron acceptor and interacts strongly with electron donors. Of all polymers studied to date, PVC is the most miscible with structurally different homopolymers and copolymers[14].

Since the sum of the effects of interactive pairs depends on their concentration, miscibility also depends on the overall ratio of components, and if a copolymer is involved, on the composition of the component itself. With a given composition, the higher the molecular weight, less favourable, is mixing. The temperatures employed in mixing, the intensity of shear employed etc. also affect the miscibility of the components.

Three types of miscibility behaviour could be differentiated in polymer blends[15]. First, there are the miscible systems, whose advantage is that properties are generally predictable because they are based on those of the constituent materials. The disadvantage, however, is that a dramatic leap in properties cannot be achieved.

A second class of polymer blends are those that are totally immiscible. Lack of miscibility is a disadvantage, because the two or more phases of the material formed do not stick together. Adhesion can be improved by the use of compatibilizers, which promote the creation of smaller, better adhering domain sizes of the incompatible components. For a typical immiscible two-component system, in general, there can be two different types of dispersion states[16]. In the first state, one component forms a continuous phase and the other component forms a discrete phase. Usually the major component in terms of volume fraction forms the continuous phase. In the second state the individual components each form continuous phase giving rise to an interlocked or interpenetrated state of dispersion.

A third class of miscibility behaviour is that of partial miscibility. Here two blended materials form two separate phases, but each phase consists of a solution of the components in different concentrations. The gradient of concentration across the phase boundaries gives good adhesion and improved properties. The material is self compatibilized, the gradual interphase taking the place of a compatibilizer. Various experimental techniques such as electron microscopy, small angle X-ray diffraction, light scattering, thermal analysis and dynamic mechanical analysis have been used to investigate the question of miscibility.

Physical and mechanical properties

In a multicomponent or composite system, a property P_C depends on an average of the properties of the constituents, usually weighed in terms of volume fraction[17,18], ϕ:

$$P_C = \phi_A f(P_A) + \phi_B f(P_B) \qquad (4)$$

The precise form of the equation depends on the system, on the interactions between the components and on the miscibility.

In the case of miscible systems that are homogeneous on a fine scale the mixture will be transparent to the eye if

A and B are essentially amorphous, only one phase will be seen in the electron microscope and only one sharp T_g will be observed.

With such homogeneous systems equation (4) can be written as the following semiempirical equation[17]

$$P_C = \phi_A P_A + \phi_B P_B + K\phi_A\phi_B \qquad (5)$$

where K is an interaction parameter. When K is positive or negative, the general curve for P_C as a function of composition will in principle fall above and below respectively, the linear rule of mixtures corresponding to K = 0. Positive and negative values of K correspond to synergistic and non-synergistic behaviour respectively (Fig.1.1). However, significant variations from the rule of mixtures, usually do not occur in the case of homogeneous blends[19].

Equation (5) describes in particular variation with composition of such properties as glass transition temperature, density, refractive index, dielectric constant, thermal conductivity, heat capacity, thermodynamic properties, elastic moduli, viscosity of liquid mixtures and surface tension. Homogeneous or miscible blends are rare: poly(vinyl chloride)/ butadiene-acrylonitrile rubber and polystyrene/poly (phenylene oxide) are examples of the commercial ones.

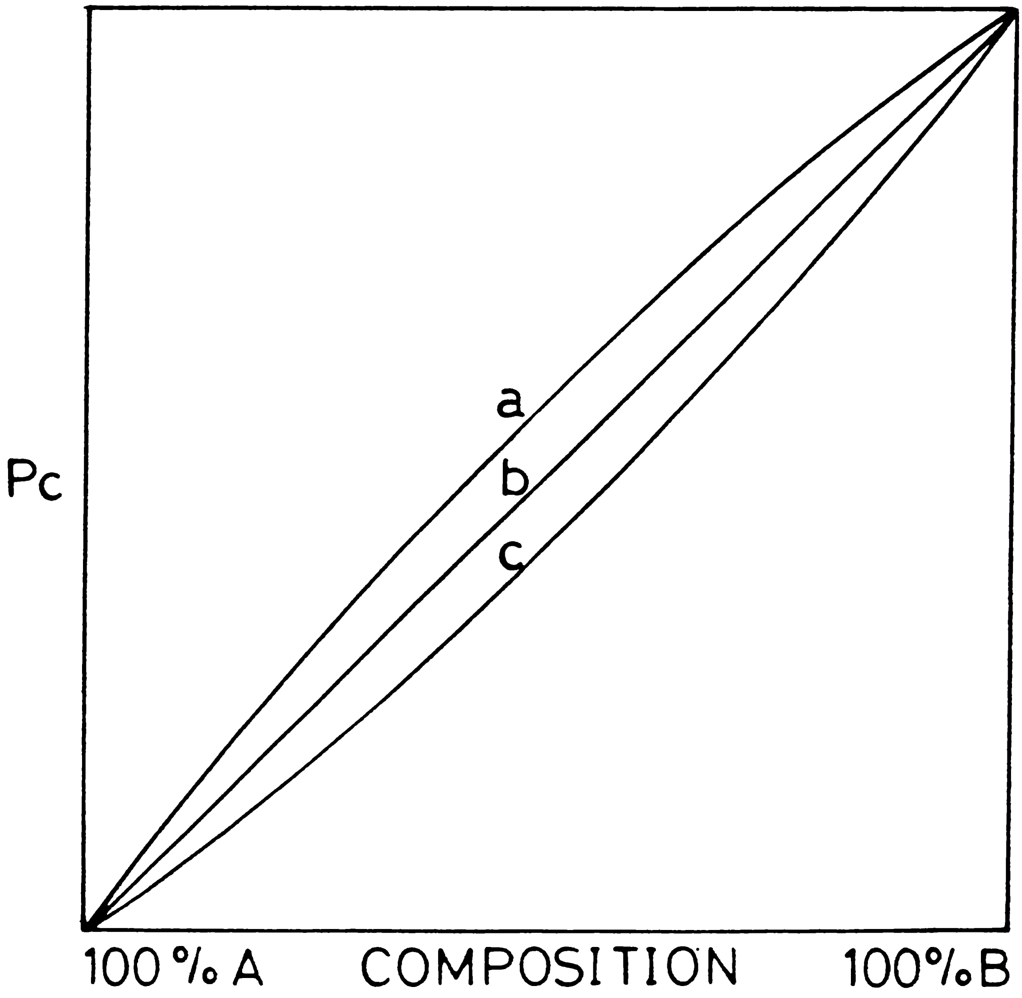


Fig. 1.1 Idealized curve for the combined property P_C, of a blend of two miscible polymers as a function of composition: (a) synergistic behaviour, (b) linear rule of mixtures, (c) non-synergistic behaviour.

Most polymer mixtures are immiscible and the properties of these heterogeneous blends are difficult to predict. Many of the equations proposed to account for the behaviour of heterogeneous blends can be expressed by[14,20]

$$\frac{P_C}{P_A} = \frac{1 + AB\phi_B}{1 - B\psi\phi_A} \qquad (6)$$

where P_A is the property of the continuous matrix, $A > 0$ depends on the shape and orientation of the dispersed phase and the nature of the interphase, B is a function of A, P_A and P_B and ψ is a reduced concentration term which is a function of the maximum packing fraction of the dispersed phase. This semiempirical mixing rule is obeyed by many physical properties such as elastic moduli, electrical conductivity, thermal conductivity, dielectric constant, thermal expansion coefficient, diffusion coefficient and the viscosity. For these blends equation (5) has also been used to describe variation with composition of such properties as moduli, impact strength, thermal and oxidative resistance, processability, environmental weatherability, colour, hardness, heat resistance, flame retardance, domain morphology, thermal expansivity, thermal conductivity, compressibility and refractive index. Because of the multiphase nature of these blends opacity is the rule.

Properties of all polymer blends but especially the heterogeneous ones strongly depend on the thermodynamic and rheological properties of the ingredient resins, the method and extent of mixing and processing. All these define the morphology in the final product and its ultimate properties and performance. Schematically these correlations can be presented as shown in Fig.1.2.

Poly(vinyl chloride) blends

Poly(vinyl chloride) has been manufactured commercially for the past 50 years and is, for calender year 1985, the second largest volume thermoplastic manufactured in the world. PVC is used in a wide range of applications because of its combined physical properties of,

compounding versatility as rigids or flexibles
high modulus (unplasticized)
ease of fabrication
low flammability and
low cost.

Because of this versatility of PVC, its blends are also attracting a lot of attention. Blending of PVC with other polymers is done for two reasons; to improve the properties of PVC and less often, to improve the properties of the other polymers.

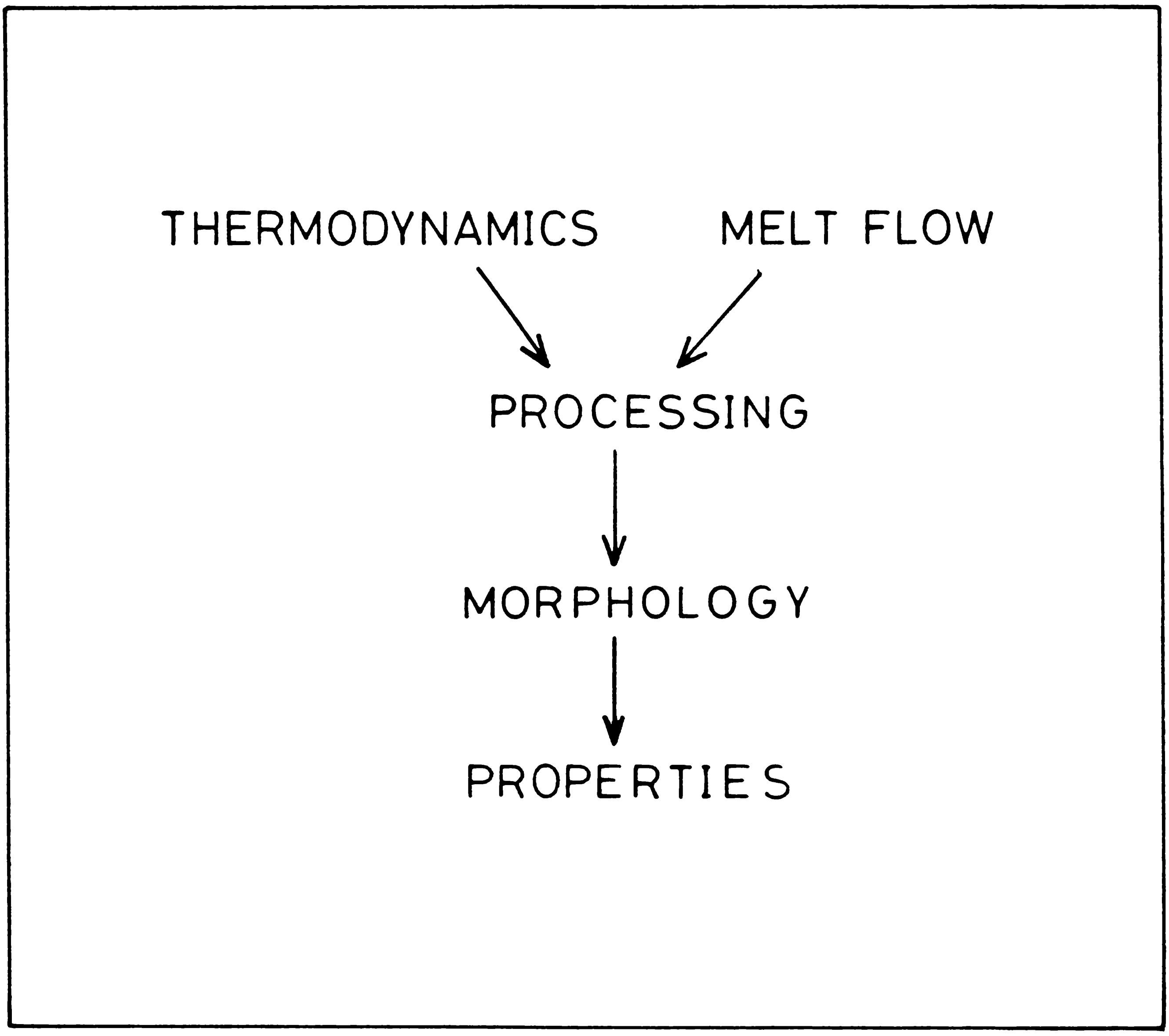


Fig. 1.2 Factors affecting properties of polymer blends.

Most PVC blends of technological interest are semimiscible or miscible. Whereas miscible blends are of most interest as polymeric plasticizers or for raising the heat distortion temperature, partial miscibility is required for most other purposes[21,22].

The variety of PVC blends and their properties are illustrated in Table 1.1.

OBJECTIVES AND SCOPE OF THE PRESENT WORK

The study was undertaken on PVC blends because of their all-round importance. One of the most prominent needs of PVC in application end-use is permanent plasticization[10]. Butadiene-acrylonitrile rubber (NBR) has been utilized as permanent plasticizer for PVC since the 1940s for wire and cable insulation, food contact, and pondliners used for oil containment[23,24]. Also plasticized PVC has been added to vulcanizable nitrile rubber, to yield improved ozone, thermal ageing, and chemical resistance resulting in applications including fuel hose covers, gaskets, conveyor belt covers, and printing roll covers. This blend is miscible in the range of 23 to 45 per cent acrylonitrile content in the butadiene-acrylonitrile copolymer[25].

The first phase of the study was directed towards modification of the existing PVC blends, especially NBR/PVC

Table 1.1

Poly(vinyl chloride) blends[20]

No.	Additive	Improved property
1.	ABS	Impact resistance, hardness, tensile strength, distortion temperature
2.	Acrylics	Impact resistance, transparency, chemical resistance, oil resistance, mouldability
3.	Poly(lactones)	Plasticization (non extractable), mouldability, impact resistance.
4.	SAN	Low temperature toughness, processability, dimensional stability
5.	Poly(imide)	Transparency, high distortion temperature, impact resistance
6.	MBA	High dimensional stability, processability
7.	Poly(urethanes)	Plasticization (non extractable) elongation, impact resistance, tensile strength, low temperature toughness
8.	Nitrile rubber (NBR)	Plasticization, toughness

No.	Additive	Improved property
9.	EVA	Plasticization, toughness, adhesiveness
10.	Chlorinated PE (CPE)	Processability
11.	Poly(vinyl chloride-g-ethyl acrylate)	Impact resistance, thermal stability, processability
12.	PE + CPE	Ductility, elongation, low temperature toughness
13.	BR	Toughness, weatherability
14.	Hytrel (copolyester)	Low temperature toughness, plasticization
15.	PVC/EVA-copolymer	Processability, mechanical properties
16.	Poly(dimethyl siloxane)	Large effect on processability, heat stability
17.	Chlorinated POM	Processability, plasticization

blends. These blends, in addition to the polymers, require a host of additives like curatives for the NBR phase and stabilizers for the PVC phase[26]. Careful consideration has to be given in the selection of these ingredients especially when the end product is to be used in applications like food containers. Further, the additives chosen for one polymer should not affect the other. It would be attractive in such a situation if common rubber compounding ingredients themselves could be successful heat stabilizers for PVC. Magnesium oxide and zinc oxide are conventional ingredients in rubber compounding. Magnesium oxide is a good acid acceptor[27] and zinc oxide is associated with good heat ageing[28]. Hence magnesium oxide/zinc oxide combination could be a potential heat stabilizer for PVC. This combination, if found successful, could be used in NBR/PVC blends.

NBR/PVC blends could be further modified with other polymers for improving the performance and properties or for economic advantage. Modifying these blends with general purpose rubbers like natural rubber (NR), styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) could produce economically advantageous ternary blends. Compared to NBR, NR has higher strength and tear strength, SBR has higher hardness and modulus and BR has higher abrasion resistance[29,30]. Hence, the ternary blends prepared by modifying NBR/PVC blends by these general purpose rubbers are also likely to display some improved physical properties. Polysulphide rubbers are outstanding in their solvent resistance. However, their processing characteristics, odour and mechanical properties are very poor[31]. If blends of polysulphide rubbers with NBR/PVC blends could be prepared without seriously affecting the solvent resistance of the former or the mechanical properties of the latter, it would be a promising method for generating high performance ternary blends. It is proposed to study these modifications of NBR/PVC blends in the present work.

The second phase of the study was directed towards the development of novel PVC based blends. Chloroprene rubber (polychloroprene) (CR) is structurally similar to PVC and hence is likely to form successful blends with PVC[32]. Polychloroprene has very good resistance to oil, ozone, oxidation, high temperatures and naked flames. It is less permeable to gases than NR and SBR and has good electrical and mechanical properties (in particular its strength and resilience). It has good strength without carbon black, but the inclusion of carbon black will improve strength even more. It is used in many critical applications like car radiator hoses, gaskets, seals, conveyor belts etc.[33,34]. If blends of CR and PVC could be made without large reductions in the useful properties of CR, it would be a cheaper substitute for CR. Further, the higher modulus, ageing resistance etc. of PVC could also be imparted to the blends. CR being a crystallizable rubber like NR, the CR/PVC blends could display good mechanical properties even without reinforcing fillers. It is proposed to study the preparation and performance of CR/PVC blends in this study.

Since plasticizers could lower the processing temperature of PVC blending of CR with plasticized PVC could be done at lower temperatures. But blending of CR with unplasticized PVC (UPVC) requires comparatively high temperatures. In the former case an MgO/ZnO based system could be effective both as the stabilizer for PVC and the curative for CR. But in the latter case a high temperature stabilizer might be required. When such a stabilizer is used we may not have, however, the advantage of using the same material(s) as stabilizer and curative. Tribasic lead sulphate ($3PbO.PbSO_4.H_2O$) (TBLS), a commonly used high temperature stabilizer for PVC[35], is a good acid acceptor and contains PbO which is a curing agent for CR[36]. Hence, TBLS might itself be a potential curative for CR. This stabilizer, if found successful, could be advantageously used in the high temperature blending of CR and PVC. It is also proposed to study the efficiency of TBLS as a curing agent for CR in the present work.

This thesis is divided into the following chapters:

Chapter 1	- Introduction
Chapter 2	- Experimental techniques
Chapter 3	- MgO/ZnO combination--Efficient stabilizer for poly(vinylchloride)
Chapter 4	- Tribasic lead sulphate--Efficient curing agent for polychloroprene
Chapter 5	- Studies on butadiene--acrylonitrile rubber/poly(vinylchloride) blends
Chapter 6	- Modification of polychloroprene with poly (vinyl chloride)
Chapter 7	- Summary and conclusions.

References

1. L.A.Utracki, Polym.Eng.Sci., 23, 602 (1983).

2. W.Witt, Int.Polym.Sci.Technol., 12, No.8, 4 (1985).

3. J.A.Manson and L.H.Sperling, "Polymer Blends and Composites", Plenum Press, New York (1976).

4. S.Krause in "Polymer Blends", D.R.Paul and S.Newmann (Eds.), Vol.1, Chap.2, Academic Press, New York (1978).

5. O.Olabisi, L.M.Robeson and M.T.Shaw, "Polymer-Polymer Miscibility", Academic Press, New York (1979).

6. C.D.Han, "Multiphase Flow in Polymer Processing", Academic Press, New York (1979).

7. J.W.Barlow and D.R.Paul, Polym.Eng.Sci., 21, 985 (1981).

8. T.K.Kwei and T.T.Wang in "Polymer Blends", D.R.Paul and S.Newmann (Eds.), Vol.1, Chap.4, Academic Press, New York (1978).

9. N.A.J.Platzer, "Copolymers, Polyblends and Composites", Advances in Chemistry Series No.143, American Chemical Society, Washington D.C. (1975).

10. L.M.Robeson, Polym.Eng.Sci., 24, 587 (1984).

11. P.A.Small, J.Appl.Chem., 3, 71 (1953).

12. H.G.Elias, "Macromolecules", Vol.2, Chap.25, Plenum Press, New York (1984).

13. J.A.Manson in "Encyclopaedia of PVC", L.I.Nass and C.A.Heiberger (Eds.), Vol.1, Chap.10, Marcel Dekker, New York (1986).

14. O.Olabisi in "Kirk-Othmer Encyclopaedia of Chemical Technology", M.Grayson and D.Eckroth (Eds.), Vol.18, p.445, Wiley-Interscience, New York (1982).

15. V.Wigotsky, Plast.Eng., 42, 19 (1986).

16. H.K.Chuang and C.D.Han, J.Appl.Polym.Sci., 29, 2205 (1984).

17. L.E.Nielson, "Predicting the Properties of Mixtures", Marcel Dekker, New York (1978).

18. L.E.Nielson, "Mechanical Properties of Polymers and Composites", 2 Vols, Marcel Dekker, New York (1974).

19. H.K.Chuang and C.D.Han in "Polymer Blends and Composites in Multiphase Systems", C.D.Han (Ed.), Chap.11, Advances in Chemistry Series 206, American Chemical Society, Washington, D.C. (1984).

20. L.A.Utracki, Polym.Plast.Technol.Eng., 22, 27 (1984).

21. B.Terselius and B.Rundy, Pure Appl.Chem., 53, 421 (1981).

22. J.A.Manson, Pure Appl.Chem., 53, 471 (1981).

24. J.E.Pittenger and G.F.Cohan, Mod.Plast., 25, 81 (1947).

25. G.A.Zakrzewski, Polymer, 14, 348 (1973).

26. A.H.Mazumdar and M.S.Majmudar, "Chemaprene Rubber Handbook", Chap.7, Synthetics & Chemicals Ltd., Bombay (1983).

27. D.N.Simmons in "Rubber Technology and Manufacture", C.M.Blow and C.Hepburn (Eds.), Chap.6, Butterworths, London (1985).

28. S.H.Morrell in "Rubber Technology and Manufacture", C.M.Blow and C.Hepburn (Eds.), Chap.5, Butterworths, London (1985).

29. F.W.Billmeyer, "Textbook of Polymer Science", Chap.19, John Wiley & Sons, New York (1984).

30. D.C.Blackley, "Synthetic Rubbers", Applied Science Publishers, London (1983).

31. W.Cooper and G.M.Doyle in "Rubber Technology and Manufacture", C.M.Blow and C.Hepburn (Eds.), Chap.4, Butterworths, London (1985).

32. K.Mori and Y.Nokamura, Plast. & Rub.Proce. & Appl., 3, 17 (1983).

33. R.J.Crawford, "Plastics and Rubbers--Engineering Design and Applications", Mechanical Engineering Publications Ltd., London (1985).

34. J.C.Bament and J.G.Pillow in "Developments in Rubber Technology - 2", A.Whelan and K.S.Lee (Eds.), Chap.5, Applied Science Publishers, London (1981).

35. L.I.Nass, "Encyclopedia of PVC", Vol.1, Chap.9, Marcel Dekker, Inc., New York (1976).

36. D.B.Forman in "Rubber Technology", M.Morton (Ed.), Chap.13, Van Nostrand Reinhold Company, New York (1973).

CHAPTER-2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

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

MATERIALS

Poly(vinyl chloride)

The poly(vinyl chloride) (PVC) used in the study was suspension polymer with a K value of 65 as powder. The resin was obtained from National Organic Chemicals Ltd., Bombay.

Butadiene-acrylonitrile rubber

Butadiene-acrylonitrile (nitrile) rubber (NBR) used in the study had an acrylonitrile content of 33% and a Mooney viscosity of 40.9 (ML(1+4) at $100^{o}C$). The rubber was obtained from Synthetics and Chemicals Ltd., Bareilly.

Chloroprene rubber

Poly(chloroprene) (neoprene) rubbers (CR) used in the study were the following general purpose grades:

1. GN type, Mooney viscosity, ML(1+4) at 100°C, 46
2. W type, Mooney viscosity, ML(1+4) at 100°C, 47

3. W type, Mooney viscosity, ML(1+4) at 100°C, 42.

All the three grades were obtained from Du Pont, USA.

Natural rubber

The natural rubber (NR) used was crumb rubber, ISNR-5 obtained from the Rubber Research Institute of India, Kottayam. The Mooney viscosity of the rubber was 85.3 (ML(1+4) at 100°C).

Styrene-butadiene rubber

Styrene-butadiene rubber (SBR) was obtained from Synthetics & Chemicals Ltd., Bareilly. The rubber had a styrene content of 23.5% and a Mooney viscosity of 49.2 (ML(1+4) at 100°C).

Polybutadiene rubber

Polybutadiene rubber (BR) was obtained from Indian Petrochemicals Corporation Ltd., Baroda. The rubber was 97% 1,4 (cis) and had a Mooney viscosity of 48.0 (ML(1+4) at 100°C).

Polysulphide rubber

Polysulphide rubber used in the study was FA type with a Mooney viscosity of 82.0 (ML(1+4) at 100°C). It was supplied by M/s.J.B.Polymers, Bombay.

Magnesium oxide

Magnesium oxide used in the study was commercial grade calcined light magnesia with a specific gravity of 3.6.

Zinc oxide

Zinc oxide used in the study was commercial grade white seal with a specific gravity of 5.5.

Stearic acid

Stearic acid used in the study was commercial grade with a specific gravity of 0.92.

Tribasic lead sulphate

Tribasic lead sulphate ($3PbO.PbSO_4.H_2O$) (TBLS) used was commercial grade with a specific gravity of 7.0.

Dibasic lead stearate

Dibasic lead stearate ($2PbO.Pb(C_{17}H_{35}COO)_2$) (DBLS) used was commercial grade with a specific gravity of 1.9.

Red lead

Red lead (Pb_3O_4) used was commercial grade supplied by M/s.Glaxo India.

Dioctyl phthalate

Dioctyl phthalate (DOP) used was commercial grade with a specific gravity of 0.986 and viscosity 60 cps.

Epoxidized soyabean oil

Epoxidized soyabean oil used was commercial grade with a specific gravity of 0.993 and viscosity 400 cps.

Calcium stearate

Calcium stearate used was commercial grade.

Lauric acid

Lauric acid used was commercial grade.

Titanium dioxide

Titanium dioxide used was commercial grade.

Sulphur

Sulphur used in the study was commercial grade which conformed to the specifications given in I.S. 8851 (1978).

MBTS

MBTS (benzothiazyl disulphide) used was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

TMTD

TMTD (tetramethyl thiuram disulphide) used was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

CBS

CBS (N-cyclohexyl-2-benzothiazyl sulphenamide) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

DPG

DPG (diphenyl guanidine) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

NA-22

NA-22 (ethylene thiourea) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

PBN

PBN (phenyl-β-naphthylamine) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

Carbon black

Carbon black used in the study was semi-reinforcing furnace black (N741) supplied by Phillips Carbon Blacks Ltd., Durgapur.

Naphthenic oil

Naphthenic oil used in the study was commercial grade procured from M/s.Hindustan Petroleum Corporation.

Aromatic oil

Aromatic oil used in the study was commercial grade procured from M/s.Hindustan Petroleum Corporation.

ASTM reference oil

ASTM reference oil used in the study was ASTM reference oil 3 which conformed to the specifications given in ASTM D471 (1983).

Solvents

Solvents used in the study (chloroform, toluene, acetone, carbon tetrachloride, methanol, acetic acid and methyl ethyl ketone) were of analytical grade.

EXPERIMENTAL PROCEDURES

Preparation of PVC compounds

The dry blending technique was employed for the preparation of PVC compounds. PVC resin and the stabilizers were subjected to vigorous stirring. When the temperature rose to about 70° - 80°C, plasticizer was added which got absorbed into the polymer particles to give dry, free flowing powders.

Studies on a Brabender Plasticorder

Brabender Plasticorder (Torque rheometer) manufactured by M/s.Brabender OHG Duisburg, West Germany has been widely used for measuring processability of polymers, rheological properties of polymer melts, for blending of polymers, modelling processes such as extrusion etc.[1-6]. A plasticorder model PL3S was used in this study.

The Brabender torque rheometer is essentially a device for measuring in metergrams the torque generated due to the resistance of a material to mastication or flow under pre-selected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model specified. Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with nogs or protrusions. The resistance which is put up by the test material against the rotating rotors in the mixing chamber is made visible with the help of a dynamometer balance. The dynamometer is attached to a precise mechanical measuring system which indicates and records the torque. By means of a lever and weight system different measuring ranges could be adjusted. For the present model the minimum span is 0-1000 metergrams, the intermediate span 0-2500 metergrams and the maximum span 0-5000 metergrams. A D.C. thyristor controlled drive is used for speed control of the rotors (range 0 to 150 rpm). The temperature of the mixing chamber is controlled by circulating hot oil. The temperature could be set at any value upto 300°C. Stock temperature thermocouple coupled with a temperature recorder is used for temperature measurement. Different types of rotors could be employed depending upon the nature of the polymers. The rotors can be easily mounted and dismounted due to the simple fastening and coupling system. Once test conditions have been decided (rotor type, rpm and temperature), and set, sufficient time should be given for the temperature to attain the set value and to become steady. Then the materials could be charged into the mixing chamber to obtain a torque-time curve or a plastogram. A typical torque-time curve for a PVC compound is shown in Fig.2.1 (for formulation A,table 3.6). The following observations could be made from the torque-time curve.

A - begin of the curve
This is the point at which the material is heated.

B - maximum torque
This is the point at which maximum torque is attained due to the melting of PVC phase.

C - torque stabilizes at a value
This is the point at which torque stabilizes to a constant value, when the fusion and homogenization is complete. The torque shown is a measure of the melt viscosity at the corresponding stock temperature.

D - degradation break
This is the point at which crosslinking of the molecules due to accelerated molecular degradation starts.

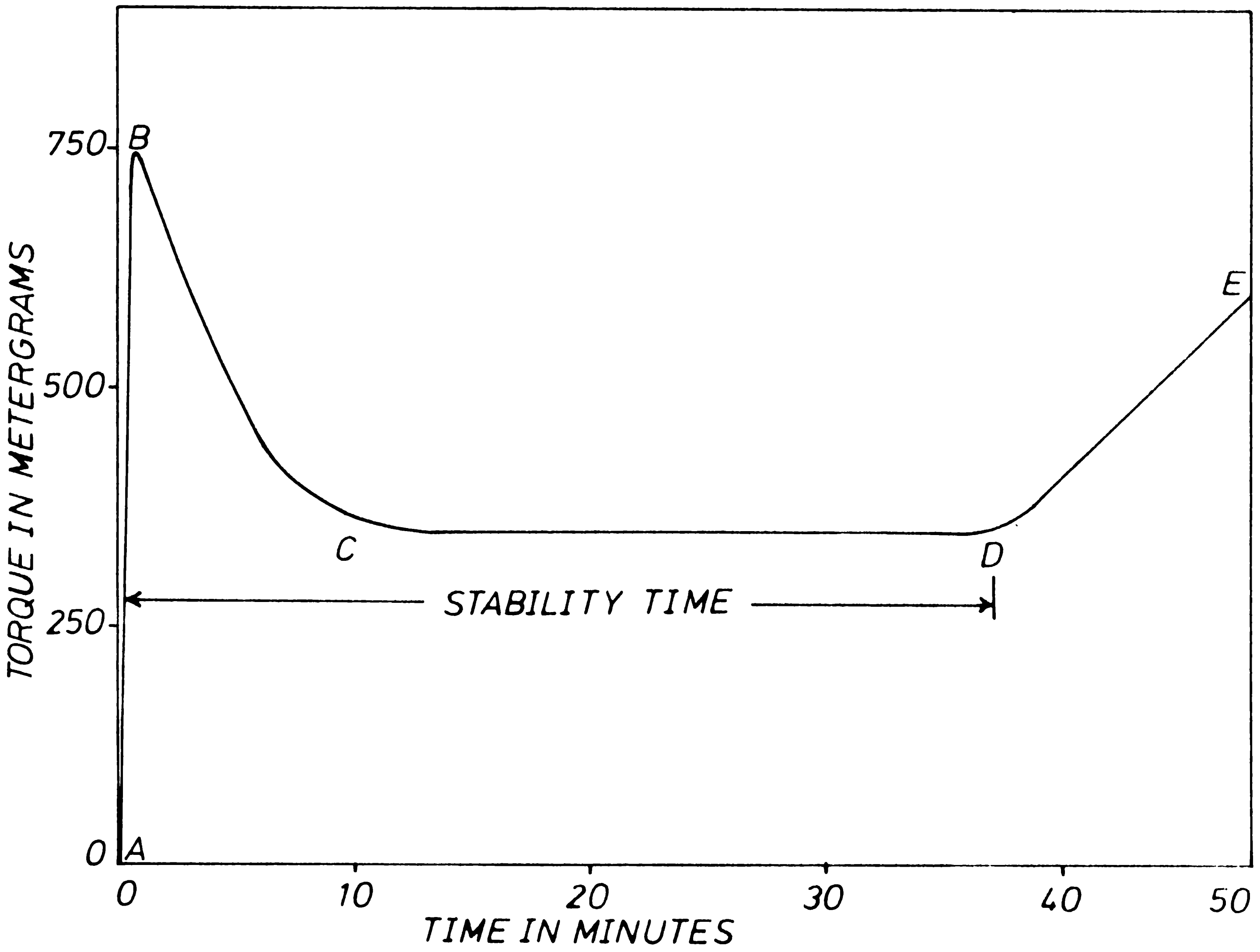


Fig. 2.1 A typical Brabender torque-time curve for a PVC compound

E - maximum crosslinking

This is the point at which the degree of crosslinking reaches maximum. Thereafter the material crumbles down to powder and the torque drops to zero.

The distance between A and D in minutes is a measure of the heat stability of the material under investigation. The stability time of the present compound is about 37 minutes. A long stability time indicates processing safety. When the material is used in processing operations such as extrusion, the complete processing time should be well below the stability time of the material. The Brabender torque rheometer could also be used for a variety of other applications such as measuring processability, rheological behaviour of polymers, blending of two polymers etc. In processes such as blending, the operation should be completed in the stable period of the polymers in order to prevent any degradations in the matrix. In the present work the Brabender plasticorder was used for the assessment of heat stability of PVC compounds, blending of PVC with other polymers, for examining the compatibility of PVC with other polymers etc. The details of the procedure adopted are given in the relevant chapters.

Heat stability testing

Heat stability tests on PVC compositions and products are important in the practical contexts of processing and service. Evaluation of the suitability and effectiveness of stabilizers, and stabilizer/plasticizer/lubricant systems in protecting PVC against degradation both under processing conditions and in use, is one of their main applications.

Determination of stability time on a Brabender plasticorder, or in other processing equipments like internal mixer, extruder or two roll mill, is specified as a dynamic test method since the stability of the material is determined in actual processing conditions. In equipments like the mill where a torque-time curve cannot be obtained, stability is assessed by periodically checking other effects used as the degradation index (commonly colour development in the material). By their nature, dynamic tests are primarily relevant to the effects of processing on PVC compositions. Indeed, the test equipment, temperature and running conditions are often chosen with a view to relating the test results to a particular process.

In static tests, the test treatment essentially consists in heating specimens of PVC material at the test temperature. The specimens are often pieces of sheet of standard size, but they may also be standard weights of powder or pellets of PVC polymer or composition.

1. Oven stability test

The oven stability test was the static test on stability conducted in this study. In this test, the heating equipment was an air-circulation oven, the specimens being placed inside the oven. The oven was set to a temperature suitable for the particular composition and stability was determined in terms of heating time to reach a certain level of the degradation index used in the test: this may be the first appearance, or attainment of a certain degree of discolouration in the composition. The results of static tests are more relevant to the effects of heat in service than in processing of PVC materials. However, because the test procedures are simpler than those of dynamic tests, oven stability test is sometimes used to obtain indications of likely stability in processing with suitable correlations. An oven used for static heating test must be reliable with good control and even distribution of temperature. ASTM D2115 (1974) gives a useful summary of requirements in this regard.

A sequence of colour change is established by preparing a series of strips of PVC sheet degraded to the colours listed below:[7]

0 clear
1 barely detectable change
2 very slight change
3 slight yellow tinge
4 pale yellow
5 yellow

6 faint tinge of red
7 pale red
8 red
9 deep red
10 very deep red/black.

2. Congo red test

Another test on heat stability conducted in this study was the Congo red test. The principle of this method is the detection or determination of HCl evolved by PVC material on heating. Enough sample of the compound was taken in a test tube to fill the test tube to a depth of 50 mm. Congo red paper strip (30 mm x 10 mm) was centrally mounted on the test tube above the specimen. Then the test tube was placed in an oil bath kept at 180^{o}C. Time in minutes for red colour to change to transient violet or permanent blue was recorded. Mean values of times obtained in duplicate determinations for each specimen was recorded as the stability time. The details of the method are given in DIN 53381.

Mixing and homogenization on the mixing mill

Mixing and homogenization of polymers and compounding ingredients were also done on a laboratory size two roll mixing mill (15 cm x 33 cm) at a friction ratio of 1:1.

The polymers were blended initially and temperature of the rolls was maintained at 40°C-50°C during this time. Proper blending of the polymers was ensured by careful control of temperature, nip gap, time of mastication and by uniform cutting operation. The compounding ingredients were then added as per ASTM D3184 (1980) and 3182 (1982) in the following order: activators, fillers, accelerators and curing agent(s). Before the addition of accelerators and sulphur, the batch was thoroughly cooled.

After completion of mixing, the stock was sheeted out and passed six times end wise through a tight nip and finally sheeted out at a nip gap of 3 mm. Mixing time and temperature were controlled during the studies.

Determination of cure characteristics

1. Using Monsanto Rheometer

The cure characteristics of the compounds were determined mostly on a Monsanto Rheometer model R 100 at 150°C. In this test, the polymer specimen is contained in a cylindrical cavity 50 mm x 10 mm and has embedded in it a biconical rotor of diameter 37 mm which is oscillated sinusoidally through a small arc amplitude. The cavity and specimen are maintained at a temperature of ±0.50°C and the force required to oscillate the disc is measured. The following data could be taken from the torque-time curve (ASTM D1646 (1981)):

(i) Minimum torque - This is the torque attained by the mix after homogenizing at the test temperature before the onset of curve.

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

(iii) Optimum cure - This is the time taken for attaining 90% of the maximum torque.

(iv) Scorch time - This is the time taken for 2 units rise above the minimum torque.

If the mix exhibits a reverting cure behaviour, the torque decreases after reaching the maximum value.

2. Using Göttfert Elastograph

This is a rotorless curemeter and the torque-time curve is generated by the oscillation of the lower half of cavity in which polymer mix is charged. An Elastograph model 67.85 was used in this study. This is a microprocessor controlled curemeter and hence has the capacity of generating so many other data such as the cure-rate curve. However, the torque-time curve of the Elastograph is similar to that of the Rheometer and all the relevant data could be taken accordingly.

Mooney viscosity measurement

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 disk rotating in a shallow cylindrical cavity set at 100°C and filled with the rubber under test. In running a viscosity test, the sample was allowed to warm up for one minute after the platens were closed. The motor was then started. Reading taken after 4 minutes was reported as the Mooney viscosity of the rubber (ML(1+4) at 100°C) (ASTM D1646 (1981)).

Moulding of test sheets

The test sheets for determining the physical properties were prepared in standard moulds by compression moulding on a single daylight electrically heated press having 30 cm x 30 cm platens at a pressure of 45 kg/cm^2 on the mould. In the case of rubber(s) and blends in which rubbers constituted the major fraction, the compounds were vulcanized upto their respective optimum cure times at 150°C. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set) additional times based on the sample thickness were used to obtain satisfactory mouldings. In the cases of mixes showing a thermoplastic nature, the mouldings were prepared in specially designed moulds which could be immediately cooled after curing with the samples still kept inside under compression. The same technique was used for compression moulding of thermoplastics. However, in the case of thermoplastics moulding temperatures and times were determined by trial and error methods (ASTM D3182 (1982)).

Physical test methods

1. Tensile strength, elongation at break and modulus

In the present work these tests were carried out according to ASTM D412 (1980) using dumb-bell specimens on a Zwick Universal Testing Machine model 1445. All the above tests were carried out at 25±2°C. Samples were punched from compression moulded sheets parallel to the grain direction 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 500 mm/minute. Tensile strength, elongation at break and modulus (stress at a given elongation) were printed out after each testing.

2. Hardness

Shore-A type Durometer was employed to find out the hardness of the moulded samples. The instrument uses a calibrated spring to provide the indenting force. Readings were taken after 15 seconds of the indentation after firm contact had been established with the specimens. The method employed was ASTM D2240 (1981).

3. Compression set

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hr in an air oven at 70°C. After the heating period, the samples were taken out, cooled to room temperature for half 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 and t_s is the thickness of the spacer bar used. The method used was ASTM D395 (1982) method B.

4. Tear resistance

This test was carried out as per ASTM D624 (1981). Unnicked, 90° angle test pieces were used. The samples were cut from the compression moulded sheets parallel to the grain direction. The test was carried out on a Zwick Universal Testing Machine. The speed of extension was 500 mm/minute and the temperature 25±2°C.

Ageing studies

Dumb-bell specimens for evaluation of physical properties were prepared and aged in an air oven at pre-determined temperatures for specified periods suitable for the test material. Physical properties like tensile strength, elongation at break, modulus etc. were measured before and after ageing and the percentage retention of these properties was evaluated for assessing the effect of ageing (ASTM D573).

Ozone resistance test

The ozone resistance of samples was assessed as per ASTM D1171 (1974) using a Mast ozone chamber. In this chamber, ozonised air is generated with the help of an ultraviolet lamp. Test pieces of triangular cross-section with specified dimensions were prepared and were then bent into a loop for keeping the samples under strain. After mounting, the samples were allowed to condition for a specified period of time at room temperature in an ozone-free atmosphere. The samples were then introduced into the ozone chamber at an ozone concentration of 50 parts per hundred million (pphm). The temperature of the test was 40±1°C. The samples were exposed for 20 hours and visual assessment of crack intensity was made at 10 hours interval.

For estimating the ozone concentration a known volume of air is passed into a 4% solution of potassium iodide buffered to pH 7. The liberated iodine is titrated against 0.002 N sodium thiosulphate solution and ozone concentration calculated.

Swelling studies

Samples of approximately 1 cm diameter, 0.25 cm thickness and 0.30 gm weight, were punched out from the central portion of the compression moulded sheets, weighed and allowed to swell in excess of the respective solvents at laboratory temperature (30±2°C) for the specified period of time. Then the samples were taken out, quickly dried with a filter paper and weighed. The percentage increase in weight was calculated. The procedure given in ASTM 471 (1983) was followed.

Infrared spectroscopy

Infrared (IR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indicative of the bond strengths and structural geometry in the molecule. Absorption at around 1700 cm^{-1} was made use of in this study because it is appropriate for carbonyl group determination[8-11]. The IR spectra given in this investigation were taken in KBr pellets using a Perkin Elmer model 983.

Scanning electron microscopy

Scanning electron microscope (SEM) was first introduced in 1965 and it has since become a very useful tool in polymer research for studying morphology[12-14]. In this technique an electron beam is scanned across 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 gold or platinum. This is done by placing the specimen in a high vacuum evaporator and vaporizing the conducting material held in a tungsten basket (vacuum dispersion).

The SEM observations reported in the present investigation were made on the fracture surface of tensile test specimens using a Philips 500 model scanning electron microscope. The fracture surfaces of the samples were carefully cut out from the failed test pieces without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made within one week after gold coating. The gold coated samples were kept in desiccators before the SEM observations were made. The shapes of the test specimens, direction of the applied force and portions from where the surfaces have been cut out for SEM observations are shown in Fig.2.2.

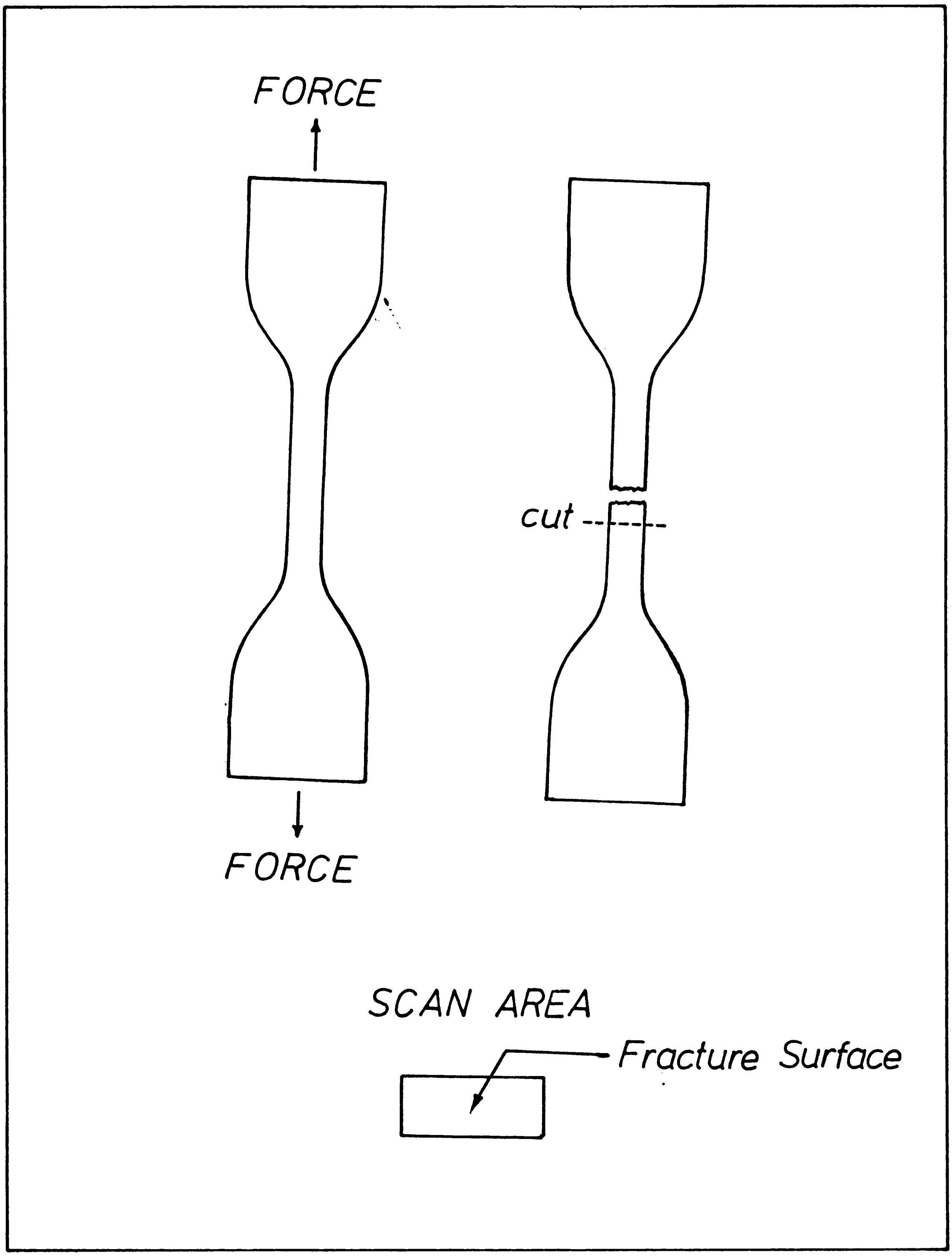


Fig. 2.2 SEM scan area of the tensile failure surface.

References

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

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

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

4. H.E.Luben, Chem.Rundschau, 27, 17 (1974).

5. C.Roja Rao and K.Ramamurthy, Popular Plast., 12, 15 (1977).

6. N.V.Zakharenko et al, Inter.Polym.Sci.,Technol., 12, No.9, 23 (1985)

7. W.V.Titow, "PVC Technology", Elsevier Applied Science Publishers, London (1984).

8. D.Braun, A.Michel and D.Sonderhof, Eur.Polym.J., 17, 49 (1981).

9. J.F.Rabek et al, J.Appl.Polym.Sci., 24, 2407 (1979).

10. F.Mori, M.Koyama nand Y.Oki, Angew.Makromol.Chem., 68, 137 (1978).

11. J.Verdu, J.Macromol.Sci.Chem., 12, 551 (1978).

12. J.R.White and E.L.Thomas, Rubber Chem.Technol., 57, 457 (1984).

13. P.R.Thornton, "Scanning Electron Microscopy", Chapman and Hall, London (1968).

14. E.Balcerzyk, J.Hockstim and S.Wlodarezyk, Int.Polym.Sci. Technol., 12, No.7, 121 (1985).

CHAPTER - 3

MAGNESIUM OXIDE/ZINC OXIDE COMBINATION EFFICIENT STABILIZER FOR POLY(VINYL CHLORIDE)

MAGNESIUM OXIDE/ZINC OXIDE COMBINATION--EFFICIENT STABILIZER FOR POLY(VINYL CHLORIDE)

Poly(vinyl chloride) (PVC) surpasses every other polymer in diversity of applications. This versatility stems from its ability to be compounded into various flexible and rigid forms with good physical, chemical and weathering properties. In addition, PVC has broad processability including calendering, extrusion, moulding (injection, compression, rotational, blow), fluid (solution, latex, organosol, plastisol) coating and impregnation. This broad menu of PVC technology has generated an almost endless formulary of PVC compounds. PVC formulations can contain varying amounts of the following ingredients in order to give the polymer the desired processing and end-use characteristics[1].

- Plasticizers
    - Monomerics
    - Oligomerics
- Polymeric modifiers
    - Solid plasticizers
    - Impact modifiers
    - Heat distortion improvers
    - Processing aids
- Fillers
- Heat stabilizers
- Lubricants

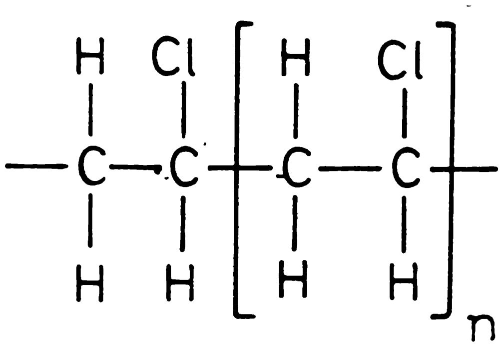
Colourants
Light stabilizers
Blowing agents
Flame retardants
Deodourants
Antistats

Heat stabilizer is singly the most important ingredient in PVC compounds and it is incorporated in all PVC compositions to protect the polymer against thermal degradation at the high temperatures of processing (generally ranging from 170°C to 220°C depending upon the amount of plasticizer and other ingredients) and also subsequently in service.

PVC degradation and stabilization

If unstabilized PVC is exposed to heat (temperature above 100°C), ultra-violet light or gamma radiation, then depending on the intensity of exposure and type of PVC, a cleavage of HCl accompanied by polyene sequence formation and crosslinking along the chain or intermolecularly, can occur[2-4]. As a result, the polymer discolours from yellow to dark brown, the solubility in various solvents decreases, and the original mechanical and electrical properties of the PVC deteriorate rapidly[5,6]. All these effects are intensified in the presence of oxygen. The thermal degradation of

PVC is effected by an auto-catalytic dehydrochlorination reaction due to the presence of labile sites in the polymer chains such as allyl chlorines and tertiary hydrogen and chlorine atoms, or by terminal end groups such as double bonds or peroxide residues[7]. If PVC in reality did correspond to the idealized concept of regular repeating units shown in Fig.3.1(A) and nothing else, it would be expected to be a polymer of remarkable inherent stability, as evidenced by thermogravimetric analysis and other studies made on similar low molecular weight model compounds such as 1,3,5-trichlorohexane[8,9]. The fact that commercial PVC does not perform in a manner predicted by the model system led investigators to examine other model systems representative of the possible structures that might logically be expected to be present in PVC as structural irregularities. These studies have shown that internal allylic chlorides are the least stable (most susceptible to replacement) of all the groups examined, followed in order by tertiary chlorides, terminal allylic chlorides and secondary chlorides[10]. From this and from other evidence, it is postulated that the degradation of PVC is due initially to a loss of hydrogen chloride, which commences at a site on the molecule either containing or adjacent to a tertiary or allylic chloride atom, either of which can function as an activating group as shown in Fig.3.1(B). The elimination of the first molecule



$$-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}\left[-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-\right]_n$$

A. PVC repeating unit

$$-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-X-$$

$$\Big\downarrow \text{-HCl}$$

$$-CH_2-CHCl-CH_2-CHCl-CH{=}CH-X-$$

B. Unzipping of HCl under the activation of group, X

$$-CH{=}CH-CH{=}CH-CH{=}CH-X-$$

C. A chain segment of poly unsaturation.

Fig. 3.1 Steps in PVC degradation.

of hydrogen chloride and the subsequent formation of an unsaturated double bond on the PVC chain then activates the neighbouring chlorine atom, which is now structurally located as an allylic chlorine, and thus facilitates the subsequent elimination of another hydrogen chloride molecule, with the process continuing to repeat itself. This progressive dehydrochlorination proceeds quite rapidly, soon leading to a chain segment of polyunsaturation[11] as shown in Fig.3.1(C). In the presence of air, the dehydrochlorination is a nonlinear process with a tendency to increase in rate in the course of the reaction, and the polyene sequence can react with O_2 to produce other structures that favour degradation[12]. For this reason degradation in the presence of heat and air is termed thermo-oxidative degradation. The mechanism of thermo-oxidative degradation of PVC is easily explained in terms of the general oxidation of saturated hydrocarbons. The dehydrochlorination reaction is also typical for the high energy radiation degradation process of PVC[13].

HCl acceptance is unquestionably the most important feature of any chemical substance used as a thermal stabilizer for PVC because of the catalytic effect of HCl on degradation[13,14]. The second preventive function of a stabilizer is the exclusion of labile starting sites for dehydrochlorination in the polymer. Other mechanisms by which heat stabilizers could function are, modification of chain reactions so as to prevent the evolution of HCl, limiting the formation of conjugated double bond sequences by promoting addition reactions or functioning as an oxidation catalyst to stabilize the colour of PVC and inactivation of impurities that may occur in the polymerization and subsequent work[15].

Heat stabilizers for PVC

In addition to providing heat stability an ideal stabilizer should also

1) be readily dispersible in the PVC compound and fully compatible with all its constituents even after prolonged service,

2) have no adverse effect on processing properties,

3) be equally effective in PVC resins of all types and from all sources,

4) be inexpensive and effective in small proportions,

5) pose no health hazards both in the general handling and processing in the factory and in the subsequent use of the stabilized PVC material.

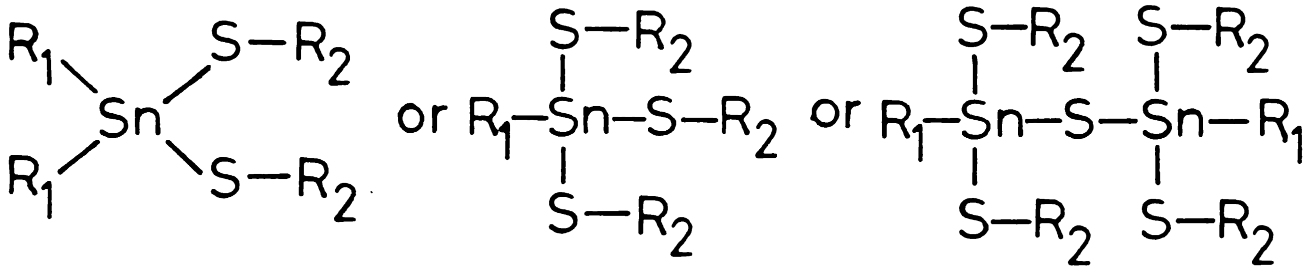
The most important classes of heat stabilizers can be briefly summarized as follows[12]:

1. Organo tin stabilizers

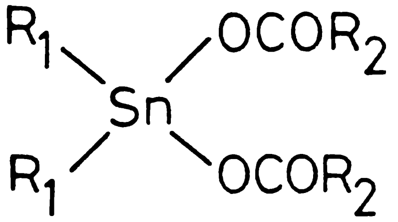
These are the most effective stabilizers available, unequalled in the degree of stabilization and the clarity they confer on PVC compounds. Their greatest drawback is their high cost. Another disadvantage is their toxicity though some of them are allowed in food-contact applications. The commonly used systems are:

(a) Sulphur - containing tin stabilizers (organo tin mercaptides and sulphides)

Because of their excellent efficiency they are used in situations where temperatures of 200°C and above occur. They can be used in all formulations, but because of the absence of a lubricative function, they have to be used with lubricants. Because of the minimum migration ascertained, they can be used in mixtures for food packaging and for pipes for drinking water. General structural formulae of sulphur containing tin stabilizers are shown in Fig.3.2(A).



A. Sulphur containing tin stabilizers



B. Sulphur free tin stabilizers

$(RCOO)_2Ba$ and $(RCOO)_2Cd$

C. Barium-Cadmium stabilizers

$(RCOO)_2Ba$ and $(RCOO)_2Zn$

D. Barium-Zinc stabilizers

Fig. 3.2 General formulae of important classes of PVC stabilizers.

(b) Sulphur free tin stabilizers (organo tin carboxylates or salts of alkyl tin oxide with maleic acid or partly esterified maleic acid)

In contrast to the sulphur containing tin compounds, the tin carboxylates have to be used with antioxidants. Their advantage over the sulphur containing ones is the good photostability and the lack of odour. These stabilizers, too, need additional lubricants. General structural formulae of sulphur free tin stabilizers are shown in Fig.3.2(B).

2. Barium-cadmium stabilizers

The two compounds are used together because of the synergism (interplay by combination of the individual actions) in the various mixture ratios. Generally costabilizers (phosphites), antioxidants (biphenols), and polyols of these mixtures are used to counteract the destabilizing effect of cadmium chloride that results from the subsequent stabilization reaction. The greatest disadvantage of this stabilizer system is the toxicity, predominantly of the cadmium part. General structural formulae of Ba-Cd stabilizers are shown in Fig.3.2(C).

3. Barium-zinc stabilizers

These are used in various mixtures because of the same synergistic effect as that of the Ba-Cd stabilizers.

The conversion of Zn carboxylate into $ZnCl_2$ during the stabilization action produces an even stronger destabilization effect than that of $CdCl_2$ ($ZnCl_2$ is a much stronger Lewis acid than $CdCl_2$). Hence the comixture with phosphites, epoxidized fatty acid esters, and polyols in compounds is indispensible. This comixture neutralizes the zinc chloride in its action. Recently, because of the toxicological action of cadmium compounds, these stabilizers have found increasing use. General structural formulae of Ba-Zn stabilizers are shown in Fig.3.2(D).

4. Calcium-zinc stabilizers

These have structural formulae similar to that of the Ba-Cd or Ba-Zn stabilizers. They have recently been finding many applications despite their very much weaker effect, because of, two non-toxic compounds; calcium and zinc stearate. They are always used in combination with costabilizers, epoxy plasticizers and antioxidants.

5. Lead stabilizers

The lead stabilizers are inorganic compounds which can be used with lead stearate in various combinations: sulphates, phosphates, or carbonates. The most important advantage of the stabilizing systems based on lead compounds is the formation of lead chloride ($PbCl_2$), which has no destabilizing effect like that of $ZnCl_2$ or $CdCl_2$ and does not increase the conductivity properties of PVC. For the latter reason, they are used in cable insulation.

6. Metal-free stabilizers

These are being increasingly discovered and investigated. The oldest of these are diphenyl thiourea and α-phenyl indole. β-amino crotonic acid and its esters are newcomers in organic stabilizers.

7. Antioxidants

Antioxidants, mostly phenolic compounds such as bisphenol A or 2,6-di-tert-butyl-p-cresol are sometimes added to improve the action of the heat stabilizers.

8. UV absorbers

When PVC is used outside (window frames, foils, sheeting, roofing etc.) UV absorbers are also generally incorporated.

MgO/ZnO COMBINATION AS HEAT STABILIZER FOR PVC

MgO is an efficient acid acceptor and ZnO is associated with good heat ageing[16]. Hence MgO/ZnO combination in presence of a common lubricant, stearic acid, was tried as a heat stabilizer for PVC.

Experimental

1. Studies on a Brabender Plasticorder

The study was conducted on a Brabender Plasticorder model PL3S. The test parameters are shown in Table 3.1. PVC plasticized with 50 phr (parts per hundred PVC resin) dioctyl phthalate (DOP) was selected for investigation to keep the mixing/test temperature around 170°C - 180°C.

Table 3.1

Test parameters

Brabender Plasticorder	
Roller Mixer	Type 30
Mixer Temperature	175°C
Rotor speed	30 rev. min^{-1}
Measuring range	0-2500 metergrams
PVC compound	
Sample weight	30 gms
Plasticizer content	50 phr
Variables	MgO, ZnO and stearic acid
Test time	15 mins.

PVC compounds with varying amounts of MgO, ZnO and stearic acid were prepared using a high speed mixer and then run on the Brabender plasticorder for 15 minutes and the torque curves were taken. Initially, formulations containing MgO and ZnO at equal concentrations of 4 phr, 3 phr and 2 phr, keeping the concentration of stearic acid constant at 2 phr were selected for study. For comparison, a formulation with 4 phr of tribasic lead sulphate (TBLS), a conventional PVC stabilizer, was also chosen. The torque curves of these compounds are shown in Fig.3.3. To find the most efficient combination of MgO and ZnO, they were then added in different concentrations of 4 phr MgO/5phr ZnO, 3phr MgO/5phr ZnO, 2phr MgO/5phr ZnO, 2phr MgO/4phr ZnO and 1 phr MgO/5phr ZnO, again keeping stearic acid at a constant level of 2 phr. The Brabender torque curves of these compounds are shown in Fig.3.4.

In order to study the effect of stearic acid on stabilization, its concentration was varied, keeping the amounts of MgO and ZnO the same. Concentrations of stearic acid tried were 2phr, 3phr, 4phr and 5phr, keeping the concentrations of MgO and ZnO constant at 3phr and 5phr respectively. To study the colour flexibility of the compounds stabilized with MgO/ZnO/stearic acid system

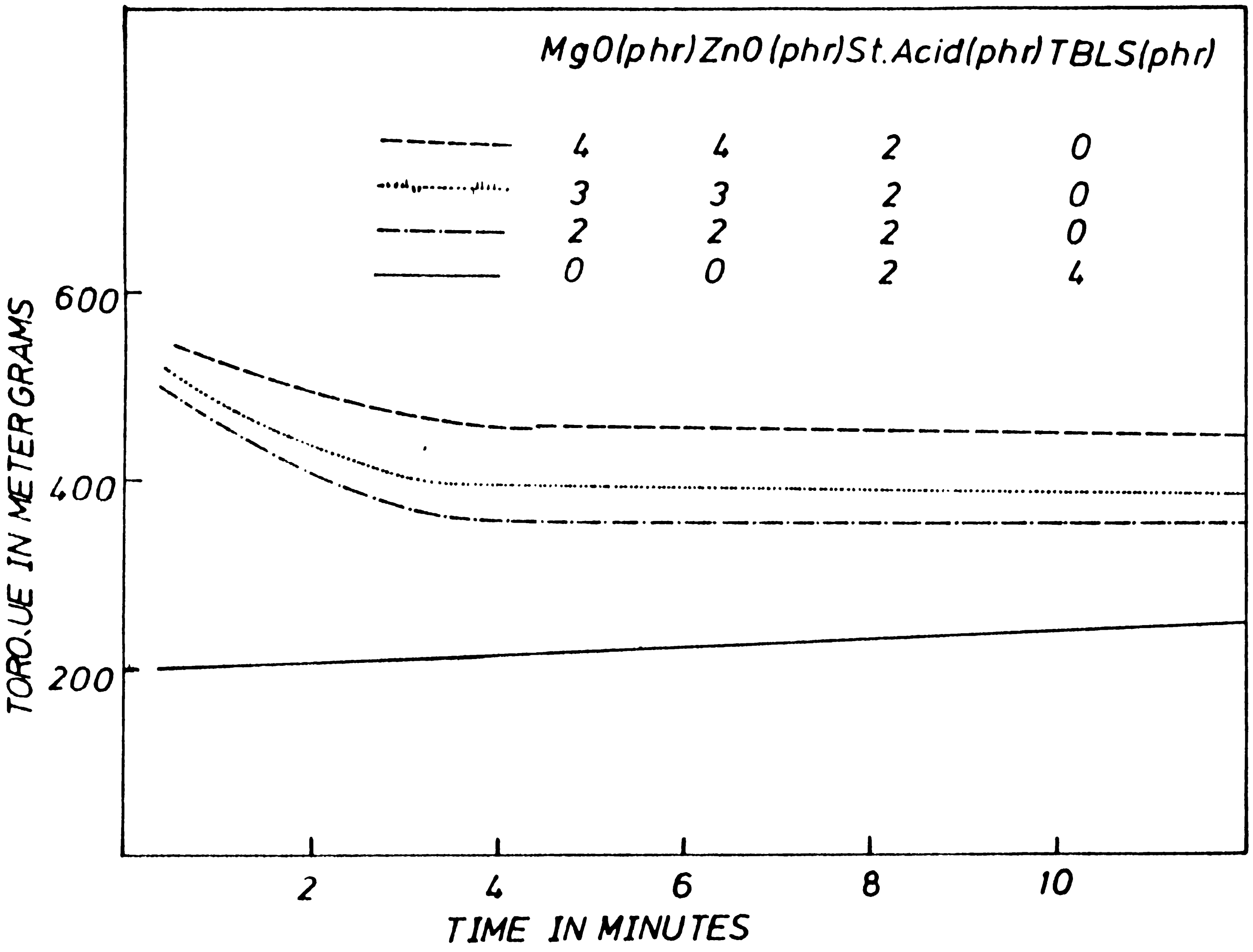


Fig. 3.3 Brabender torque-time curves of PVC compounds containing MgO and ZnO in equal concentrations in presence of 2 phr stearic acid (initial rising part of the curves not shown)

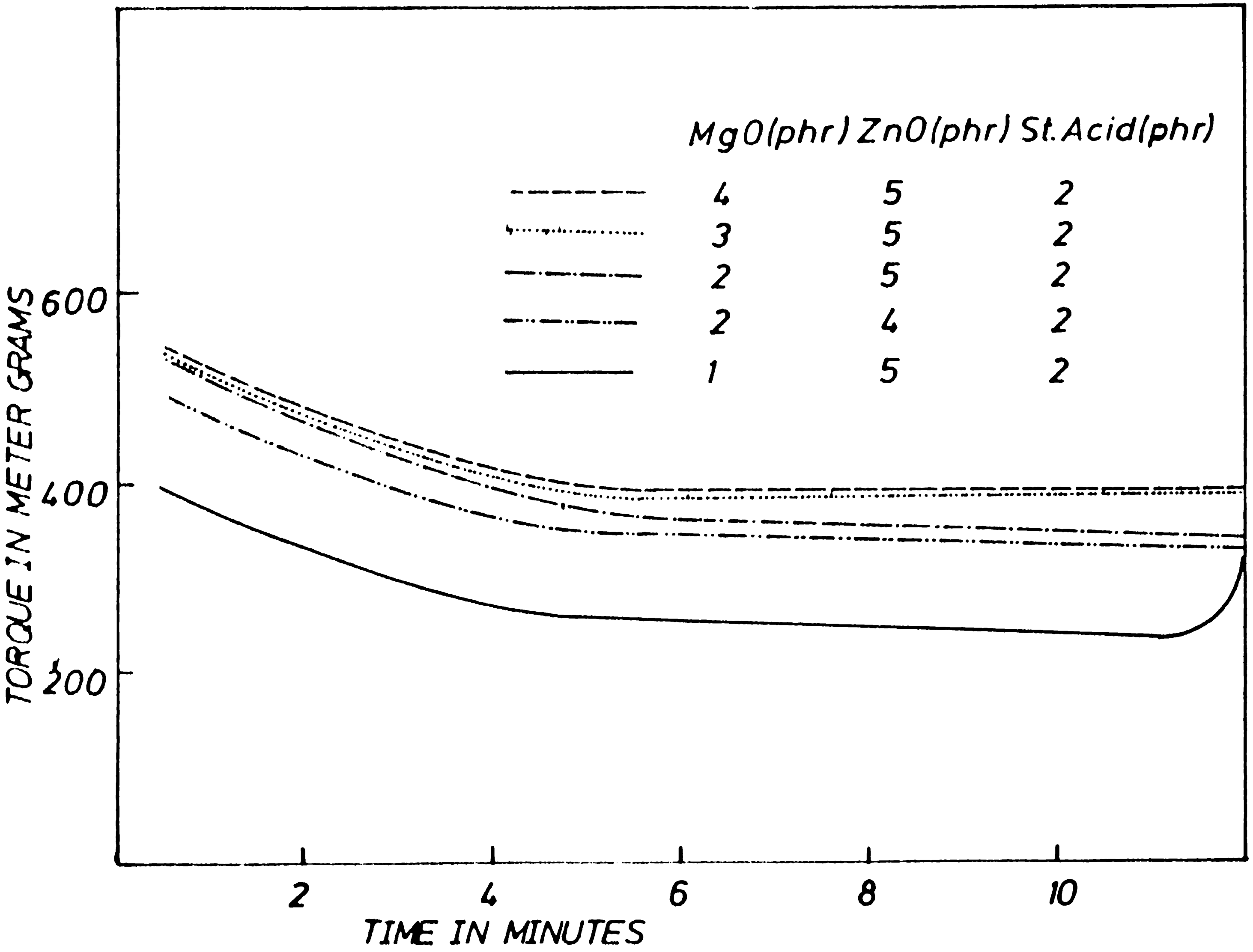


Fig. 3.4 Brabender torque-time curves of PVC compounds containing MgO and ZnO in varying concentrations in presence of 2phr stearic acid (initial rising part of the curves not shown)

a formulation containing 2 phr titanium dioxide was also selected. The Brabender torque curves of these compounds are shown in Fig.3.5.

Finally each of the three additives, MgO, ZnO and stearic acid was also completely withdrawn to assess the importance of each additive on stabilization. The formulations tried were 3 phr MgO and 5 phr ZnO with no stearic acid, 4 phr ZnO and 2 phr stearic acid with no MgO, and 4 phr MgO and 2 phr stearic acid with no ZnO. The Brabender torque curves of these compounds are shown in Fig.3.6.

The sequence of colour development for each of the above compound during the 15 minutes of test run on the Brabender Plasticorder was visually observed. The numbers in Fig.3.7 represent the degree of colour development over a scale[17] 0-10 (0 = colourless, 10 = black).

2. Oven stability test[18,19]

The compounds, after the test run on the Brabender Plasticorder, were subjected to the oven stability test at 180°C (±5°C). The sequence of colour changes of the material was observed at intervals of 10 minutes for 110 minutes. The results are shown in Fig.3.8. Formulations for Figs.3.7 and 3.8 are given in Table 3.2.

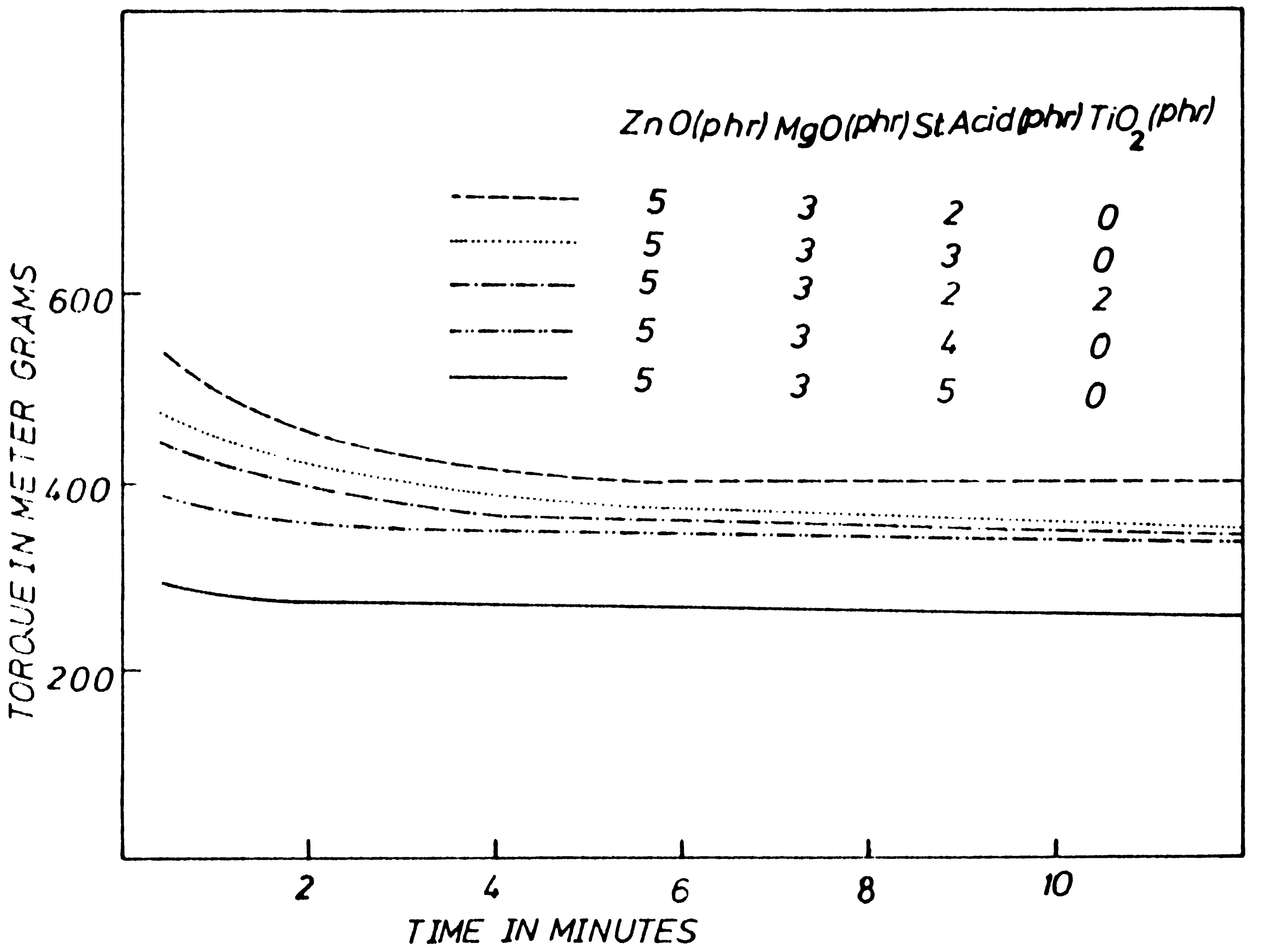


Fig. 3.5 Brabender torque-time curves of PVC compounds containing stearic acid in varying concentrations in presence of 3phr MgO and 5 phr ZnO (initial rising part of the curves not shown).

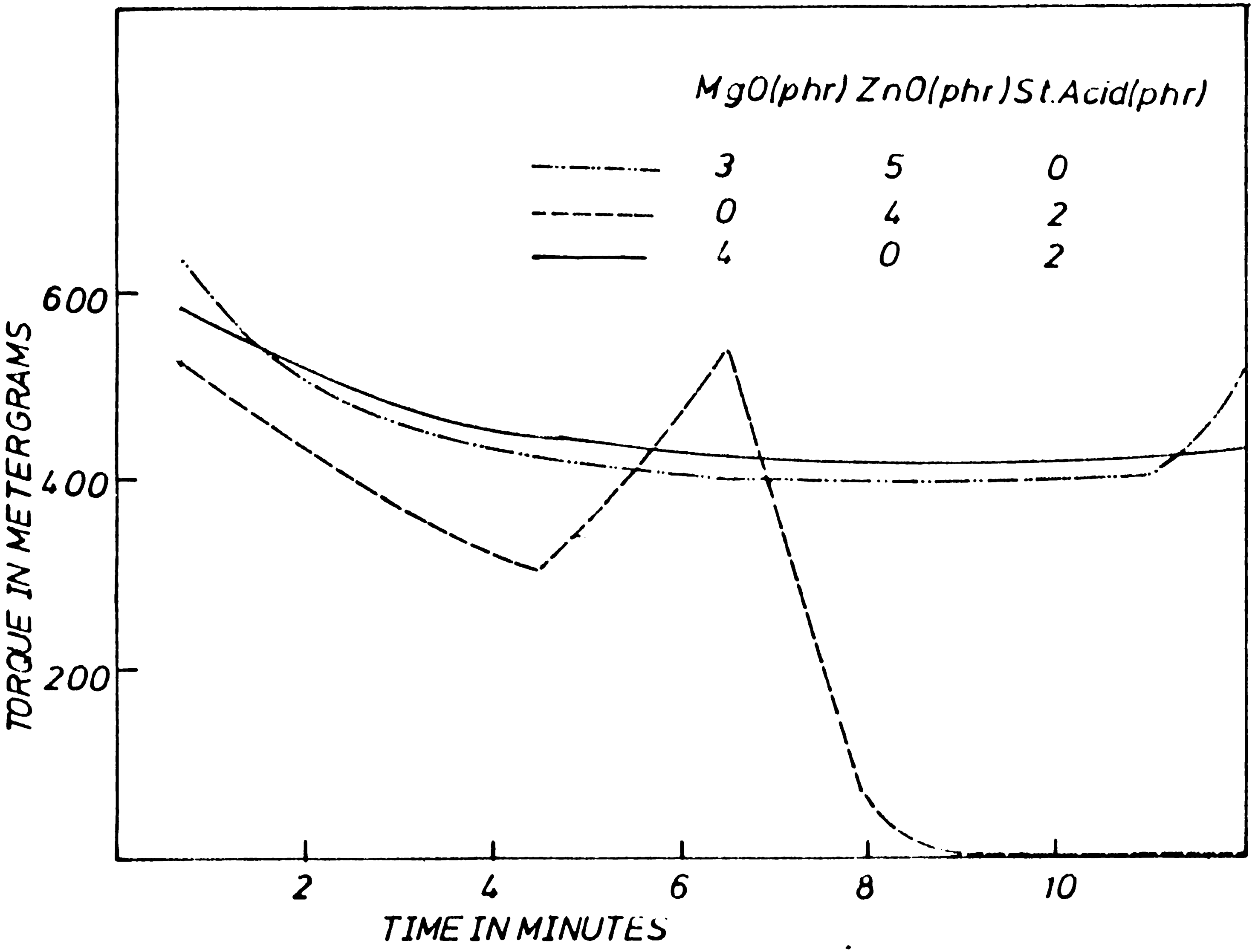


Fig. 3.6 Brabender torque-time curves of PVC compounds in the absence of any one of the ingredient, MgO, ZnO or stearic acid (initial rising part of the curves not shown).

Degree of colour
0=Colourless
10=Black

TIME IN MINUTES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
15	5	3	1	3	5	1	1	1	1	3	1	1	1	10	10	5
10	3	1	1	1	4	1	1	1	1	1	1	1	1	10	10	5
5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

FORMULATION

Fig. 3.7 Sequence of colour changes of PVC compounds observed during the test on the Brabender plasticorder.

Degree of colour: 0=Colourless 10=Black

TIME IN MINUTES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
110	8	4	3	6	10	6	2	2	3	4	2	2	2	10	10	9
100	8	4	2	5	10	5	2	2	3	4	2	2	1	10	10	9
90	7	4	2	4	6	4	2	1	2	4	2	2	1	10	10	8
80	6	4	2	4	6	3	2	1	2	4	1	1	1	10	10	7
70	6	4	2	3	5	3	1	1	2	4	1	1	1	10	10	7
60	6	3	1	3	5	2	1	1	1	3	1	1	1	10	10	7
50	6	3	1	3	5	2	1	1	1	3	1	1	1	10	10	6
40	6	3	1	3	5	1	1	1	1	3	1	1	1	10	10	6
30	6	3	1	3	5	1	1	1	1	3	1	1	1	10	10	6
20	5	3	1	3	5	1	1	1	1	3	1	1	1	10	10	5
10	5	3	1	3	5	1	1	1	1	3	1	1	1	10	10	5
0	5	3	1	3	5	1	1	1	1	3	1	1	1	10	10	5

FORMULATION

Fig. 3.8 Sequence of colour changes of PVC compounds observed during the oven stability test.

Table 3.2

Formulations for Figs.3.7 and 3.8

Formulation	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
PVC	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
DOP	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
MgO	2	3	4	2	1	2	3	4	4	6	3	3	3	3	0	4
ZnO	2	3	4	4	5	5	5	5	6	4	5	5	5	5	4	0
Stearic acid	2	2	2	2	2	2	2	2	2	2	3	4	5	0	2	2

3. Congo red test[18]

Around 2 gms of the PVC compounds prepared for the tests on the Brabender Plasticorder were subjected to the Congo red test to assess whether there was any visual evidence of HCl evolution for 15 minutes.

Results and discussion

Torque curves of compounds with MgO and ZnO at equal concentrations rose to a high torque level initially, dropped a little and then stabilized to a constant torque level (Fig.3.3). The initial unstable part may be the time taken for fusion and homogenization. Hence, to a first approximation, the period over which the constant torque level continues may be taken to be a measure of the efficiency of the stabilizing system. For all the three compounds with MgO/ZnO system, this period extends over the test time of 15 minutes. However, the stable torque value is slightly different for the three compounds. This might indicate that the PVC phase is not fully homogenized at the temperature and/or shear rates encountered in the study. The higher torque values displayed by the compounds with higher amounts of MgO and ZnO might imply that a larger amount of PVC melts when the concentration of MgO and ZnO are increased due to their lubricant action. The compound with 4 phr TBLS also shows a stable behaviour as expected. However, its torque curve is below those of the compounds containing MgO and ZnO, which indicates that the lubricant action of 4 phr TBLS is not sufficient to homogenize the PVC phase fully at the temperature and/or shear rate employed. For this compound the torque is found to rise gradually during the test run which further shows that the amount of fused and homogenized PVC increases during the test run.

The behaviour of the PVC compounds with MgO and ZnO at different concentrations is more or less similar (Fig.3.4). All the compounds, except the one with 1 phr MgO/5 phr ZnO display stable behaviour. The torque curve of the compound which contains 1 phr MgO and 5 phr ZnO stabilizes to a constant torque level after the initial unstable part. But just before the end of the test-time, the torque is found to increase rapidly. This may be due to the degradative crosslinking of the PVC matrix in turn due to the low level of MgO which is insufficient to provide efficient stabilization.

All the torque-curves in Fig.3.5 show a stable behaviour. Varying the concentration of stearic acid, keeping the amounts of MgO and ZnO at the constant levels of 3 phr and 5 phr respectively, does not seem to affect stability. 2 phr of stearic acid seems to be sufficient for efficient stabilization. Increasing the amount of stearic acid from 4 phr to 5 phr brings down the stable torque value noticeably, indicating that at these levels of stearic acid, the fusion of PVC particles is almost complete and hence the lubricant action alone has the say in the torque value. Presence of 2 phr titanium dioxide does not seem to affect the stability or colour. This might imply that the colour flexibility of PVC compounds will not be impaired when this stabilizer system is employed.

The behaviour of the compounds when each of the additives, MgO, ZnO and stearic acid, is completely withdrawn is interesting (Fig.3.6). The stability is found to be least when there is no MgO. Even before stabilizing properly to a constant level, the torque curve rises again to a maximum value. This is obviously due to the increase in torque resulting from degradative crosslinking. After crosslinking, the material breaks down to powder and hence the torque reduces to zero. When there is no ZnO, the stable period seems to extend over the test time. However, the compound becomes yellow in the Brabender plasticorder indicating inefficient stabilization. However the onset of crosslinking, indicating large scale degradation is not evident from the torque curve in this case. When there is no stearic acid, the stable period does not extend over the test time. The torque increases before the end of test time indicating severe degradation. Thus all the three ingredients MgO, ZnO and stearic acid are found to be essential for efficient stabilization.

An examination of the sequence of colour changes observed while the compounds were under the test run on the Brabender plasticorder (Fig.3.7 and Table 3.2) shows that the compounds that became highly discoloured were those in which MgO or stearic acid was completely absent (formulations 14 and 15). This further shows that these two are the most essential ingredients of the stabilizer system. The compound without ZnO (formulation 16) also becomes discoloured indicating that ZnO is also an indispensible ingredient. Other formulations which got badly discoloured indicating insufficient stabilization were formulation 5 in which concentration of MgO was only 1 phr and formulation 1 in which the concentration of ZnO was only 2 phr. These concentrations seem to be less than the minimum levels of MgO and ZnO required for efficient stabilization. It may be inferred that a minimum of 2 phr MgO and 3 phr of ZnO are required for efficient stabilization.

Results from the oven stability test (Fig.3.8 and Table 3.2) confirm the observations made above. It further shows that compounds with 4 phr MgO/4 phr ZnO/2 phr stearic acid, 3 phr MgO/5 phr ZnO/2 phr stearic acid, 4 phr MgO/ 5 phr ZnO/2 phr stearic acid are very stable. Using MgO above 4 phr and ZnO above 5 phr does not seem to improve the efficiency any further. It seems that the optimum concentration of MgO is about 3 to 4 phr and that of ZnO about 4 to 5 phr. The concentration of stearic acid needs to be only 2 to 3 phr.

The above conclusion was further substantiated by the results of the Congo red test. Compounds in which MgO, ZnO or stearic acid was completely absent or MgO and ZnO present in less than the minimum required level (formulations 1, 5, 14, 15 and 16 of Table 3.2) were seen to be the least stable.

The products from the tests on the Brabender Plasticorder were subjected to natural weather conditions for six months. Compounds containing more than the minimum levels of MgO or ZnO with stearic acid showed barely any detectable change. This might imply that this stabilizer system has reasonable resistance against ultraviolet light and weathering.

Mechanism of stabilization

An attempt was made at explaining the possible mechanism of stabilization by the MgO/ZnO/stearic acid combination by

Infrared (IR) spectroscopy. IR spectra of the combinations given in Table 3.3 were taken in KBr pellets on a Perkin Elmer model 983 spectrophotometer. The concentration of the ingredients in the combinations was based on one of the best formulations obtained by the studies on the Brabender Plasticorder (4 phr MgO/4 phr ZnO/2 phr stearic acid).

Table 3.3

Combinations employed for IR scan

1. Stearic acid (Fig.3.9)
2. MgO + Stearic acid, heated at 175°C for 5 minutes (Fig.3.10)
3. ZnO + Stearic acid, heated at 175°C for 5 minutes (Fig.3.11)
4. MgO + ZnO + Stearic acid (Fig.3.12)
5. MgO + ZnO + Stearic acid, heated at 175°C for 5 minutes (Fig.3.13)
6. MgO + ZnO + Stearic acid heated at 175°C for 5 minutes + HCl* (Fig.3.14)

*Mixture and PVC samples were sealed in extreme ends of the same glass tube, and the side containing PVC inserted into an oven so as to form HCl which can be reacted by the thermal stabilizer.

Fig.3.9 shows the IR spectrum of stearic acid alone and the absorption at around 1700 cm^{-1} of the carbonyl group[20]

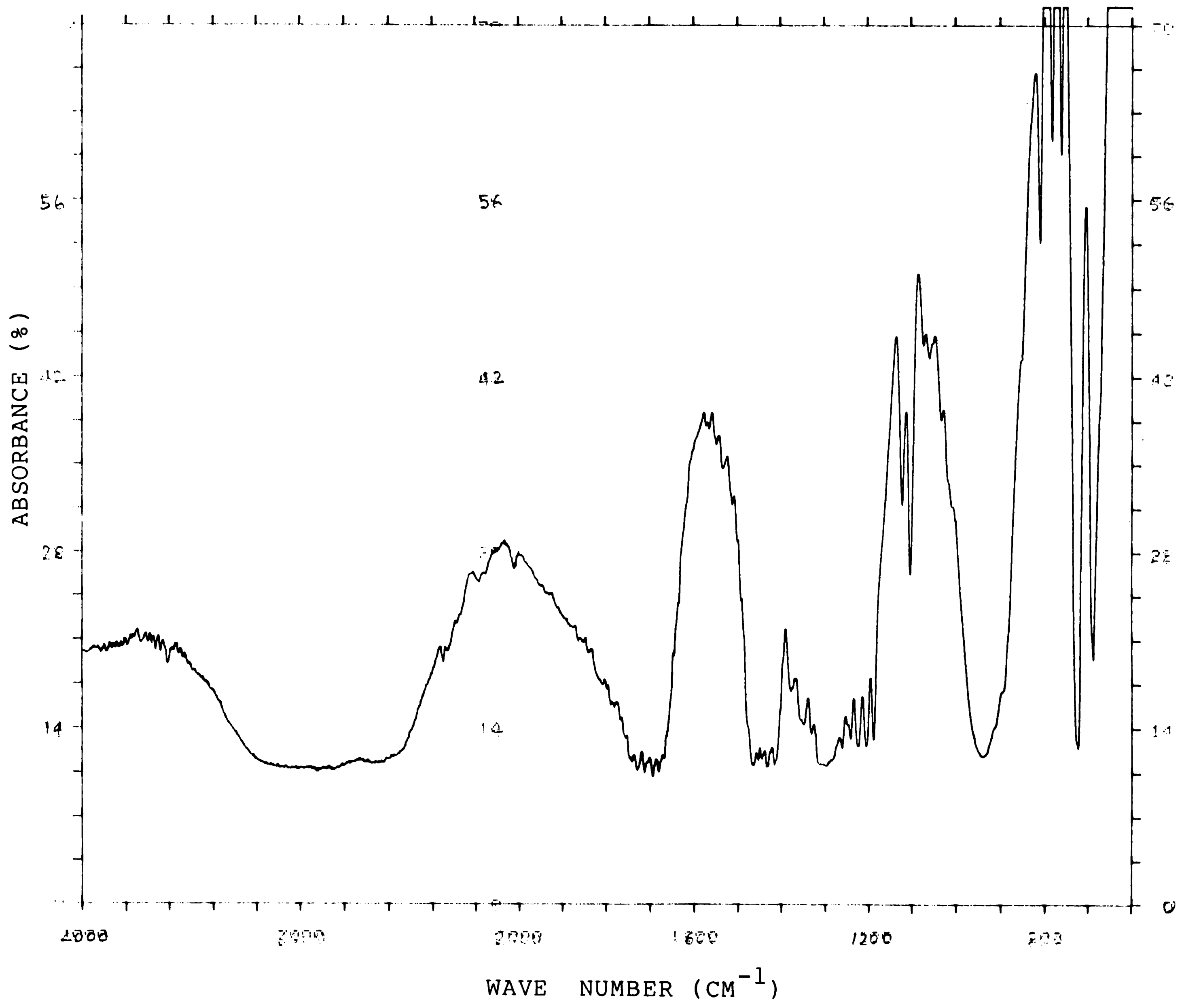


Fig. 3.9 IR Spectrum of stearic acid

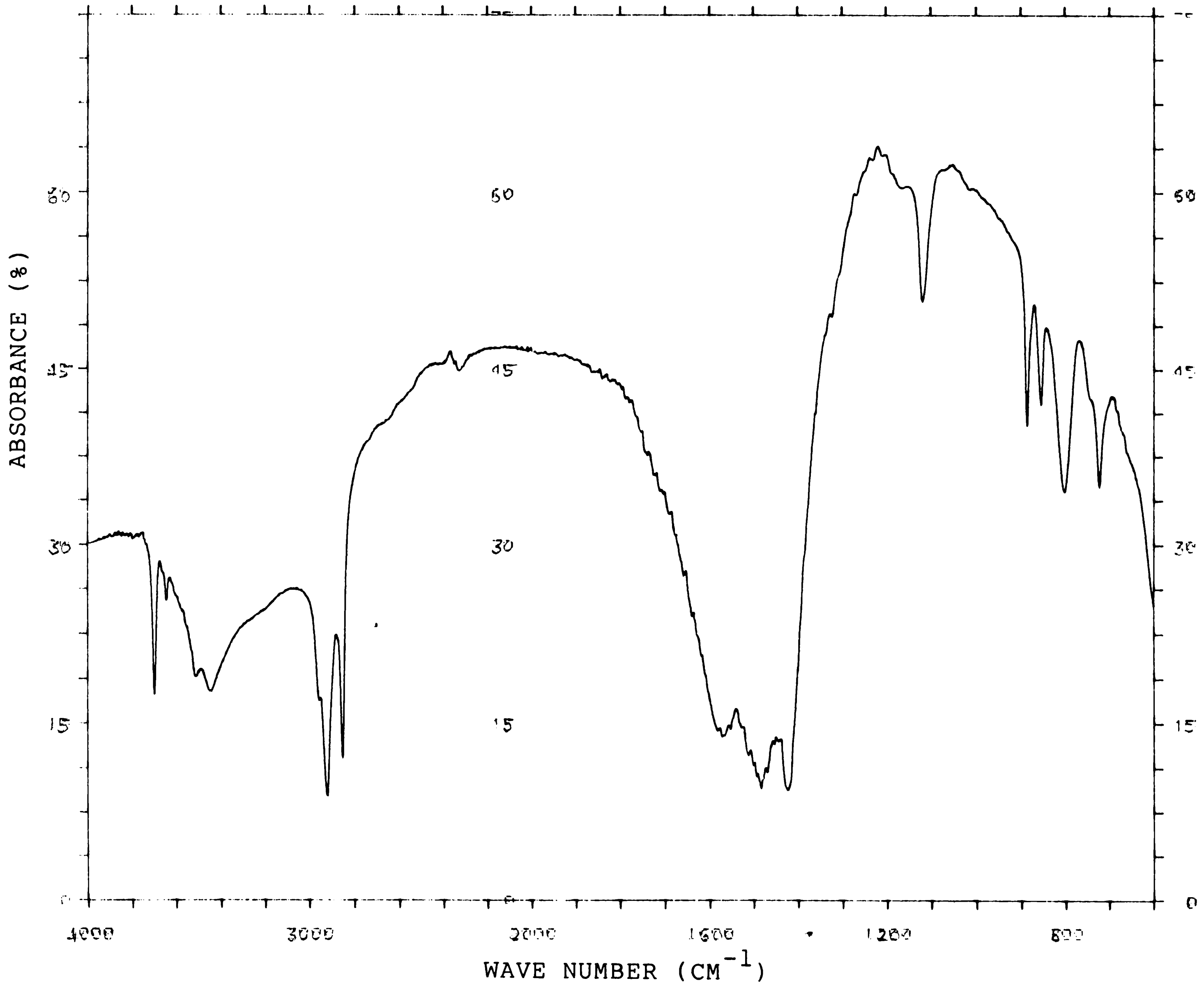


Fig. 3.10 IR spectrum of MgO + stearic acid (heated together at 175°C for five mins.)

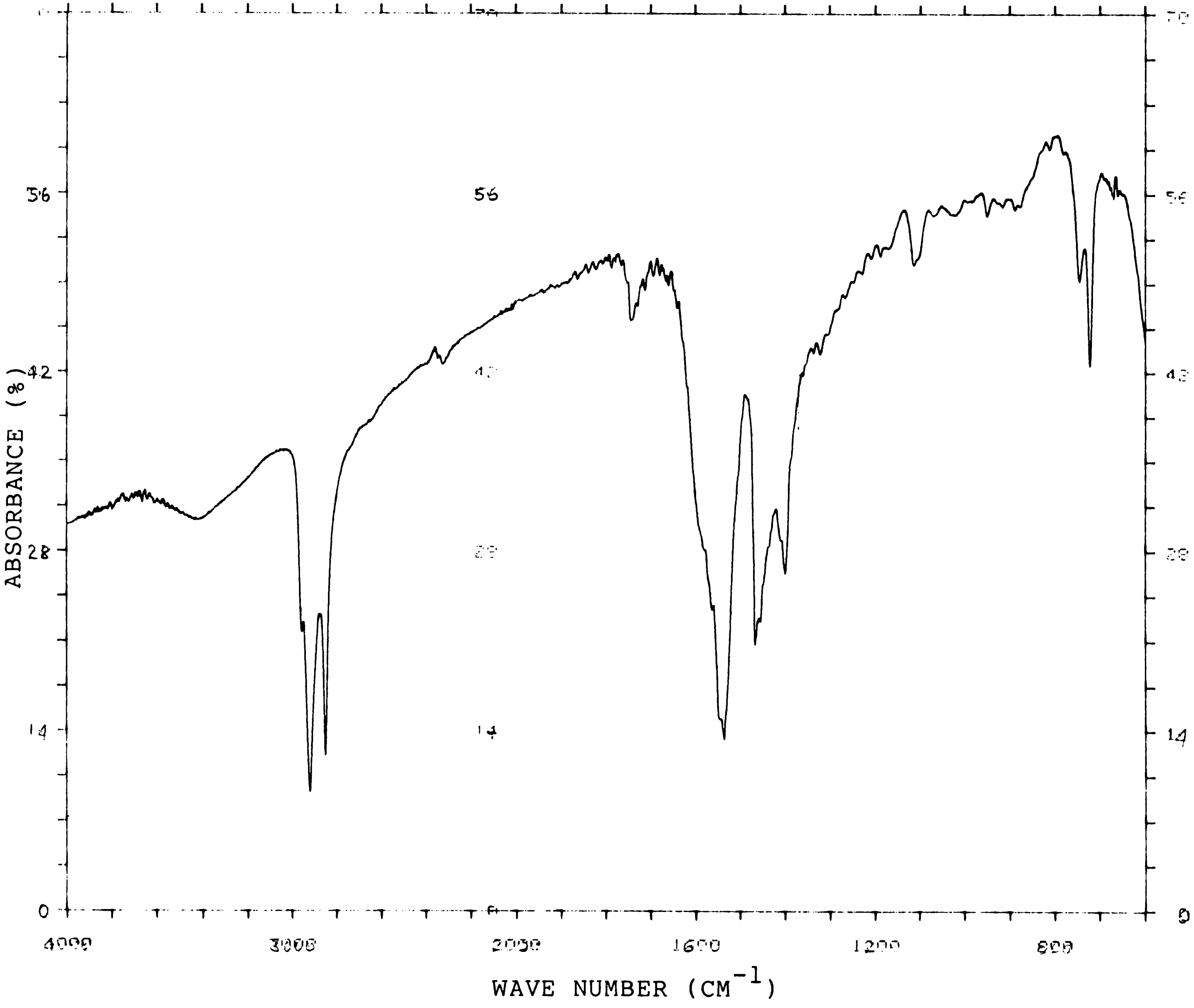


Fig. 3.11 IR spectrum of ZnO + stearic acid (heated together at 175°C for five mins.)

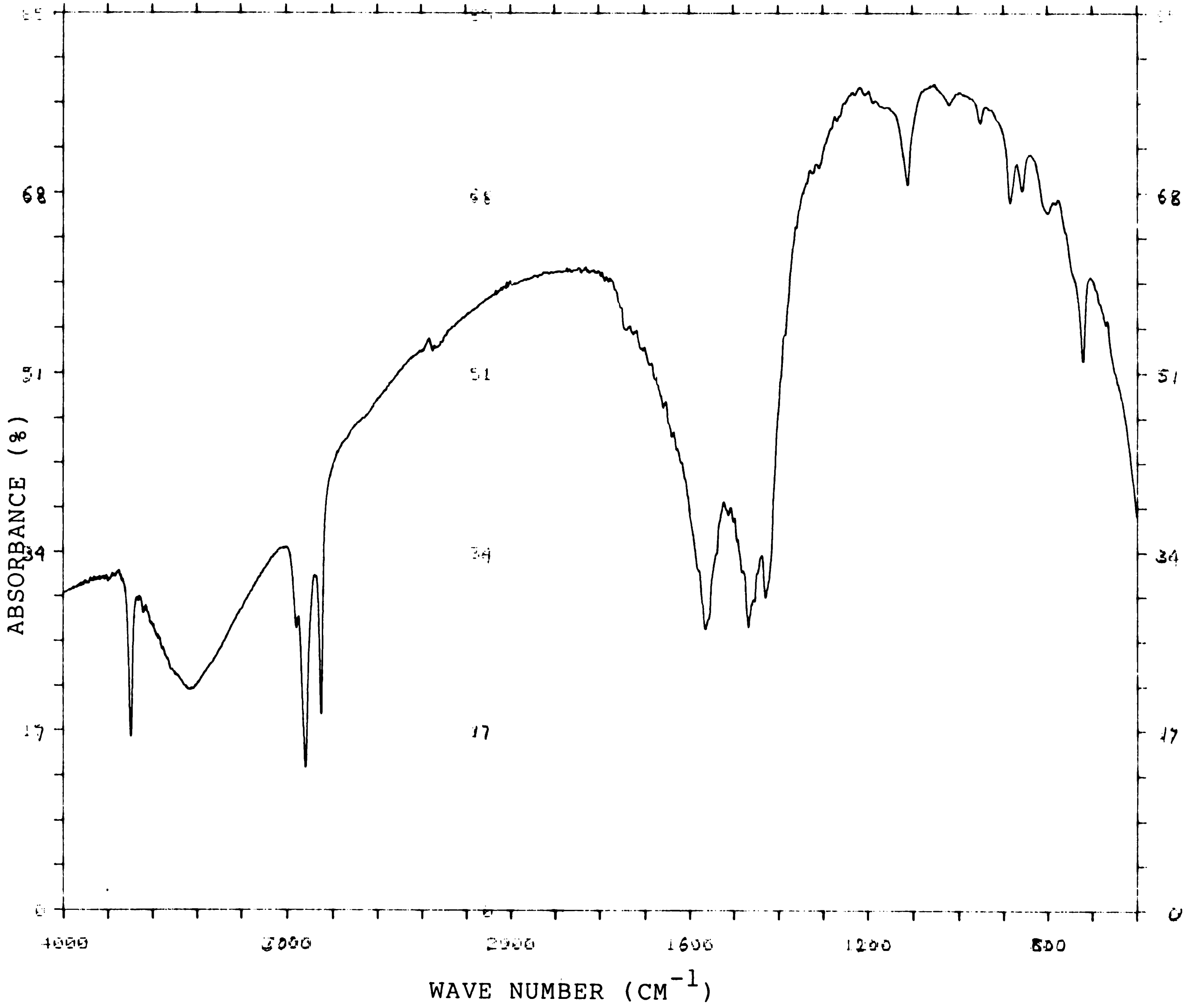


Fig. 3.12 IR spectrum of MgO + ZnO + stearic acid.

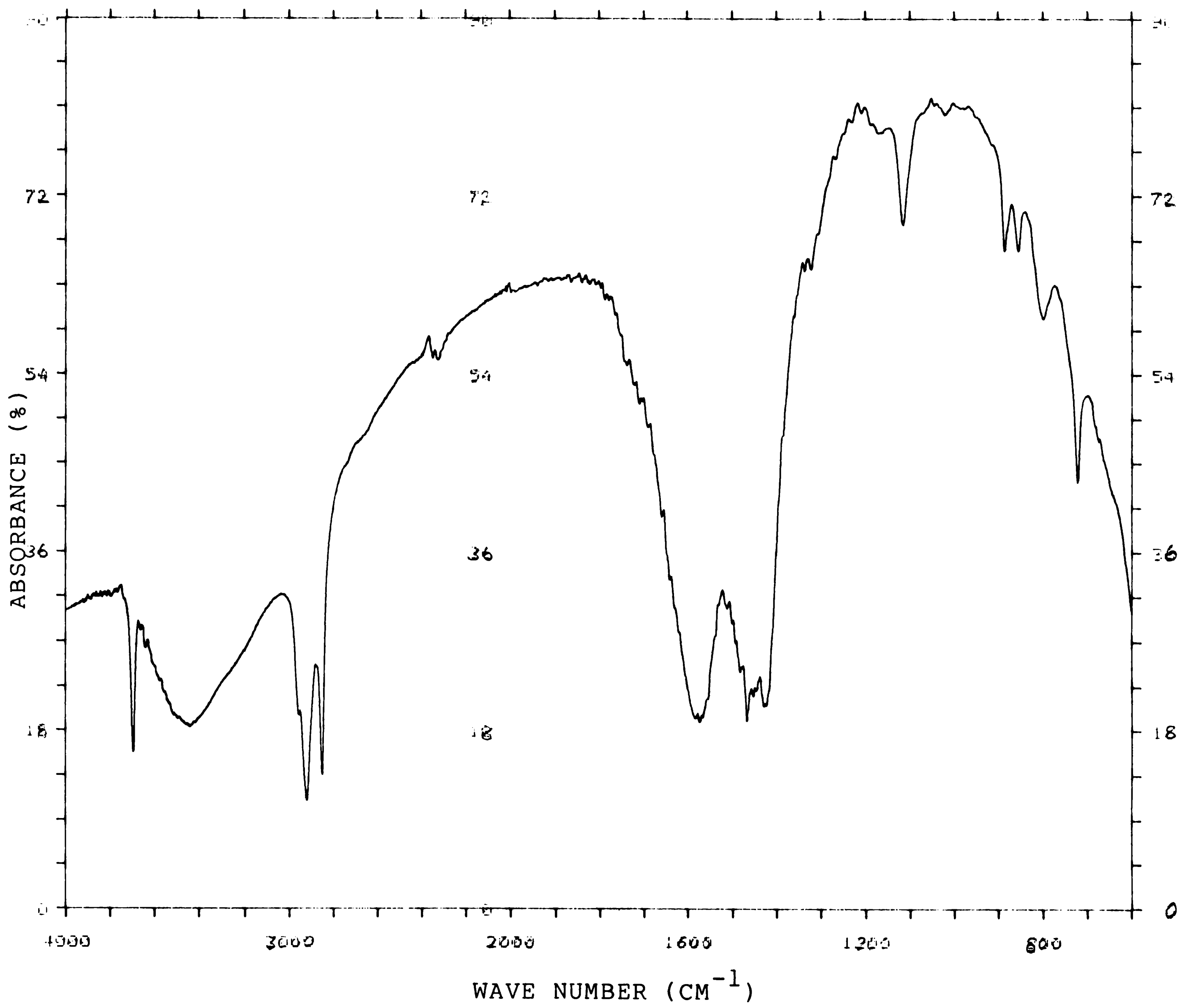


Fig. 3.13 IR spectrum of MgO + ZnO + stearic acid (heated together at 175°C for five mins.)

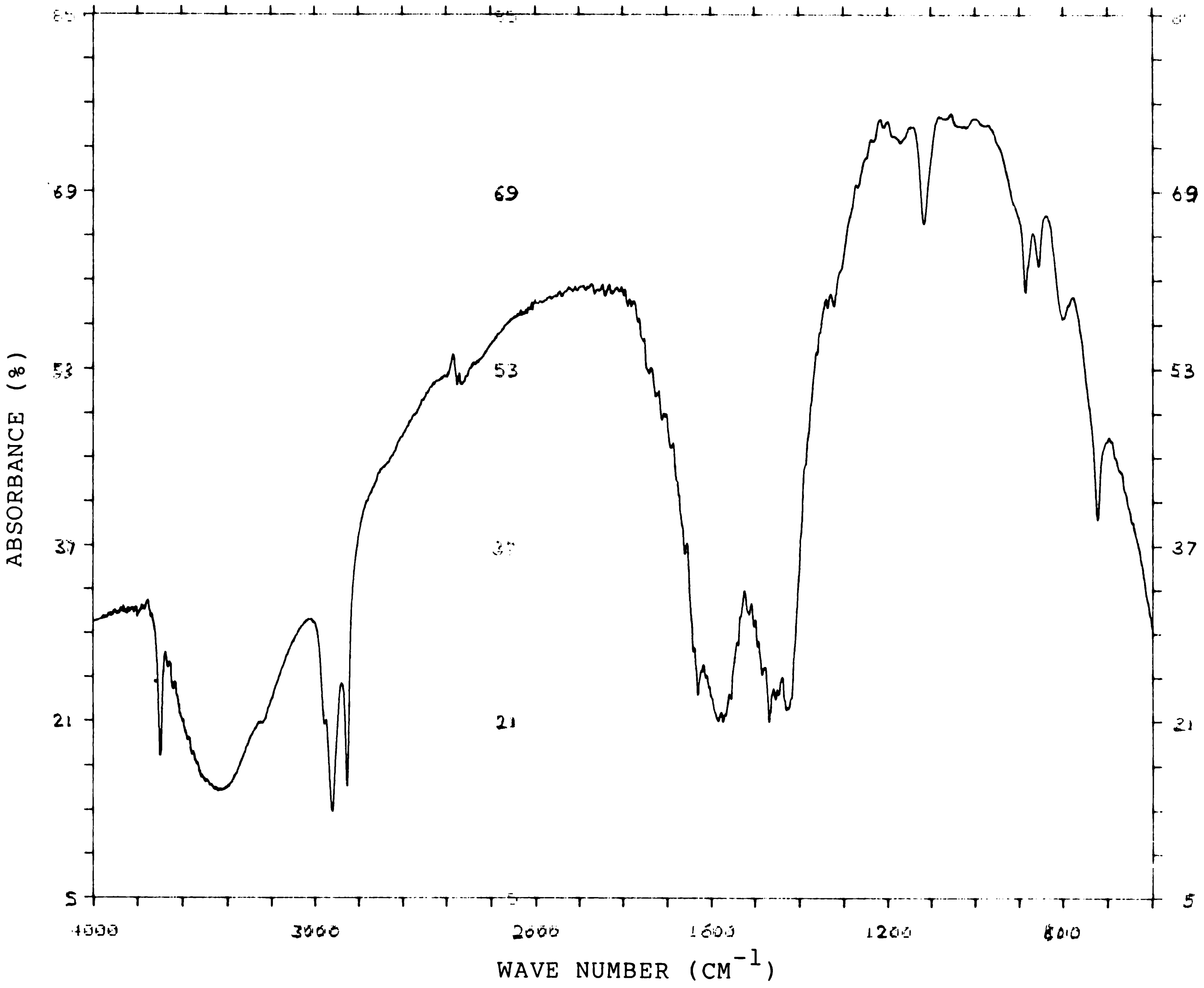


Fig. 3.14 IR spectrum of MgO + ZnO + stearic acid (heated together at 175°C for five mins.) + HCl.

was made use of for this study. The reaction of MgO and stearic acid produces magnesium stearate as shown by the shifting of the carbonyl group to the new position[20] (Fig.3.10). The reaction between ZnO and stearic acid also forms zinc stearate (Fig.3.11). Fig.3.12 and Fig.3.13 look similar which indicates that the stearate formation could take place even at room temperature. This shows that the stabilization action of the MgO/ZnO/stearic acid system might be similar to that of a mixture of magnesium stearate and zinc stearate which in turn might be similar to the action of the barium-zinc stabilizers or the calcium-zinc stabilizers. Hence this study shows that instead of using magnesium and zinc stearates proper, it is enough to use the corresponding metal oxides and stearic acid. When HCl, evolved by the degradation of PVC, is passed over the mixture, stearic acid is produced (Fig.3.14) necessarily with the formation of the corresponding chlorides. The presence of chloride in the mixture has also been confirmed by chemical analysis. The overall chemical reaction could thus be represented as

$$\mathrm{MgO + 2C_{17}H_{35}COOH \longrightarrow Mg(OCOC_{17}H_{35})_2 + H_2O}$$

$$\mathrm{ZnO + 2C_{17}H_{35}COOH \longrightarrow Zn(OCOC_{17}H_{35})_2 + H_2O}$$

$$\mathrm{Mg(OCOC_{17}H_{35})_2 + 2HCl \longrightarrow MgCl_2 + 2C_{17}H_{35}COOH}$$

$$\mathrm{Zn(OCOC_{17}H_{35})_2 + 2HCl \longrightarrow ZnCl_2 + 2C_{17}H_{35}COOH}$$

The overall mechanism might then be a synergism between the magnesium and zinc stearates as in the case of barium-zinc stabilizers or calcium-zinc stabilizers. Hence the observations made from the Brabender studies could be explained as follows.

1. The system was found to be least efficient when there was no MgO. In this case, the zinc stearate formed could rapidly fix the HCl evolved due to PVC degradation. However, the zinc chloride formed produces a strong destabilization effect[12].

2. Stearic acid was found to be the second most important ingredient in the system. In the absence of stearic acid, the fixation of HCl by the metal oxides would be slow reducing the efficiency of stabilization.

3. When all the three ingredients were present in optimum concentrations, the system was found to be an efficient stabilizer for plasticized PVC. In this case also zinc stearate rapidly fixes the HCl evolved. However, zinc chloride formed could immediately react with magnesium stearate forming magnesium chloride and thereby regenerating zinc stearate. Thus the system neutralises the destabilizing effect of zinc chloride. Such a mechanism based on the regeneration of cadmium or zinc alkyl-

carboxylate from their chlorides by the action of barium or calcium alkylcarboxylate is considered to be the synergistic effect of barium-cadmium and calcium-zinc soap mixtures[21-23].

Yet another mechanism by which this system provides stability could be by the replacement of labile tertiary chlorine atoms by ZnO and thereby crosslinking two PVC molecules as in the case of the crosslinking of polychloroprene rubber by ZnO[24]. It has been verified by swelling studies that a small amount of crosslinking, which does not interfere with processing, does occur in the PVC matrix when the MgO/ZnO/stearic acid system is used for stabilization. Further, it has been established that zinc oxide could act as a crosslinking agent for PVC in presence of tetra methylthiuram disulphide (TMTD)[25]. Such a small degree of crosslinking might be present in the PVC phase stabilized by conventional stabilizers like tribasic lead sulphate (TBLS) also. This is in conformity with the observation that TBLS could act as a potential curative for polychloroprene rubber[26] (Chapter 4).

Mechanical properties of plasticized PVC stabilized with MgO/ZnO/Stearic acid system

4 phr MgO/4 phr ZnO/2 phr stearic acid, one of the best combinations was chosen for determining the mechanical

properties of plasticized PVC with this stabilizer system. One compound with the conventional stabilizer, tribasic lead sulphate was also chosen for comparison. The formulations used for preparing test samples are shown in Table 3.4.

Table 3.4

Formulations used for determining mechanical properties

Formulation	A	B
PVC	100	100
DOP	50	50
MgO	4	--
ZnO	4	--
TBLS	--	4
Stearic acid	2	2

The compounds were prepared on the Brabender Plasticorder at 175°C and pressed on a laboratory press at the same temperature for 2 minutes using a mould which could be water cooled immediately after pressing, keeping the sample still under compression. The dumb-bell specimens for testing tensile properties were punched from these sheets. The tensile properties were determined on a Zwick Universal Testing Machine as per ASTM D412 (1980). The resistance to thermal ageing of the samples was measured by keeping the samples at 100°C for 48 hours in an air oven and then measuring the retention in the tensile properties. The properties are shown in Table 3.5.

Table 3.5

Tensile properties of plasticized PVC

Property	A	B
Before ageing		
Tensile strength (MPa)	14.7	14.1
Elongation at break (%)	260.10	276.26
100% modulus (MPa)	8.8	8.3
After ageing		
Tensile strength (MPa)	16.0	15.1
Elongation of break (%)	232.12	245.54
100% modulus (MPa)	9.1	8.7

The tensile properties of both samples A and B are comparable. The PVC stabilized with MgO/ZnO system shows slightly higher tensile strength but slightly lower elongation at break. This might be due to a slightly higher degree of crosslinking in the former sample. The properties after thermal ageing suggest that the polymer has not been adversely affected by the ageing conducted at 100°C. Tensile strength has slightly improved in both samples A and B and elongation at break has come down a little. This suggests an increase in the crosslink density in the PVC matrix for both A and B during ageing.

Efficiency of MgO/ZnO stabilizers in presence of other plasticizers and lubricants

Some plasticizers like epoxidized soyabean oil has a stabilizing action on PVC in addition to the plasticizing action[27,28]. The migration resistance of this plasticizer is also high, comparable to that of the polymeric plasticizers. MgO/ZnO/stearic acid stabilizers were tried in presence of epoxidized soyabean oil to determine whether there was any improvement in the efficiency of stabilization. Calcium stearate has a dual role in PVC formulations both as a lubricant and heat stabilizer[17]. Hence it was also examined whether calcium stearate could improve the efficiency of the MgO/ZnO/stearic acid system if substituted in place of stearic acid. It has been stated that MgO and ZnO get converted to their corresponding stearates and then fix the HCl. Hence, it would be interesting to note whether the same efficiency would be retained if stearic acid is substituted with other fatty acids like lauric acid. To compare the efficiency of stabilization of these systems a dynamic stability test[29] was performed on the Brabender Plasticorder. The stability times of the various systems are given in Table 3.6. The mixer temperature was 175°C and rotor speed 30 rev/minute, and the sample weight 30 gms.

The stability time observed for MgO/ZnO/stearic acid system (A) is 37 minutes (Fig.2.1). When DOP is substituted by epoxidized soyabean oil (B) the stability time goes upto 47 minutes. Hence as with other systems, epoxidized soyabean oil behaves synergistically with the MgO/ZnO/stearic acid system also. When stearic acid is substituted with calcium stearate (C) there is a marked improvement in the efficiency of stabilization, as expected. Almost the same stability time is obtained, when stearic acid is substituted by lauric acid (D). This shows that the MgO/ZnO system could function as an efficient stabilizer in presence of fatty acids other than stearic acid.

Advantages of MgO/ZnO/stearic acid system compared to other conventional stabilizers

The MgO/ZnO/stearic acid system has been identified as an efficient stabilizer system for plasticized PVC. It has the following advantages.

Table 3.6

Stability times of MgO/ZnO based stabilizer systems

	Formulations		Stability time, mins.
A	PVC	- 100	37
	DOP	- 50	
	MgO	- 4	
	ZnO	- 4	
	Stearic acid	- 3	
B	PVC	- 100	47
	Epoxidized soyabean oil	- 50	
	MgO	- 4	
	ZnO	- 4	
	Stearic acid	- 3	
C	PVC	- 100	55
	DOP	- 50	
	MgO	- 4	
	ZnO	- 4	
	Calcium stearate	- 3	
D	PVC	- 100	37
	DOP	- 50	
	MgO	- 4	
	ZnO	- 4	
	Lauric acid	- 3	

1. Non-toxic; hence could be used in food contact applications
2. Could be used in blends of rubbers with PVC, since all the three ingredients MgO, ZnO and stearic acid are conventional ingredients in rubber compounding
3. Inexpensive
4. Does not impair colour
5. Odourless
6. Stable in the range of processing temperatures for PVC
7. Non-sulphide staining, hence could be used in blends of PVC with sulphur vulcanizable rubbers.

References

1. G.H.Hofmann, "Polymer Blends and Mixtures", D.J.Walsh et al (Eds.), Martinus Nijhoff Publishers, Dordrecht (1985).

2. F.Chevassus and R.de Broutelles, "The Stabilization of PVC", Edward Arnold, London (1963).

3. D.Braun and M.Thalimaier, J.Polym.Sci., Part C, No.16, 2351 (1967).

4. D.Braun, Pure Appl.Chem. 26, 173 (1971).

5. W.C.Geddes, Rubber Chem.Technol., 40, 177 (1967).

6. J.Brandup and E.H.Immergut, Polymer Handbook, Sec.II, p.475, Wiley Interscience, New York (1975).

7. Z.Mayer, J.Macromol.Sci., Rev.Macromol.Chem., 10, 263 (1974).

8. J.H.P.Standinger, Plast.Progr., 9, 15 (1953).

9. H.V.Smith, J.Rubber Int.Plast., 138, 966 (1960).

10. M.Asahina and M.Onozuka, J.Poly.Sci., Part A, No.2, 3505 (1964).

11. M.E.Abuzeid et al, J.Appl.Polym.Sci., 29, 2431 (1984).

12. D.Braun and E.Bezdadea, "Encyclopedia of PVC", L.I.Nass and C.A.Heiberger (Eds.), Chap.8, Marcel Dekker, New York (1986).

13. Wypych, "Polyvinyl Chloride Degradation", pp.146 and 166, Elsevier, New York (1985).

14. L.I.Nass, "Encyclopedia of PVC", Vol.1, p.271, Marcel Dekker, New York, (1976).

15. J.S.H.Daoust, "Additives for Plastics", p.150, Springer Verlag, New York (1983).

16. C.M.Blow and C.Hepburn (Eds.), "Rubber Technology and Manufacture", pp.222 and 173, Butterworth Scientific, London (1982).

17. W.V.Titow, "PVC Technology", p.325, Elsevier Applied Science Publishers, London (1984).

18. W.S.Penn, "PVC Technology", p.195, Applied Science Publishers, London (1971).

19. D.J.Dunne, Plast. & Rub.Proc. & Appl., 3, 337 (1983).

20. R.M.Silverstein, G.C.Bassler and T.C.Murrie, "Spectroscopic Identification of Organic Compounds", John Wiley & Sons, New York (1981).

21. D.Braun and D.Hepp, Angew.Makromol.Chem., 44, 131 (1975).

22. D.F.Anderson and D.A.Mekenzie, J.Polym.Sci., 8, 2905 (1970).

23. M.Onozuka, J.Appl.Polym.Sci., Part A, No.5, 2729 (1967).

24. S.W.Schmitt, "Rubber Handbook", R.O.Babbit (Ed.), p.144, R.T.Vanderbilt Company, CT (1978).

25. V.Duchacek and A.Kuta, J.Appl.Polym.Sci., 27, 1549 (1982).

26. R.Joseph, K.E.George and D.J.Francis, Angew.Makromol.Chem., 148, 19 (1987).

27. J.Wypych, J.Appl.Polym.Sci., 23, 39 (1979).

28. J.Gilbert and J.R.Startin, Eur.Polym.J., 16, 73 (1980).

29. H.E.Luben, Chem.Rundschau, 27, 17 (1974).

CHAPTER - 4

TRIBASIC LEAD SULPHATE

EFFICIENT CURING AGENT FOR POLYCHLOROPRENE

TRIBASIC LEAD SULPHATE--EFFICIENT CURING AGENT FOR POLYCHLOROPRENE

Chloroprene rubber (neoprene) (CR) is a special purpose synthetic rubber manufactured by polymerizing 2-chloro-1,3 butadiene (chloroprene). E.I. dupont de Nemours & Co. Inc. is the principal manufacturer of polychloroprene in the world. Because of the electronegative chlorine on the 1,4-trans double bond, the resistance of polychloroprene to air oxidation, ozone attack, high temperature and naked flames is higher than that of a typical diene rubber such as natural rubber or styrene-butadiene rubber[1-4]. Hence CR is used in many critical applications such as car radiator hoses, gaskets, seals, cable covering, conveyor belts, shoe soles etc.

Today essentially all polychloroprenes are manufactured by emulsion polymerization. Because chloroprene polymerizes rapidly and tends to branch or gel as conversion or temperature excursions occur, control of polymerization parameters such as temperature, short stopping, chain transfer etc. is essential. The growing chloroprene chain can be modified by copolymerization with sulphur followed by peptization. It can also be modified by a chain transfer agent such as alkyl xanthogen disulphide $(ROCSS)_2$, organic polyhalide (e.g., CHI_3) or a combination of both[5,6]. In some applications the gel polymer is prepared to meet specific needs.

The various types of polychloroprenes may be conveniently divided into two general classes depending on their versatility and overall usefulness[6-9]. The best known and most widely used are the general or all purpose types which are recommended wherever the general characteristics of CR vulcanizates are desired. The other class of polychloroprenes is specifically designed for outstanding performance in selected physical properties for applications such as adhesives, sealants etc.

The general purpose CR rubbers fall into three classes, the G, W and T groups, according to the Dupont grading system. Within each group a number of polymers are available varying in Mooney viscosity, rate of crystallization and other features.

The G types (e.g., GN, GW, GNA, GRT), generally termed sulphur modified, are interpolymerized with sulphur to give C-S-C links and contain thiuram disulphide stabilizer and show fairly wide molecular weight distribution ranging from 20,000 to 950,000. The molecular weight is adjusted by the addition of sulphur and thiuram disulphide to reduce chain length to obtain a processable polymer[6-9]. GN type CR was the first sulphur modified grade to win large scale commercial acceptance.

The W types (e.g., W, WRT etc.), generally termed non-sulphur modified, are mercaptan modified to give C-C links in the polymer and, containing no sulphur or sulphur-yielding substances, they have excellent raw polymer stability and better heat resistance than the G types. Their more uniform molecular weight distribution imparts better processability.

CR vulcanizes in a considerably different manner from that of natural rubber and such synthetic rubbers like styrene-butadiene rubber. Unlike normal vulcanization with sulphur, metallic oxides are necessary to vulcanize CR. The metallic oxides most often used are zinc oxide as crosslinking agent and magnesium oxide which is mainly used as an acid acceptor. The effects obtained differ greatly in the G and W types of CR. In G types, metallic oxides generally give satisfactory vulcanization by themselves. On the other hand W types have less tendency to crosslink and therefore require not only metallic oxides but also special accelerators like ethylene thiourea[10-12].

Polychloroprene can be vulcanized with several other metallic oxides apart from magnesium oxide and zinc oxide.

Lead oxide (PbO) and red lead (Pb_3O_4) are used particularly when low water absorption and high resistance to acids are required. However, with the exception of these lead oxides, none of the other metallic oxides whether used alone or in combination gives properties that even approximate to those obtained with MgO/ZnO vulcanization system[13].

Tribasic lead sulphate ($3PbO.PbSO_4.H_2O$) (TBLS), a common heat stabilizer for PVC, is a good acid acceptor[14] and contains PbO which is a special purpose crosslinking agent for CR. Hence TBLS was tried as a curing agent for polychloroprene. It is comparatively cheaper than the conventional curing agents for polychloroprene and is likely to produce good resistance to water, acids, and other solvents similar to the lead oxide cured vulcanizates.

Experimental

1. Determination of cure characteristics

The formulations of the mixes employed for determining the cure characteristics are shown in Table 4.1. The compounds were prepared on a Brabender Plasticorder model PL3S, using a roller type mixer with a rotor speed of 30 rpm, at near ambient temperature (30°C). The cure characteristics were determined on the Monsanto Rheometer at 150°C. The cure curves are shown in Figs.4.1, 4.2, 4.3 and 4.4.

Table 4.1

Formulations employed for determining the cure characteristics

Formulations	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Polychloroprene(W)*	100	100	100	100	--	--	--	--	--	--	100	100	100	100	100
Polychloroprene (GN)	--	--	--	--	100	100	100	100	100	100	--	--	--	--	--
MgO	4	--	4	--	4	--	4	--	--	--	--	--	--	--	--
ZnO	5	--	5	--	5	--	5	--	--	--	--	--	--	--	--
TBLS	--	5	--	5	--	5	--	5	10	15	5	5	5	5	5
NA-22	--	--	0.5	0.5	--	--	0.5	0.5	--	--	0.2	0.4	0.6	0.8	1.0

*Type 2 (Chapter 2).

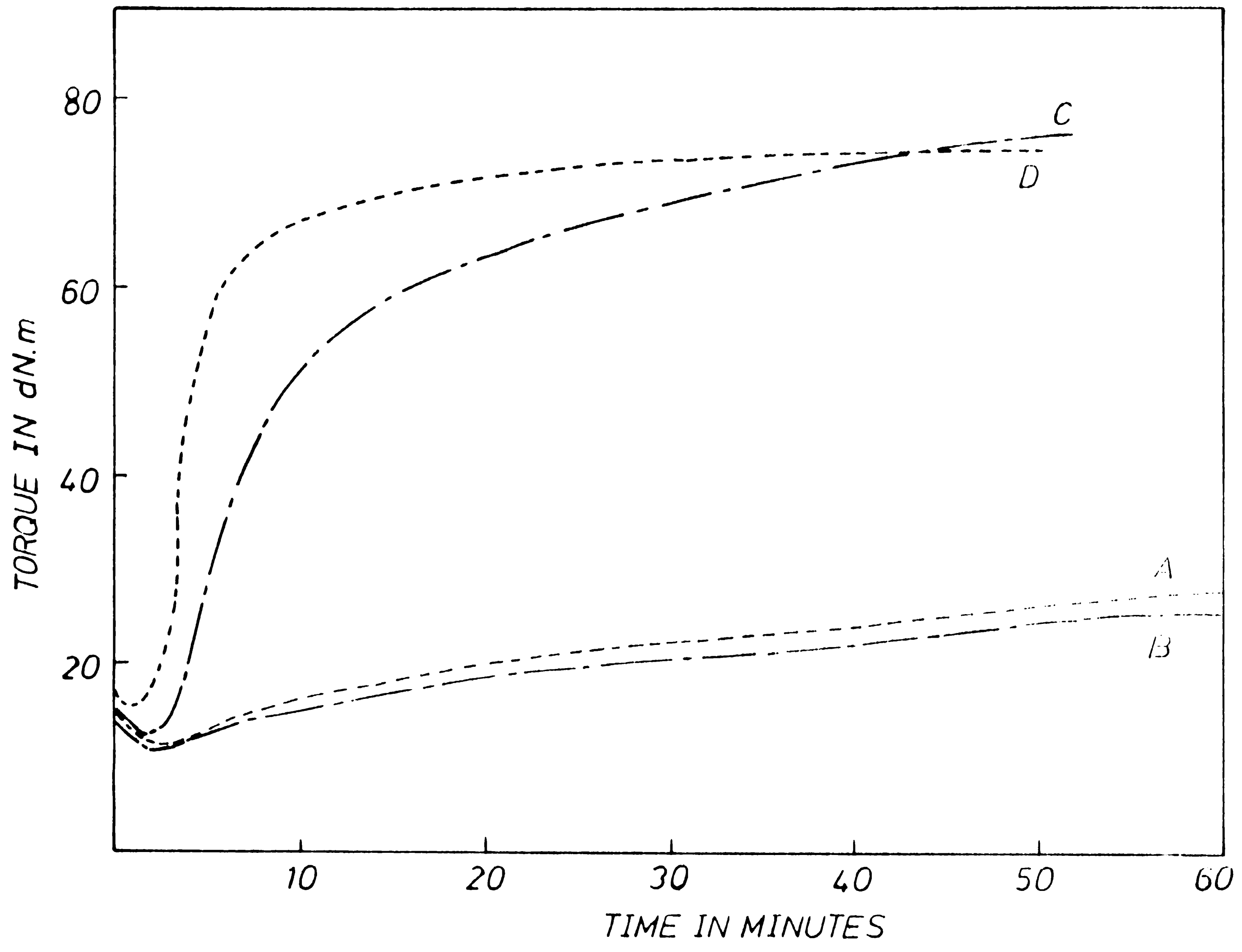


Fig. 4.1 Cure curves of W type CR in presence of (A) MgO/ZnO, (B) TBLS, (C) MgO/ZnO + NA-22, (D) TBLS + NA-22.

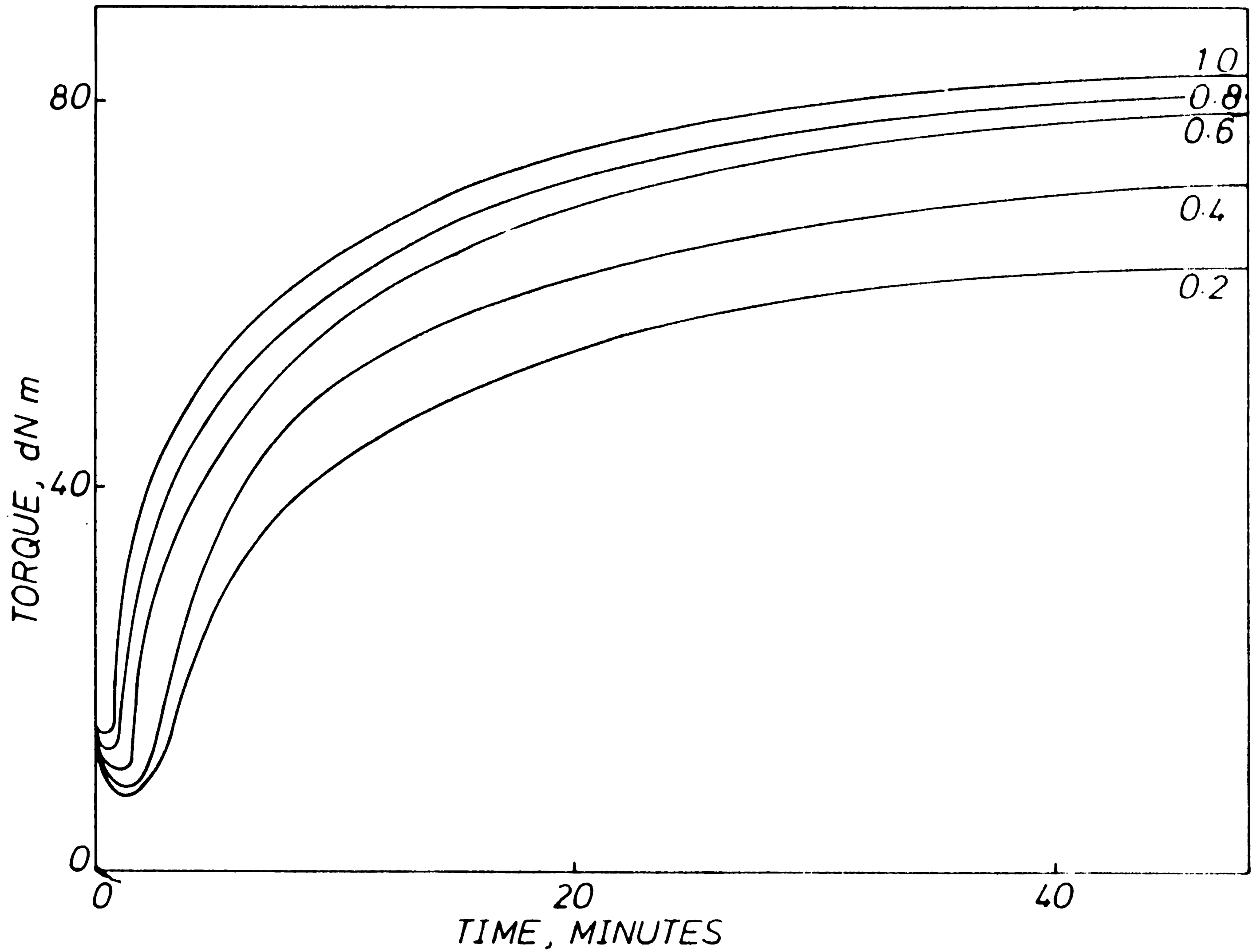


Fig. 4.2 Effect of NA-22 concentration (phr) on the curing of W type CR in presence of 5 phr TBLS.

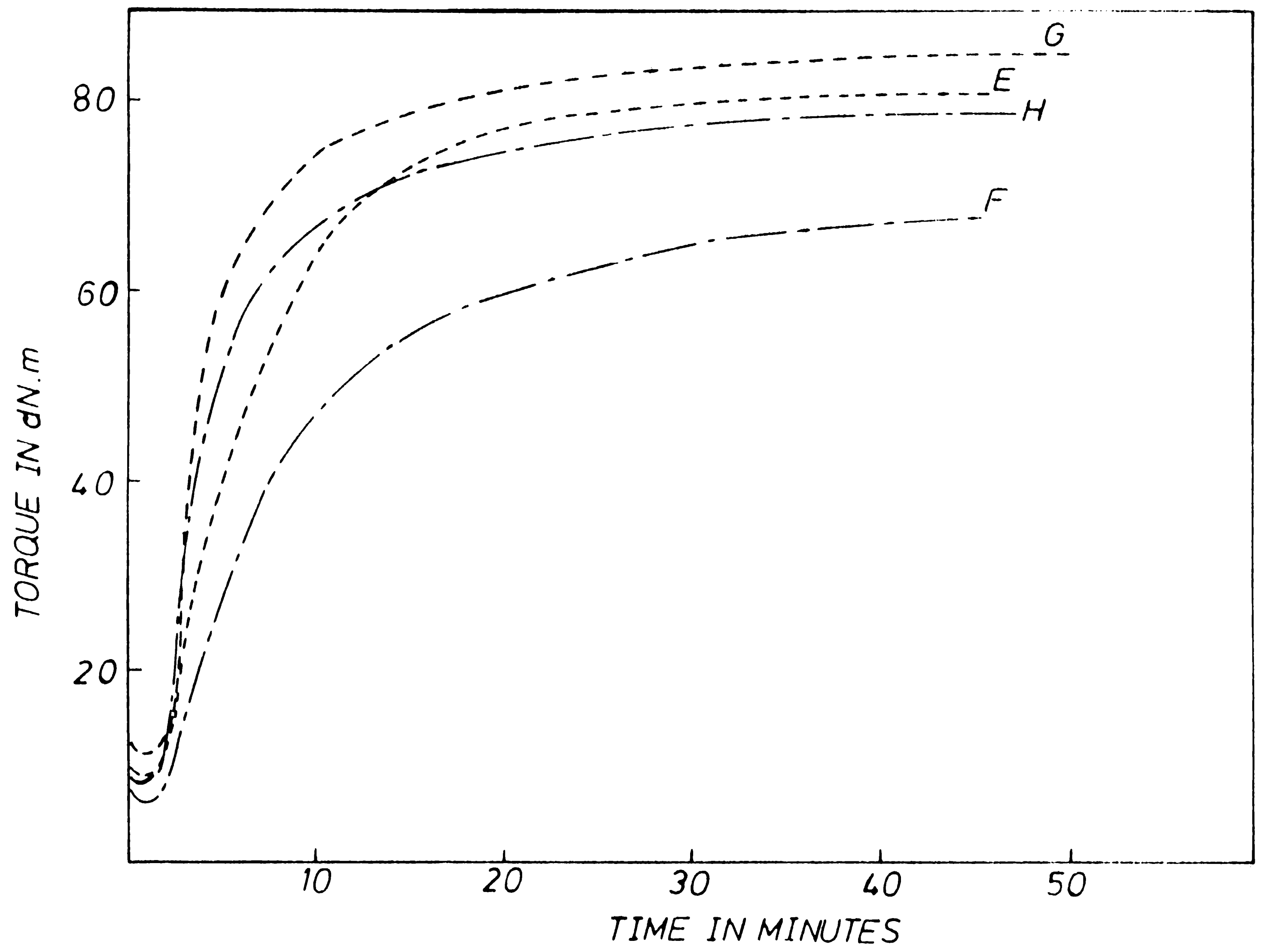


Fig. 4.3 Cure curves of GN type CR in presence of (E) MgO/ZnO, (F) TBLS, (G) MgO/ZnO + NA-22,(H) TBLS + NA-22.

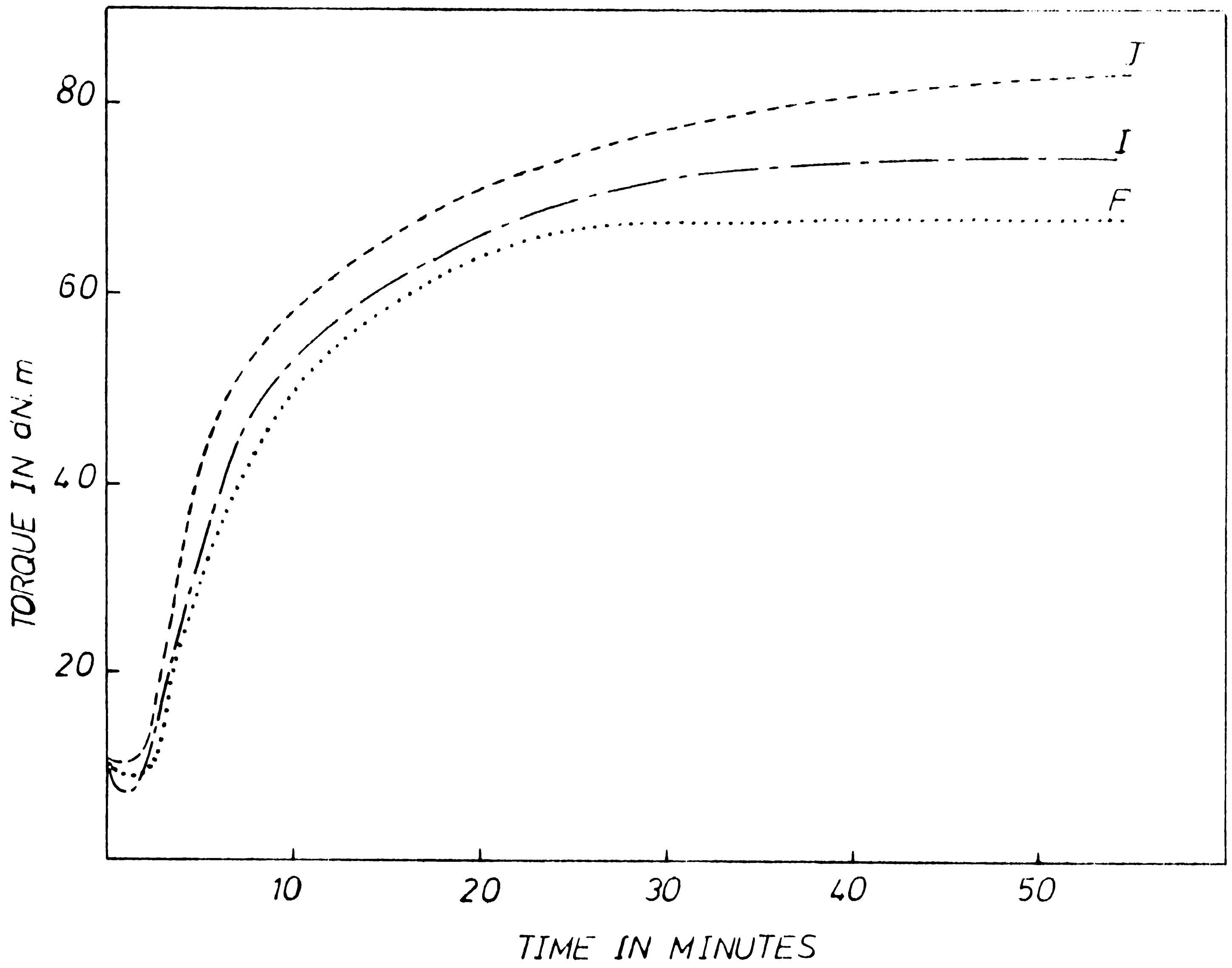


Fig. 4.4 Cure curves of GN type CR with varying amounts of TBLS: (F) 5 phr,(I)10 phr, (J) 15 phr.

2. Determination of technical properties

The formulations employed for determining the technical properties and their cure characteristics are shown in Table 4.2. The compounds were prepared on a laboratory mixing mill and then the cure characteristics were determined on the Monsanto Rheometer at 150°C. The compounds were then vulcanized upto the respective optimum cure times on a laboratory press. The tensile properties were determined as per ASTM D412 (1980). The ageing characteristics of the samples were determined by keeping them at 100°C for 48 hours in an air oven and then measuring the retention in the tensile properties. The hardness of the vulcanizates was determined according to ASTM 2240 (1981) and expressed in shore A units. The compression set was determined according to ASTM D395 (1982)under constant deflection. The solvent resistance of the vulcanizates was determined by allowing circular specimens to stand in excess of water, acetic acid, acetone, toluene and carbon tetrachloride at 30°C for 20 days and then measuring the percentage change in weight.

Results and discussion

Fig.4.1 shows the cure characteristics of W type CR. The MgO/ZnO system in the absence of an accelerator cures very inefficiently and at a very slow rate as expected. The

Table 4.2

Formulations employed for determining the technical properties

Formulations	I	II	III	IV
Polychloroprene (GN)	100	100	100	100
Mgo	4	--	--	--
ZnO	5	--	--	--
Pb_3O_4	--	15	--	--
TBLS	--	--	5	10
SRF	50	50	50	50
Naphthenic oil	10	10	10	10
PBN	1.5	1.5	1.5	1.5
Stearic acid	2.0	2.0	2.0	2.0
Cure characteristics				
Scorch time (mins.)	2.0	1.5	1.5	1.25
Optimum cure time (mins.)	14.0	37.5	26.5	32.0
Maximum torque (dN.m)	92.0	102.0	71.0	90.0
Reversion (No.of units dropped in 10 mins.)	Nil	Nil	Nil	Nil

behaviour of TBLS without an accelerator, is found to be more or less same. The curing rate is very low and the maximum torque, a measure of the amount of crosslinks, is also very low. The curing of this type of CR with MgO/ZnO system in presence of 0.5 phr (per hundred rubber) NA-22 is faster and efficient as expected. The behaviour of TBLS in presence of 0.5 phr NA-22 is also found to be similar implying that TBLS could act as a potential curative for W type CR in presence of an accelerator like NA-22. However, the scorch safety of the compound with TBLS and NA-22 is found to be a little less than that of the compound with MgO/ZnO and NA-22. This behaviour seems to be similar to that of other lead oxide curing systems[13]. The amount of the accelerator was varied keeping the amount of TBLS at 5 phr (Fig.4.2). Higher amount of accelerator produced marginal increase in the maximum torque but at the expense of the scorch safety.

Fig.4.3 shows the cure characteristics of GN type CR. MgO/ZnO system acts as an efficient curative in this case even without an accelerator as expected. Addition of an accelerator produce only marginal increase in the maximum torque. The behaviour of TBLS is also similar implying that TBLS could act as a potential curative for GN type CR even without an accelerator. The amount of crosslinks, as reflected in the maximum torque values, seems to be a little less at this level of TBLS than that obtained with the MgO/ZnO system. Fig.4.4 shows the effect of varying the amount of TBLS in the curing behaviour of GN type CR. It is found that increasing the amount of TBLS produces marginal increase in the maximum torque values without much decrease in the scorch safety.

For estimating the mechanical properties of TBLS cured CR, GN type rubber was chosen since TBLS could act as the sole curative in that case. A typical MgO/ZnO compound and a Pb_3O_4 compound were selected for comparison. Since the industrially important chloroprene rubber compounds contain fillers and antioxidants, 50 phr SRF black along with 10 phr naphthenic oil and 1.5 phr PBN were also added in each case (Table 4.2). An examination of the mechanical properties (Table 4.3) reveals that the TBLS cured vulcanizate shows the maximum tensile strength and elongation at break even at 5 phr concentration. Increasing the amount of TBLS to 10 phr shows marginal increase in tensile strength but at the expense of elongation at break. This again shows that additional crosslinks are introduced in the matrix with increase in the amount of TBLS. The hardness and compression set values confirm this observation. The vulcanizate cured by Pb_3O_4 seems to be the best in ageing resistance. However,

Table 4.3

Mechanical properties of the vulcanizates

Properties	Vulcanizate			
	I	II	III	IV
Tensile strength (MPa)	15.8	15.9	16.5	16.7
Elongation at break (%)	580	475	670	490
300% Modulus (MPa)	8.7	9.7	6.5	9.8
Hardness (Shore A)	63.0	65.0	55.0	63.0
Compression set (%)	50	35	45	40.5
<u>Tensile properties after ageing</u>				
Tensile strength (MPa)	14.4	15.0	15.0	15.5
Elongation at break (%)	425	420	500	400
300% Modulus (MPa)	10.6	11.0	7.8	11.6

the values shown by the TBLS cured vulcanizates are also within reasonable limits for practical applications.

The TBLS cured vulcanizate exhibits very good resistance to solvents (Table 4.4) even at 5 phr concentration particularly in water and acetic acid, compared to the MgO/ZnO, and Pb_3O_4 cured vulcanizates. Increasing the amount of TBLS produces further improvements in solvent resistance as shown by the vulcanizate which contains 10 phr TBLS.

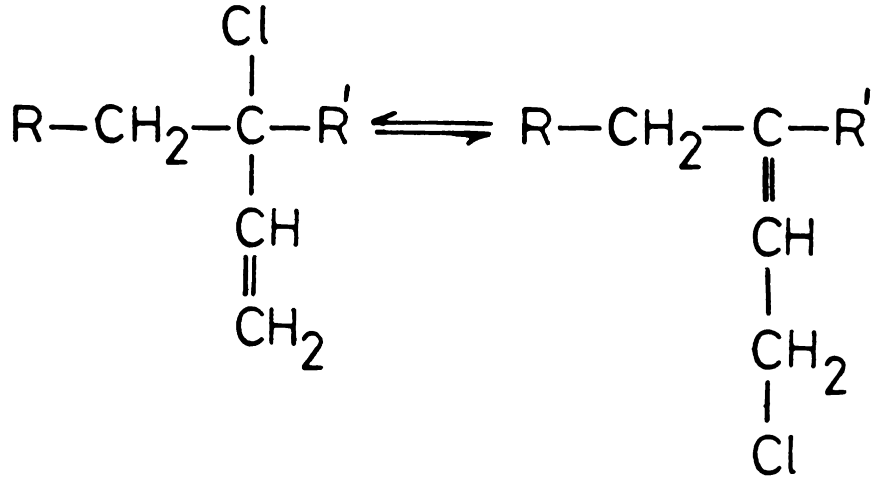
Mechanism of crosslinking

The polymer chain of polychloroprene is built up through addition of monomer units of which approximately 98% add in the 1,4 positions. About 1.5% add in the 1,2 position and these are utilized in the vulcanization process since in this arrangement they are tertiary and allylic and hence labile. The equilibrium in Fig.4.5(A) is probably the first step in the vulcanization of polychloroprene[15,16]. The PbO in the tribasic lead sulphate could then react as given in Fig.4.5(B)[15,16]. The $PbCl_2$ formed is a highly stable compound compared to that of $ZnCl_2$ and $MgCl_2$. The catalytic action of $PbCl_2$ similar to that of $ZnCl_2$[16] on the crosslinking could be the reason for the decrease in scorch safety of the compounds.

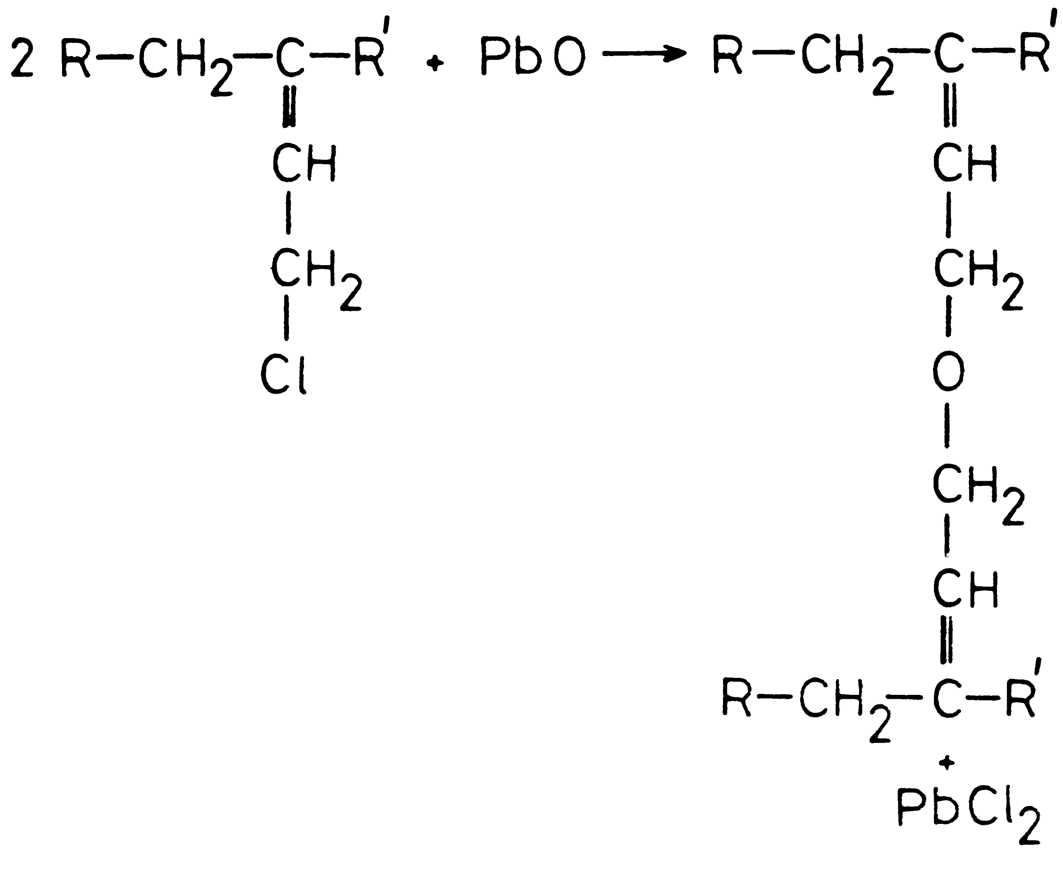
Table 4.4

Solvent resistance of the vulcanizates
(% increase in weight in 20 days)

Solvent	Vulcanizate			
	I	II	III	IV
Water	12.85	1.42	3.97	1.75
Acetic acid	62.88	8.49	7.20	4.35
Acetone	13.45	14.96	13.70	11.20
Toluene	165.5	134.49	169.34	136.53
Carbontetrachloride	274.93	227.82	289.10	238.68



A. Equilibrium



B. Crosslinking

Fig. 4.5 Mechanism of crosslinking of polychloroprene in presence of TBLS.

Vulcanization of polycloroprene with dibasic lead stearate

Similar to TBLS, dibasic lead stearate (2PbO. Pb($C_{17}H_{35}COO)_2$)(DBLS) is also a good acid acceptor and contains PbO. Hence DBLS was also tried as a curing agent for polychloroprene. The cure characteristics of CR compounds containing DBLS were compared with those of CR compounds containing TBLS on Göttfert Elastograph at 160°C. The formulations used for the study are shown in Table 4.5. The cure curves are shown in Figs.4.6 and 4.7. The curing behaviour of DBLS is also found to be similar to that of TBLS in that it effects the crosslinking of W type CR in presence of an accelerator (NA-22) (Fig.4.6) and GN type CR even without an accelerator (Fig.4.7). However, the maximum torque, a measure of the crosslink density is less in the case of DBLS both for W type CR and GN type CR. This might indicate that DBLS is less efficient, compared to TBLS, as a crosslinking agent for polychloroprene rubber.

Summary

Tribasic lead sulphate has been identified as a potential curative for CR. Compared to conventional curatives of CR, TBLS is found to be effective in comparatively lower concentrations and to impart better mechanical properties and solvent resistance to the CR vulcanizates.

Table 4.5

Formulations employed for comparing the cure characteristics of CR with TBLS and DBLS

Formulations	A	B	C	D
Polychloroprene (W)*	100	100	---	--
Polychloroprene (GN)	--	--	100	100
TBLS	10	--	10	--
DBLS	--	10	--	10
NA-22	0.5	0.5	--	--

* Type 2 (Chapter 2).

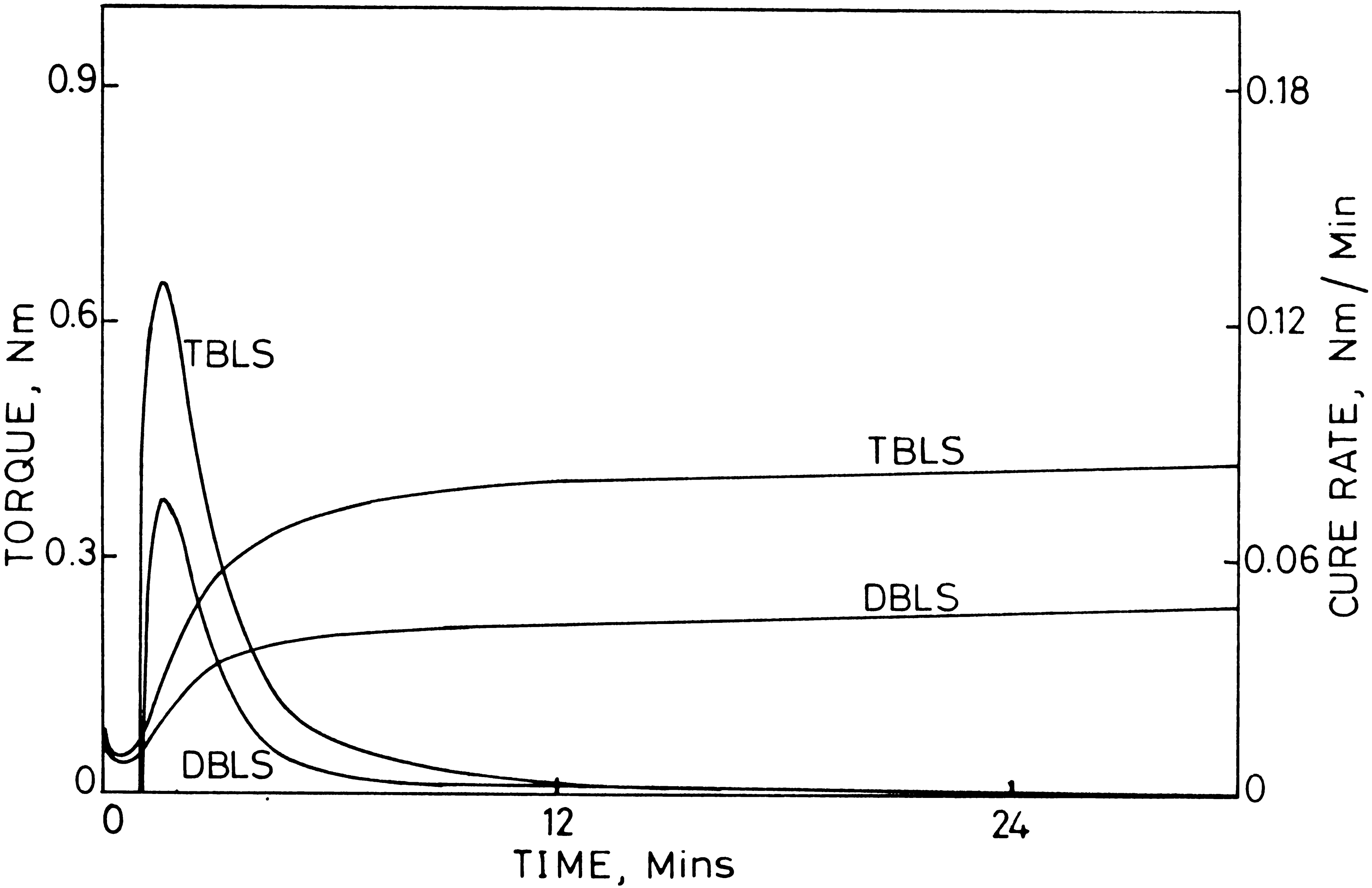


Fig. 4.6 Comparison of efficiency of TBLS & DBLS as curatives for W type CR in presence of 0.5 phr NA-22.

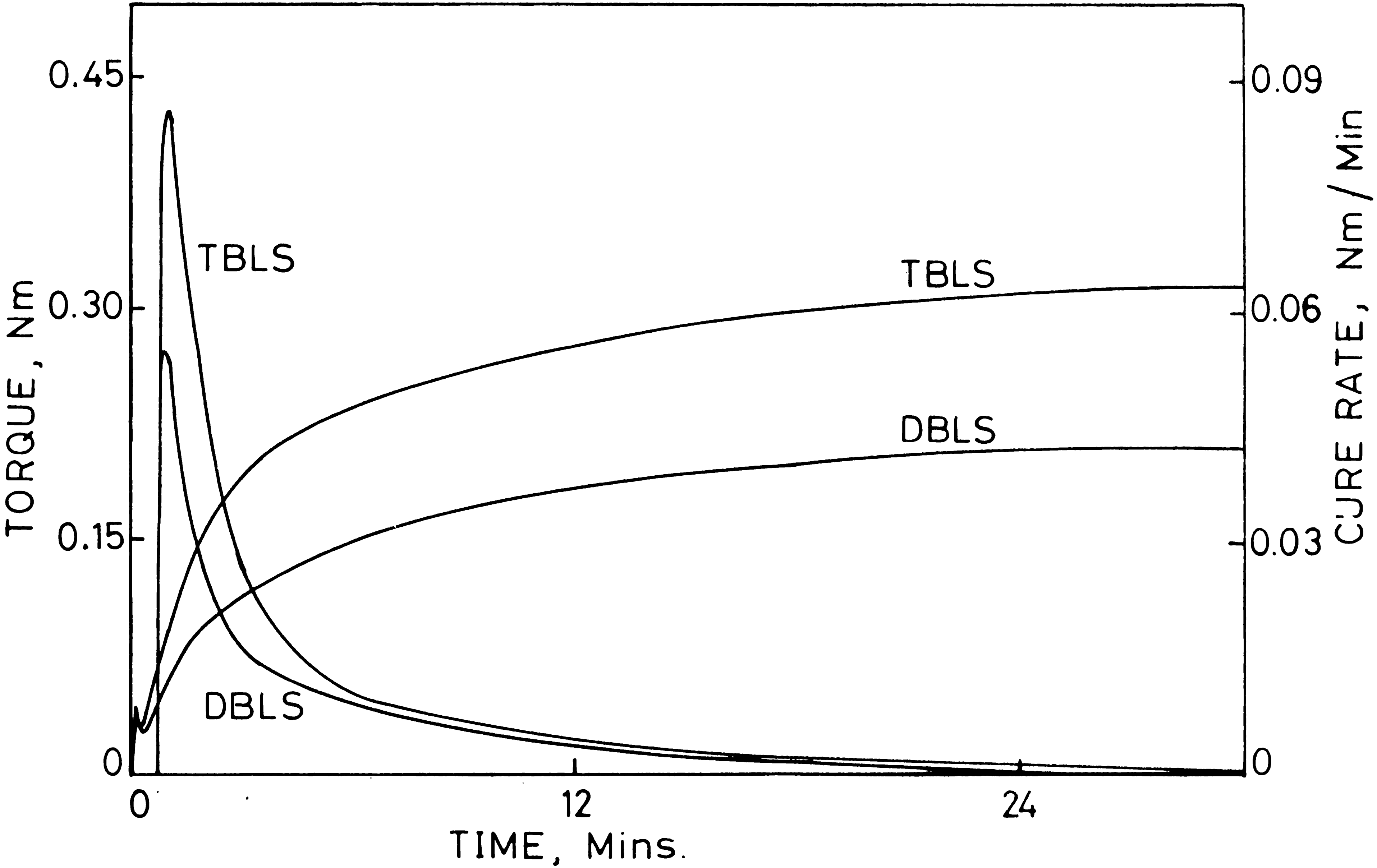


Fig. 4.7 Comparison of curing of GN type CR in presence of TBLS and DBLS

References

1. P.R.Johnson, Rubber Chem.Technol., 49, 650 (1976).
2. A.F.Nosnikove, A.A.Nosnikov and G.A.Blockh, Int.Polym.Sci. Technol., 10, No.10, 54 (1983).
3. G.A.Lysova, V.M.Artenov and F.A.Galil - Ogly, Int.Polym. Sci. Technol., 7, No.10, 35 (1980).
4. R.J.Crawford, "Plastics and Rubbers--Engineering Design and Applications", Mechanical Engineering Publications Ltd., London (1985).
5. S.W.Schmitt and C.Anelick, Rubb.Chem.Technol., 51, 888 (1978).
6. H.Mark et al (Ed.), Encyclopedia of Polymer Science & Engineering, Vol.3, pp.441-460, John Wiley & Sons, New York (1985).
7. N.L.Catton, "The Neoprenes", E.I.dupont de Nemours & Co.,Inc., Wilmington, Del. (1953).
8. W.P.Fletcher in "Rubber Technology and Manufacture", C.M.Blow and C.Hepburn (Eds.), pp.118-125, Butterworths, London (1985).
9. M.M.Murray and D.C.Thompson, "The Neoprenes", E.I.du Pont de Nemours & Co., Inc., Wilmington, Del. (1963).
10. W.Hofmann, "Vulcanization and Vulcanizing Agents", Maclaren and Sons Ltd., London (1967).
11. H.Kato and H.Fajima, Rubber Chem.Technol., 48, 19 (1975).
12. Y.Nakamura, K.Mori and T.Nakamura, Rubber Chem.Technol., 49, 1031 (1976).
13. D.B.Forman in "Rubber Technology", M.Morton (Ed.), Van Nostrand Reinhold Company, New York (1973).

14. L.I.Nass, "Encyclopedia of PVC", Vol.1, Chap.9, Marcel Dekker, Inc., New York (1976).

15. S.W.Schmitt in "Rubber Handbook", R.O.Babbit (Ed.), pp.144 and 145, R.T.Wanderbilt Company, Inc., CT (1978).

16. D.C.Blackley, "Synthetic Rubbers", pp.185-190, Applied Science Publishers, London (1983).

CHAPTER-5

STUDIES ON BUTADIENE-ACRYLONITRILE RUBBER/POLY(VINYL CHLORIDE) BLENDS

STUDIES ON BUTADIENE ACRYLONITRILE RUBBER/POLY (VINYL CHLORIDE) BLENDS

The range of application of traditional polymers can be considerably broadened by their physical modification, that is, by blending the polymer being modified with other low or high - molecular weight compounds. Such multicomponent blends often possess interesting properties which is the reason for the observed increasing interest in their investigation and application. Because of its low cost and versatility, poly(vinyl chloride) (PVC) has received great attention in further improving its processability, heat distortion temperature, impact strength, and service life etc. by blending with other polymers[1]. The polymeric modifiers added to PVC may be divided into four categories: solid plasticizers, impact modifiers, heat distortion improvers and processing aids.

The property modification is highly dependent upon the miscibility of the modifying polymer with PVC[2]. In general, blends of PVC with polymers that show high miscibility will be microscopically homogeneous (single phase) and display a single glass transition temperature (T_g) of intermediate value between the T_g's of the pure component polymers. In cases where the blend T_g is lower than that of PVC, plasticization is said to occur. When the blend T_g is increased then heat distortion temperature improvement is obtained. An additional benefit that can be imparted by miscible polymers is an improvement in processability. These polymers can increase the rate of fusion of the PVC powder leading to a more rapid formation of a homogeneous melt having higher melt strength.

By far the widest range of polymeric additives for PVC fall into a broad category that can be classified as partially miscible[3,4]. A broad range of properties may be obtained depending on the degree of miscibility. Partially miscible blends display some phase separation (microscopically heterogeneous) but a significant degree of polymer segment mixing on a molecular scale occurs producing mechanically compatible phases (high interfacial addition) with useful properties. Each phase will display a distinct T_g but because of the partial intermixing, the T_g's will be moved closer together and become progressively suppressed in intensity reflecting the ability of the high T_g component to raise the T_g of the low T_g component and vice versa. On the other hand, immiscible polymer blends will be microscopically heterogeneous (multiphase) and will display a distinct and unshifted T_g for each phase. In practice, truly incompatible polymer-PVC blends are of little interest since they yield poor properties especially if the interfacial adhesion between the phases is poor.

Butadiene-acrylonitrile (NBR)/Poly(vinylchloride) (PVC) blends

Miscibility of polymer blends was first observed with NBR/PVC systems. These blends probably have been the most widely studied, having significant commercial interest[5]. They have been described as miscible, partially miscible and even immiscible based on the different experimental techniques and copolymer compositions. Miscible blends are widely used as flexible compositions with the NBR acting as a permanent plasticizer. In general the acrylonitrile content sufficient to yield maximum miscibility appears to fall in the range of 25-40% with gradual immiscibility occurring with either decreasing or increasing acrylonitrile levels[6].

Low levels of NBR added to PVC yield impact modified rigid PVC with optimum properties. Moderate levels of NBR can act as a permanent plasticizer for PVC in critical applications, where the migration of low molecular weight plasticizer is a severe problem. On the other hand, PVC added to

NBR improves ozone, thermal, ageing and chemical resistance of NBR. PVC also vastly improves abrasion resistance, tear resistance and tensile properties[7-9]. It also adds gloss and improves finish of the extruded stock and imparts flame retardant character. NBR/PVC blends can be conveniently milled, extruded, and compression moulded using traditional processing equipments for natural and synthetic rubbers[10].

OPTIMIZATION OF BLENDING PARAMETERS FOR THE PREPARATION OF NBR/PVC BLENDS

Mixing in the molten state is often the method of choice for the preparation of polymer blends[11]. The primary disadvantage of melt mixing, however, is that the components must be in the molten state, which can mean that temperatures may be high enough to cause degradation. Hence, care should be exercised to do the blending at the minimum temperatures possible. In the case of NBR/PVC blends, NBR acts as a permanent plasticizer for PVC and hence depending upon the amount of NBR, there might be a minimum temperature at which the PVC phase fully homogenizes. If blending is done at this temperature, the degradations occurring in the polymer phases could be kept to a minimum. This means that there exists an optimum temperature of preparing a blend of a particular composition provided, the other blending parameters are fixed. An attempt has been made to estimate this optimum temperature by studies conducted on a Brabender Plasticorder. MgO/ZnO/Stearic acid combination was used as the stabilizer for the PVC phase in this study.

Experimental

1. Studies on the Brabender Plasticorder

The study was conducted on a Brabender Plasticorder Model PL3S using a roller type mixing head (rotor) at a speed of 30 rpm. A total weight of 34 gms was selected as the sample weight for each run on the plasticorder after carefully observing the torque curves for different sample weights[12]. Six combinations of blends were made by taking PVC 10, 20, 30, 40, 50 and 60% of the total weight. 4.0 parts per hundred PVC (phr) MgO, 4.0 phr ZnO and 3.0 phr stearic acid were taken together with PVC as stabilizer. The rest of the weight constituted NBR and its curatives - 1.5 phr sulphur and accelerators (1.5 phr MBTS and 0.5 phr TMTD) and activators (2.0 phr ZnO and 1.0 phr stearic acid). The recipe for the blend containing 20% PVC is shown in Table 5.1 as an example. For all the test runs on the plasticorder, NBR was added initially, after the mixer attained the required temperature. After giving 1 minute for the rubber to heat up and homogenize in the mixer, PVC and its stabilizer were added. The polymers were blended for 5.5 minutes and then the curatives were added. Once the mass broke down to crumbs it was removed. The study was repeated for the six combinations of blends at different temperatures.

Table 5.1

Recipe for the NBR/PVC blend with 20% PVC

PVC and stabilizer	
PVC	6.80 gm (20% of total wt.)
MgO	0.27 gm (4.0 phr PVC)
ZnO	0.27 gm (4.0 phr PVC)
Stearic acid	0.20 gm (3.0 phr PVC)
NBR and curatives	
NBR	24.85 gm
ZnO	0.50 gm (2.0 phr NBR)
Stearic acid	0.25 gm (1.0 phr NBR)
MBTS	0.37 gm (1.5 phr NBR)
TMTD	0.12 gm (0.5 phr NBR)
Sulphur	0.37 gm (1.5 phr NBR)
	34.00 gm

2. Evaluation of mechanical properties

For measuring the mechanical properties the blend containing 20% PVC was made at 135, 145 and 155°C and the blend containing 50% PVC at 145, 155 and 165°C. These blends were prepared on the Brabender Plasticorder using the same recipe as that used for Brabender studies. However, a blending time of 10 minutes was employed[13] and the curatives in each case were added later on a two roll laboratory mixing mill at about 50°C. The curatives were not added in the plasticorder, since the torque involved in handling the polymers at this low temperature was very high. The cure curves of the various compounds were taken at 150°C on the Monsanto Rheometer. Test samples for evaluating the physical properties were vulcanized upto the respective cure times at 150°C. The tensile properties were determined on a Zwick Universal Testing Machine as per ASTM D412 (1980). Shore-A type durometer was used for determining the hardness of the vulcanizates as per ASTM D2240 (1981).

Results and discussion

Fig.5.1 shows the Brabender torque curves of the NBR/PVC blend containing 20% PVC and that of NBR alone at 155°C. The curve for the blend may be explained as follows. NBR is charged into the mixing chamber in the region A to B, and hence the torque rises. Once the addition of NBR is over, the rubber homogenizes and the torque begins to decrease at B mainly due to degradation in the rubber, especially mechanical. At C, PVC is added. As the PVC melts, the torque rises again upto D and thereafter remains almost steady upto E.

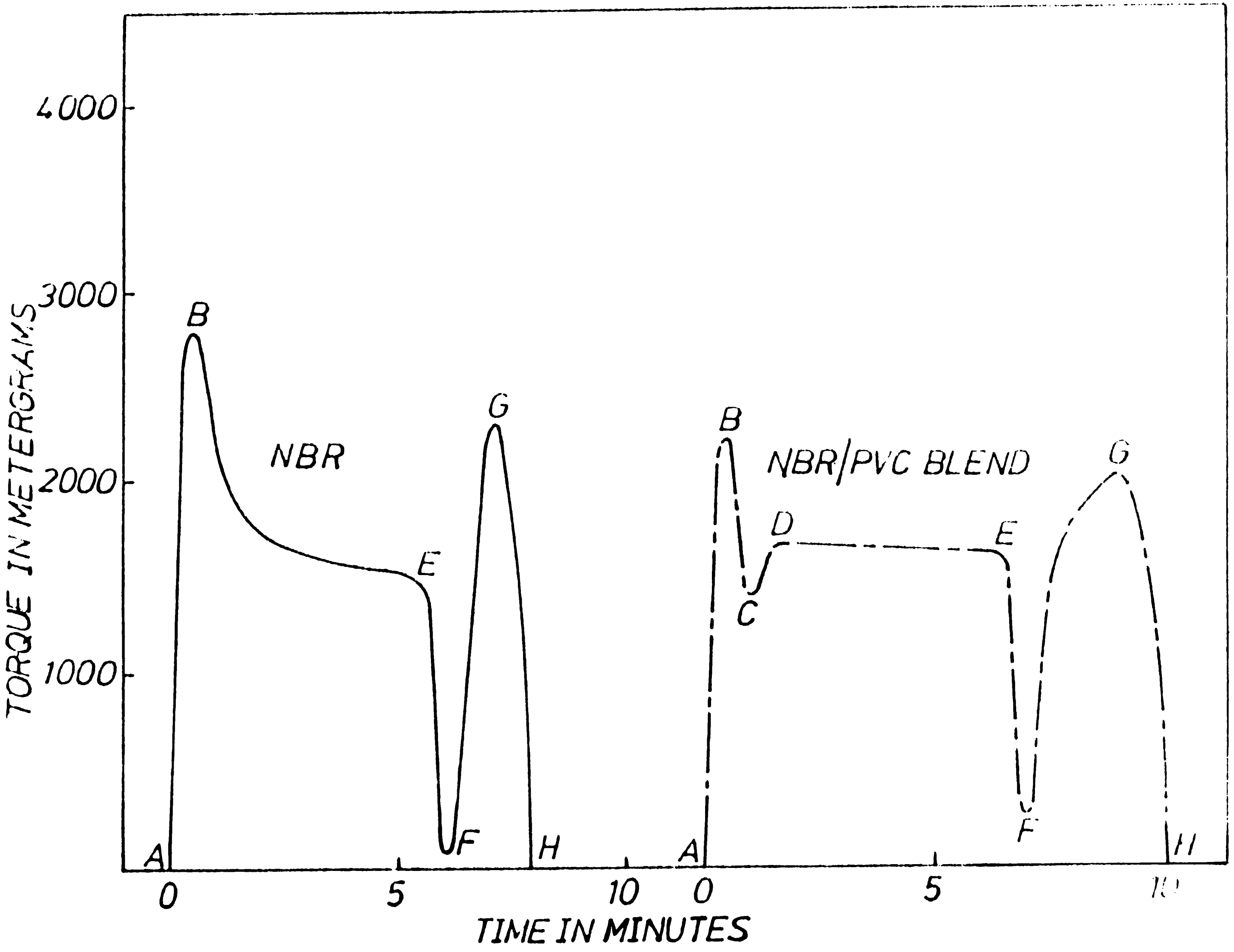


Fig. 5.1 Brabender torque-time curves of NBR and NBR/PVC blend containing 20% PVC at 155°C: (A,B) addition of rubber, (C) addition of PVC; (E) addition of curatives.

It may be observed that the tendency for degradation in the blend is not so obvious as before, and this might be due to the protection offered by the PVC phase. Curatives are added at E. The torque decreases to a minimum value F due to the lubricant action of these additives. Once crosslinking starts, the torque rises again. At G, the curing is completed and the material breaks down, which accounts for the sudden decrease in torque upto H. The torque curve for NBR alone shows that the decrease in torque due to degradation continues from the point B upto the point E. However, the rate of decrease in torque falls off from B to E due to the decrease in shear as a result of the degradation. Table 5.2 shows the torque at the points B, C, D, E and G of the blends containing different percentages of PVC at 155°C. In the case of the blend containing 10% PVC there is some decrease in torque from D to E. This shows that this amount of PVC is not enough to protect the rubber phase under the conditions existing in the mixer. The 20% PVC blend shows only a slight decrease in torque from D to E. For the blends containing 30, 40, and 50% PVC, the torque rises again after the point D, and then stabilizes to the torque value at E, which suggests that the melting of PVC is not complete at point D, but continues in the mixing time. In the case

Table 5.2

Brabender torque values of NBR/PVC blends at 155°C*

Blend composition % of PVC	Torques at various points (metergrams)				
	B	C	D	E	G
10%	2500	1500	1800	1550	2000
20%	2200	1400	1650	1600	2000
30%	1900	1100	1750	1750	2200
40%	1600	800	1750	1850	2200
50%	1200	500	1700	1950	2300
60%	1100	300	1400	1850	2200

* Ref.Fig.5.1.

of the blend containing 60% PVC, the torque continues to rise till the end of the mixing time, indicating insufficient mixing time and/or mixing temperature. The torque observed at point E increases with the percentage of PVC as expected, and this torque may be assumed to reflect the mechanical strength of blends. However, the 60% blend shows a lesser torque at E than that of the 50% blend. Clearly, the PVC has not melted properly to show the full torque. The torque shown by the blends after curing (torque at G) seems to be only a rough measure of the mechanical strength. This may be due to the tendency of the mass to break down once curing starts.

Fig.5.2 shows the Brabender torque curves of the blend containing 20% PVC at various temperatures (curing part is not shown for clarity). The torque curve at 115°C drops down slightly after D, and then stabilizes to the torque value at E. This delay in stabilizing may be due to the presence of a good amount of unfused PVC. The torque curves at 125 and 135°C also behave similarly but stabilize to the torque at E after a shorter time. At 145°C, the torque curve stabilizes to the torque at E immediately after D. At 155°C, the melting of PVC seems to be almost complete at D itself, since there is no initial unstable period. The torque curves at 165°C and 175°C do not stabilize to a particular torque, but show a trend to fall of continuously after D

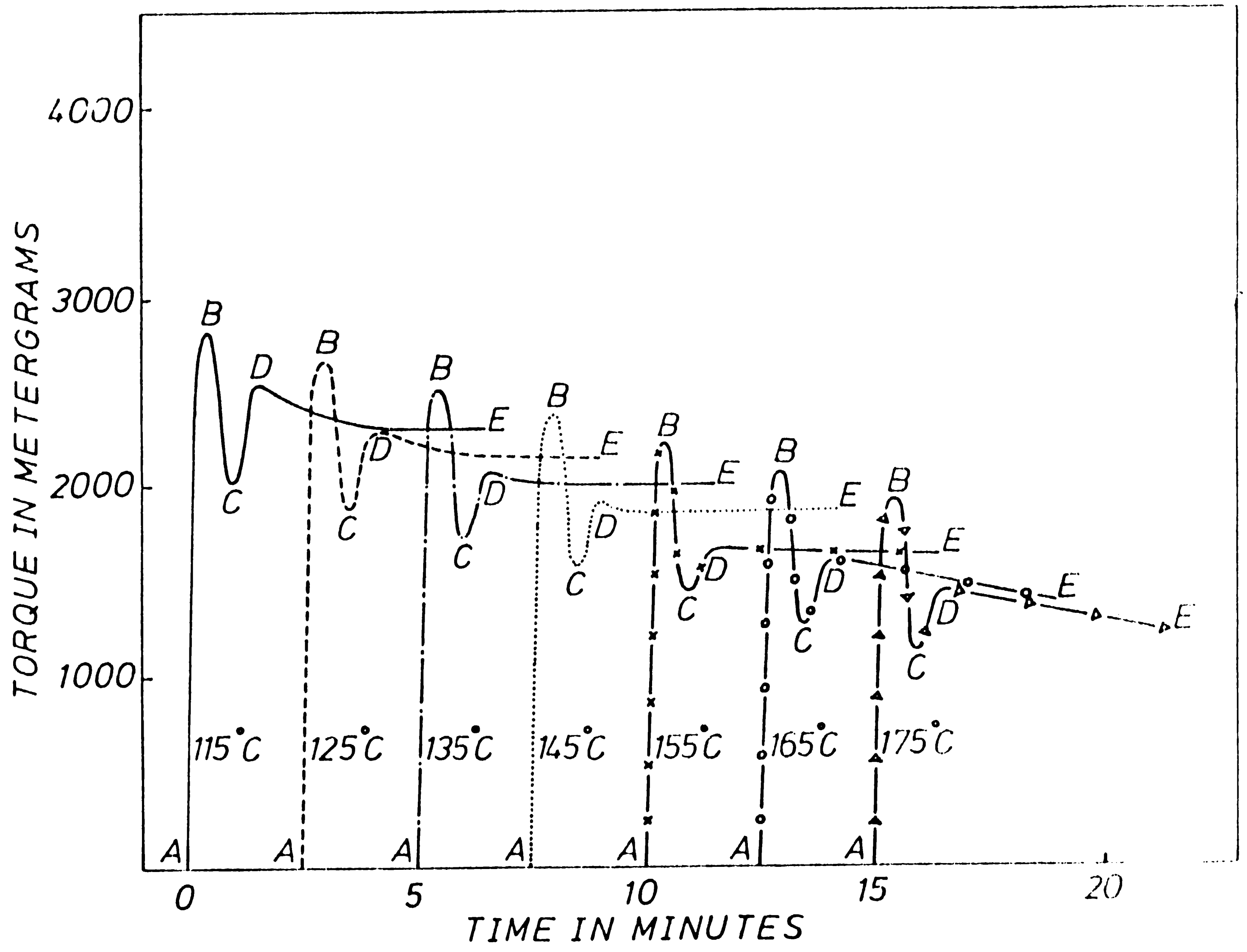


Fig. 5.2 Brabender torque-time curves of NBR/PVC blend containing 20% PVC at different temperatures (curing part not shown): (A,B) addition of rubber, (C) addition of PVC. Times marked in the abscissa refers only to the curve at115°C. For the others, zero starts from the point marked A. The scale, however, is the same.

which means that some degradative processes become active at these temperatures. This might suggest that there is an optimum temperature at which a particular blend is to be made under identical rotor speed and blending time. A comparison of the torque values at E of the 20% blend at various temperatures (Table 5.3) shows that when the temperature goes up from 115 to 125°C, the torque goes down by 150 metergrams. Since the PVC might not be fully melted at this temperature even at the point E, this difference in torque might have occurred predominantly from two factors; an overall tendency for the viscosity to come down due to the rise in temperature and the tendency of the PVC phase to enhance the viscosity by melting more of that phase. From 125 to 135°C and from 135 to 145°C the difference in torque remains the same, indicating that these two factors continue to exert almost the same influence. Between 145 and 155°C the difference in torque rises to 250 metergrams, which might suggest that the effect of more PVC melting is almost negligible in this case. Since some degradative processes might be under operation at higher temperatures as observed earlier, 145°C might be the best temperature for making 20% blends. Table 5.3 also shows the torque at the point E of the 50% blend at various temperatures. Again, comparison of the torques indicates that 155°C might be the minimum temperature at which this blend fully homogenizes

Table 5.3

Brabender torque values of 20% PVC and 50% PVC blends at different temperatures*

Temperature (°C)	Torque at the point E of 20% PVC blend (metergrams)	Torque at the point E of 50% PVC blend (metergrams)
115	2300	2050
125	2150	2250
135	2000	2200
145	1850	2100
155	1600	1950
165	1400	1625
175	1225	1450

* Ref. Figs.5.1 and 5.2.

and hence this may be the optimum temperature for making 50% blend.

Table 5.4 gives the scorch time, cure time, tensile strength, elongation at break, and hardness of the 20 and 50% PVC blends made at different temperatures. The 20% blend made at 145°C and the 50% blend made at 155°C show the maximum scorch safety in agreement with the Brabender evaluation. But for this slight change in the scorch times, the cure curves of the blends look very similar (Fig.5.3). The tensile strengths observed for the blends is much higher than that observed for NBR alone (1.81 MPa). For the 20% blend, maximum tensile strength is observed for the blend taken at 145°C and for the 50% blend maximum is observed for the blend taken at 155°C, again in agreement with the observation made on the Brabender Plasticorder. The elongation at break of the blends is higher than that of NBR alone (285%). But this property seems to fall off after a particular percentage of PVC since the 50% blend shows a lower value than the 20% blend. In this case also the highest value is observed for the blend made at 145°C for the 20% blend and for the blend made at 155°C for the 50% blend. The hardness of the blends increases with the percentage of PVC, as expected. Although the change in hardness of a blend made at different temperatures is small, the 20%

Table 5.4

Cure characteristics and mechanical properties of NBR/PVC blends made at different temperatures

Temperature (°C)	20% PVC blend					50% PVC blend				
	Scorch time (mins.)	Cure time (mins.)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore-A units)	Scorch time (mins.)	Cure time (mins.)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore-A units)
135	6.5	14	5.3	425	53	--	--	--	--	--
145	7.5	14	6.1	490	52	9.0	14.5	14.2	420	78
155	7.0	14.5	5.5	470	51	9.5	14.5	15.2	440	78
165	--	--	--	--	--	9.0	15.0	14.8	380	78

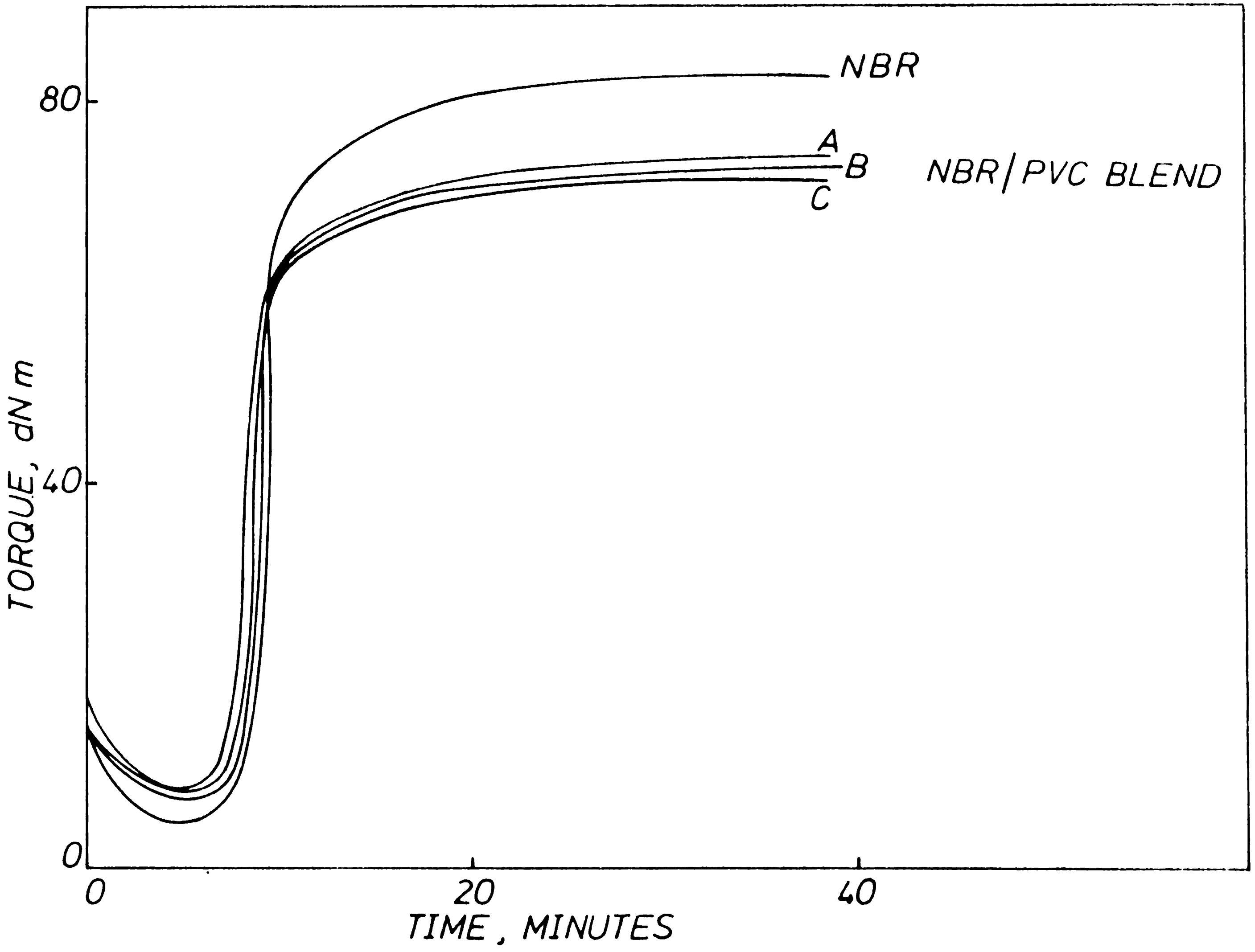


Fig. 5.3 Cure curves of NBR and NBR/PVC blends containing 20% PVC made at 135°C (A), 145°C (B) and 155°C (C).

PVC blend made at 135°C shows a higher hardness than that made at 145°C which might indicate inferior homogenity. Further, the blend made at 155°C shows a lesser value, which indicates that some degradations have occurred.

MODIFICATION OF NBR/PVC BLEND USING NATURAL RUBBER, STYRENE-BUTADIENE RUBBER AND POLYBUTADIENE RUBBER

Blending of two or more rubbers is carried out for three main reasons: improvement in technical properties, better processing and/or lower compound cost[14]. Many products in the rubber industry are based on blends in all or part of their construction. General purpose rubbers, natural rubber (NR), styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) have been used to replace NBR partly in a 70/30 NBR/PVC blend in this study mainly to lower the compound cost. Since these general purpose rubbers are not likely to be compatible with either NBR or PVC[15], the physical properties of the resulting ternary blends cannot be easily predicted[13]. However, the products are likely to show some improvement in technical properties since NR has higher tensile strength and tear strength, SBR has higher hardness and modulus and BR has higher abrasion resistance, compared to NBR[16]. MgO/ZnO/Stearic acid combination was used as the stabilizer for the PVC phase.

Experimental

1. Studies on the Brabender Plasticorder

An attempt was made to determine the relative effect of substituting part of NBR in a 70/30 NBR/PVC blend with NR, SBR and BR on a Brabender Plasticorder model PL3S (rotor speed: 30 rpm, sensitivity 0-5000 metergrams, mixer temperature 160°C). The total weight of polymers taken for each run was 40 gms. In addition to the polymers, 4 parts of MgO per hundred parts of PVC resin (phr), 4 phr ZnO and 3 phr stearic acid were also added as stabilizer for PVC. Initially, the mixing characteristics of an NBR/PVC blend which contained 70% NBR (of the total polymer weight) was studied. NBR was added initially and homogenized for two minutes. Then PVC together with its stabilizer was added. The blending was continued for ten minutes after the torque passed the maximum value. The blending characteristics of the terpolymer blends, made by replacing NBR partly (30% of the total weight of polymers) by NR, SBR and BR, were investigated next. NR, SBR or BR was added initially and homogenized for two minutes. Then NBR was added and mixed for another two minutes. Then PVC along with its stabilizer was added. After the torque passed the maximum value, the blending was continued for another ten minutes as before. The Brabender torque curves along with the amounts of polymers added are shown in Fig.5.4.

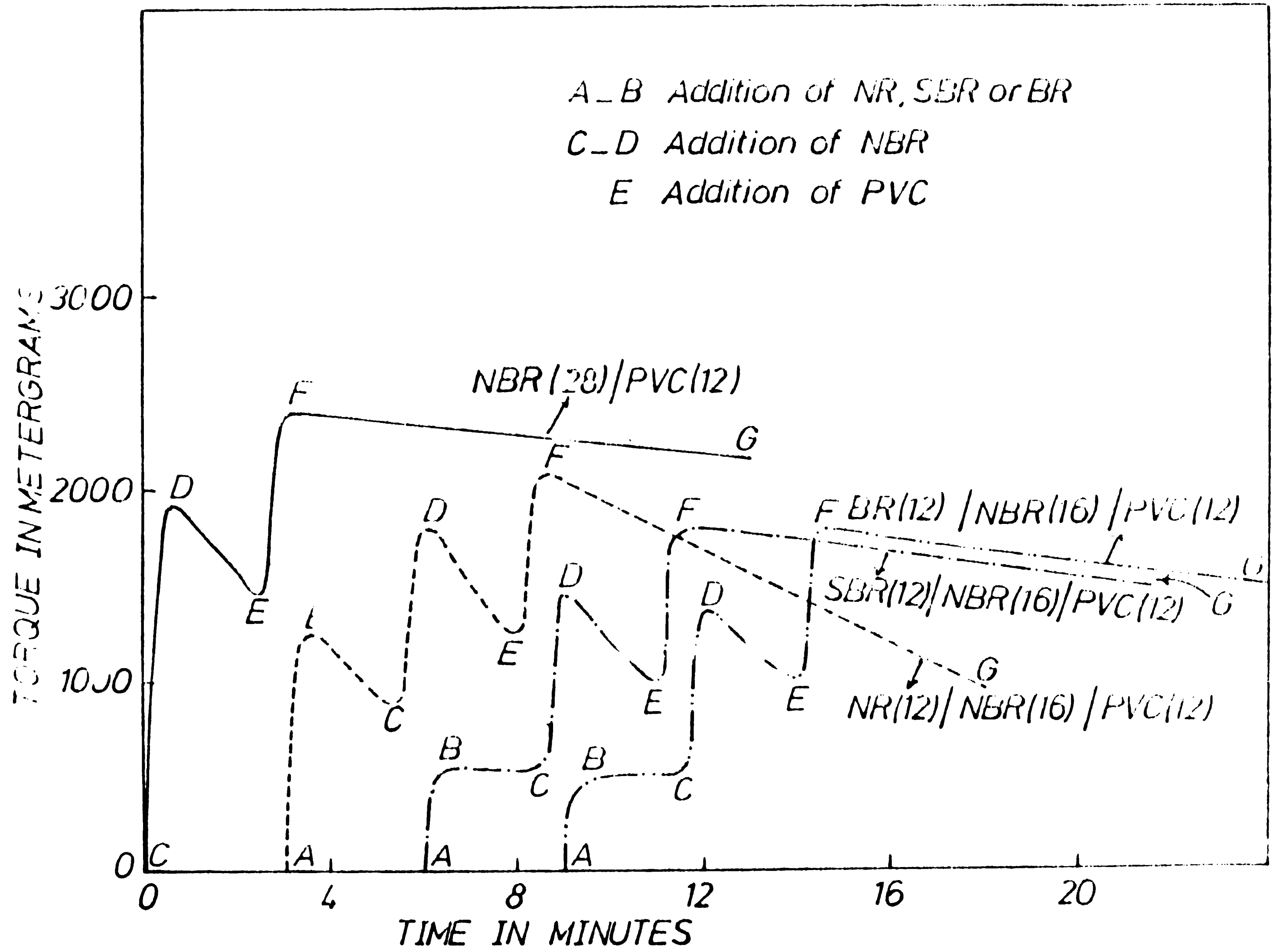


Fig. 5.4 Brabender torque-time curves of polymer blends: weight in gms of each polymer added is shown in brackets Times marked in the abscissa refers only to the torque curve of the NBR/PVC blend. For the others zero starts from the point marked A. Scale, however,is the same.

2. Determination of mechanical properties

For measuring the mechanical properties also, an NBR/PVC blend containing 70% NBR (of the total polymer weight) was chosen as the standard. Effect of modifying this blend by NR, SBR and BR on the mechanical properties was determined by replacing parts of NBR (15% and 30% of the total polymer weight) by each of these rubbers and then measuring the change in the properties. However, the polymers were not melt mixed for preparing the test samples, since the Brabender studies have shown that this leads to some degradations particularly in the NR, SBR and BR phases. Hence NBR/PVC blend alone was made on the Brabender Plasticorder initially at the optimum temperature[17], together with the stabilizer for PVC (4 phr MgO, 4 phr ZnO and 3 phr stearic acid). The terpolymer blends were then made by adding NR, SBR and BR to the NBR/PVC blend on a warm laboratory mixing mill. The vulcanizing agents for the rubber(s) were also added on the mill. The formulations employed for the preparation of the various compounds are shown in Table 5.5.

The cure characteristics of the compounds were determined at 150°C on the Monsanto Rheometer (Table 5.6). Test samples were vulcanized upto the respective optimum cure times at 150°C. The tensile properties were determined on a Zwick Universal Testing Machine as per ASTM D412 (1980). Tear

Table 5.5

Modification of NBR/PVC blends using NR, SBR and BR--formulations used for preparing test samples

Polymers (weight percentage of total polymers)		
PVC	30.00	
NR, SBR or BR	0.00	(for NBR/PVC blend)
	15.00	(for blends containing 15% of NR, SBR or BR)
	30.00	(for blends containing 30% of NR, SBR or BR)
NBR	70.00	(for NBR/PVC blend)
	55.00	(for blends containing 15% of NR, SBR or BR)
	40.00	(for blends containing 30% of NR, SBR or BR)
Stabilizers for PVC (parts per hundred parts of PVC)		
MgO	4.00	
ZnO	4.00	
Stearic acid	3.00	
Curatives for the rubber(s) (parts per hundred parts of total rubber(s))		
ZnO	2.50	
Stearic acid	1.50	
CBS	1.25	
TMTD	0.20	
Sulphur	2.25	

Table 5.6

Properties of NBR/PVC blends modified with NR, SBR and BR

Properties	NBR/PVC	NR/NBR/PVC		SBR/NBR/PVC		BR/NBR/PVC	
		15% NR	30% NR	15% SBR	30% SBR	15% BR	30% BR
Tensile strength (MPa)	10.3	13.0	8.4	11.0	11.5	12.3	5.6
Elongation at break (%)	513	550	350	488	510	515	230
Tear strength (N/mm)	45.90	55.75	32.82	42.72	41.0	42.40	28.9
Hardness (Shore-A)	58.0	57.0	56.0	62.0	62.0	60.0	62.0
Resistance to solvents (% increase in weight in 20 days)							
(a) Chloroform	732.03	667.57	639.10	710.67	664.6	617.86	596.18
(b) Toluene	148.00	165.40	190.80	155.50	164.80	162.40	172.50
(c) Aromatic oil	1.39	4.44	9.28	7.19	13.40	5.34	9.33
Cure characteristics							
(a) Scorch time (mins.)	6.50	5.50	4.50	8.00	7.00	6.50	5.00
(b) Cure time (mins.)	12.00	8.50	7.50	12.00	10.50	10.00	8.00
(c) Reversion (No.of units dropped in five mins.)	Nil	Nil	1.0	Nil	Nil	Nil	Nil

strength of the samples was determined as per ASTM D624 (1981). The hardness of the samples was measured and expressed in Shore-A units. The swelling characteristics were determined in chloroform, toluene and an aromatic oil as per ASTM 471 (1983). The properties of the blends are shown in Table 5.6.

Results and discussion

The Brabender torque curve for the NBR/PVC blend in Fig.5.4 may be explained as follows. NBR is added in the region C to D and hence the torque rises. Once the addition is over, the rubber homogenizes and the torque begins to decrease at D due to mechano-chemical degradation. PVC is added at E and due to its melting the torque rises to F. Again there is a tendency for the torque to drop slightly upto G. However, the rate of decrease in torque from F to G is much less than that from D to E indicating that PVC offers good protection to NBR against the degradation, obviously due to the compatible nature of the polymers. There is also no visual evidence for any degradation of the blend during blending. A comparison of the four torque curves in Fig.5.4 indicates that maximum torque rise from E to F occurs in the case of the NBR/PVC blend. This shows that even though the same amount of PVC (12 gms) was added in each case the maximum amount melted in this case showing again the good compatibility of NBR and PVC. These observations might indicate that the relative compatibility of PVC with the rubber(s) may be approximately estimated from the following factors:

(a) Amount of PVC melting (torque rise from E to F).

(b) Extent of protection offered by the PVC phase against the degradation of the rubber(s)
(Rate of decrease in torque from F to G compared to the rate of decrease from D to E and visual examination of the blend for any colour development during the test run on the plasticorder).

If similar tests are conducted at a lower temperature the former is likely to give more useful information and the latter if the tests are conducted at a higher temperature. In the case of NR/NBR/PVC blend, the addition of a mere 12 gms of NR initially produces a fast rate of degradation, as seen from the torque curve from B to C. This is due to the high molecular weight of NR. When NBR is also added, the net rate of decrease in torque from D to E increases due to the larger amount of rubber. With the addition of PVC, the torque rises from E to F. However, this difference in torque is less than that observed in the case of the NBR/PVC blend. Further, the protection offered by PVC against the degradation of the rubbers seems to be low, judging from the rate of decrease in torque from F to G, indicating poor compatibility. The degradation of the blend inside the plasticorder could also be observed visually from the colour development. In the case of SBR/NBR/PVC blend, the initial rate of decrease in torque from B to C is very little, due to the lower molecular weight of SBR compared to that of NR. However, with the addition of NBR, the degradation becomes obvious (D to E) due to the greater amount of rubber. But with the addition of PVC, the rate of degradation is reduced (F to G) indicating better adhesion between the phases in this case than the NR/NBR/PVC blend. However, the rise in torque from E to F is similar to that of NR, and there is a slight colour development indicating lesser compatibility than the blend of NBR and PVC alone. The behaviour of the BR/NBR/PVC blend is similar to that of the SBR/NBR/PVC blend but indicates lower level of blending.

An examination of the tensile properties of the blends (Table 5.6) shows that when NBR/PVC blend is modified with NR, SBR and BR at 15% level, the properties are improved. It may be inferred that at this level the incompatibility of the polymers does not seriously affect the mechanical properties. NR/NBR/PVC blend shows the maximum tensile strength and elongation as expected. However, when NR or BR is present at 30% level, the tensile properties deteriorated severely, obviously indicating the incompatible nature of the polymers. This shows that the optimum amount of NR or BR which could be added to NBR/PVC blends is much less than this quantity. SBR which has similar tensile properties as NBR exhibits more or less steady behaviour even when added at 30% level. This again shows that SBR blends better with NBR/PVC blends than NR or BR and that SBR could be added to the blend in larger amounts than NR or BR. The tear strength of the blends also shows similar trend as the tensile properties. SBR and BR blends show a higher hardness than the NR blend as expected. The percentage increase in weight of the blends in solvents show that the swelling of NBR/PVC blends in polar solvents like chloroform could be reduced by the addition of NR, SBR and BR. Considering the enormous swelling of NBR in polar solvents[18] this could be an advantage in some applications. However, there is some increase in the swelling of NBR/PVC blends in non-polar solvents and oils with the addition of NR, SBR and BR as shown by the swelling of the blends in toluene and aromatic oil.

MODIFICATION OF NBR/PVC BLEND USING POLYSULPHIDE RUBBER

Polysulphide rubber is a costly speciality rubber which is well-known for its outstanding resistance to solvents such as ketones, alcohols, acids, hydrocarbon solvents, water etc. But processing of polysulphide rubber is difficult, its mechanical properties are poor and it has an unpleasant odour[19-21]. Hence, it would be worthwhile to attempt improving the processing and mechanical properties of polysulphide rubber without sacrificing much of its excellent solvent resistance for use in critical applications. Attempts have already been made in this direction by blending polysulphide latices with other synthetic latices[22]. Compared to hydrocarbon rubbers, polysulphide rubber is more polar in nature and hence is likely to form successful blends with other polar polymers or polymer blends. Hence in this study, polysulphide rubber upto 50% of its weight was replaced with 50/50 NBR/PVC blend and the properties were compared. MgO/ZnO/stearic acid system was used as the stabilizer for PVC.

Experimental

1. Preparation of polysulphide/NBR/PVC vulcanizates

50/50 NBR/PVC blend was made on the Brabender Plasticorder employing a rotor speed of 30 rpm at the optimum temperature[17]. In addition to the equal weights of NBR and PVC, stabilizers for PVC (MgO - 4 parts per hundred parts of PVC resin (phr), ZnO - 4 phr and stearic acid 3 phr) were added at this stage. Blending of the polysulphide rubber and the NBR/PVC blend along with the additives for the rubbers was done on a tight, warm (about 50°C) laboratory mixing mill. The formulations employed for the various mixes are shown in Table 5.7. The cure characteristics of the mixes were determined on the Monsanto Rheometer at 150°C. The cure characteristics are shown in Table 5.8. The mixes were vulcanized upto the respective optimum cure times at 150°C on a laboratory press in a specially designed mould which could be cooled immediately after moulding, keeping the sample still under compression.

2. Determination of technical properties

The tensile properties of the vulcanizates were determined as per ASTM D412 (1980) test method on a Zwick Universal Testing Machine. The ageing characteristics of the samples were determined by keeping them at 100°C for 24 hours in an air oven and then measuring the retention in the tensile properties. The hardness of the vulcanizates was determined according to ASTM 2240 (1981) and expressed in shore-A units. The compression set was determined according to ASTM D395 (1982) under constant deflection. The solvent resistance of the vulcanizates in various solvents was determined as per ASTM 471 (1983).

Results and discussion

Mill mixing of the polysulphide rubber was found to be difficult even when a tight, warm mill was used.

Table 5.7

Modification of polysulphide rubber with NBR/PVC blend--
Formulations of mixes

Mix	A	B	C	D	E	F
<u>Polysulphide rubber and additives</u>						
Polysulphide rubber	100.00	90.00	80.00	70.00	60.00	50.00
ZnO	10.00	9.00	8.00	7.00	6.00	5.00
MBTS	0.50	0.45	0.40	0.35	0.30	0.25
DPG	0.10	0.09	0.08	0.07	0.06	0.05
Stearic acid	0.50	0.45	0.40	0.35	0.30	0.25
<u>NBR and additives</u>						
NBR	0.00	5.00	10.00	15.00	20.00	25.00
ZnO	--	0.1	0.2	0.3	0.4	0.50
Stearic acid	--	0.05	0.1	0.15	0.2	0.25
MBTS	--	0.075	0.15	0.225	0.3	0.375
TMTD	--	0.025	0.05	0.075	0.1	0.125
Sulphur	--	0.075	0.15	0.225	0.3	0.375
<u>PVC and additives</u>						
PVC	--	5.00	10.00	15.00	20.00	25.00
MgO	--	0.20	0.40	0.60	0.80	1.00
ZnO	--	0.20	0.40	0.60	0.80	1.00
Stearic acid	--	0.15	0.30	0.45	0.60	0.75

Table 5.8

Cure characteristics of polysulphide/NBR/PVC mixes

Mix	A	B	C	D	E	F
Optimum cure time (mins.)	16.5	8.5	11.5	22.5	23.5	28.5
Scorch time (mins.)	3.5	2.5	2.5	3.0	3.5	4.0
Reversion (units dropped in 5 mins.)	1.0	1.0	1.0	Nil	Nil	Nil

However, with the addition of increasing amounts of NBR/PVC mill mixing became progressively easier which might indicate that the processing characteristics of the polysulphide rubber could be improved with the addition of NBR/PVC. Further, the conventional method of curing and opening the mould while hot was found to be unsuitable especially for the blends with low concentrations of NBR/PVC. This might be due to the thermoplastic nature of the polysulphide rubber, particularly in the presence of the zinc salt of MBTS[21].

The tensile properties of the blends are shown in Figs.5.5, 5.6 and 5.7. The tensile strength and modulus of polysulphide rubber are found to improve with the addition of NBR/PVC, while elongation at break decreases slightly as expected. Other physical properties are also found to improve with the addition of NBR/PVC as evidenced by the increase in the hardness values and the decrease in the compression set values (Fig.5.8). The ageing resistance of the blends (Figs.5.5, 5.6 and 5.7) is interesting. Polysulphide rubber shows reasonably good resistance to heat ageing. The ageing resistance of the blends is found to improve with the concentration of NBR/PVC and the tensile strengths after ageing of the blends with higher concentration of NBR/PVC are found to be higher than their original values. Since the tensile strengths of polysulphide rubber

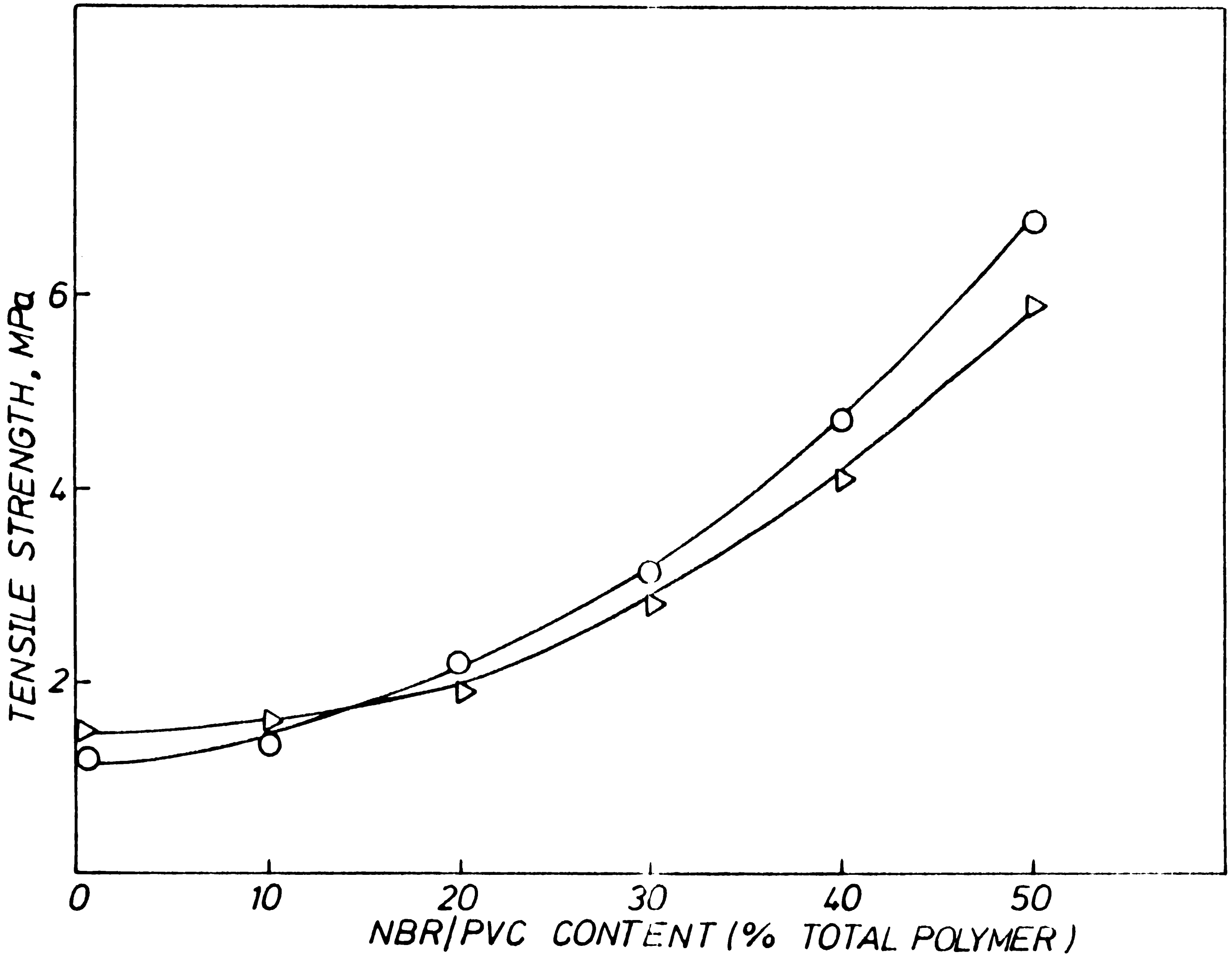


Fig. 5.5 Variation of tensile strength of polysulphide/NBR/PVC blend with NBR/PVC content: (△) before ageing, (○) after ageing.

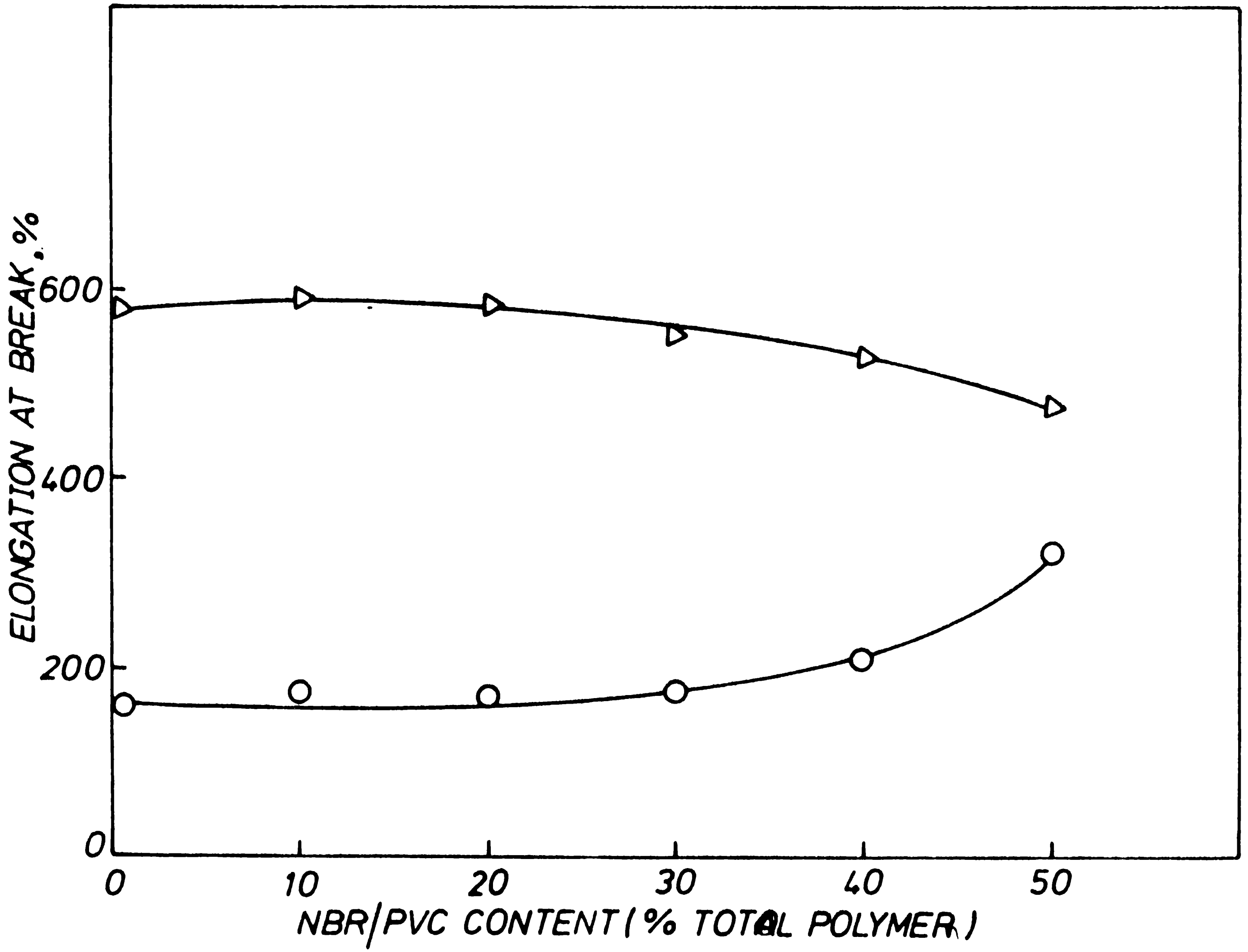


Fig. 5.6 Variation of elongation at break of polysulphide/NBR/PVC blend with NBR/PVC content: (△) before ageing, (○) after ageing.

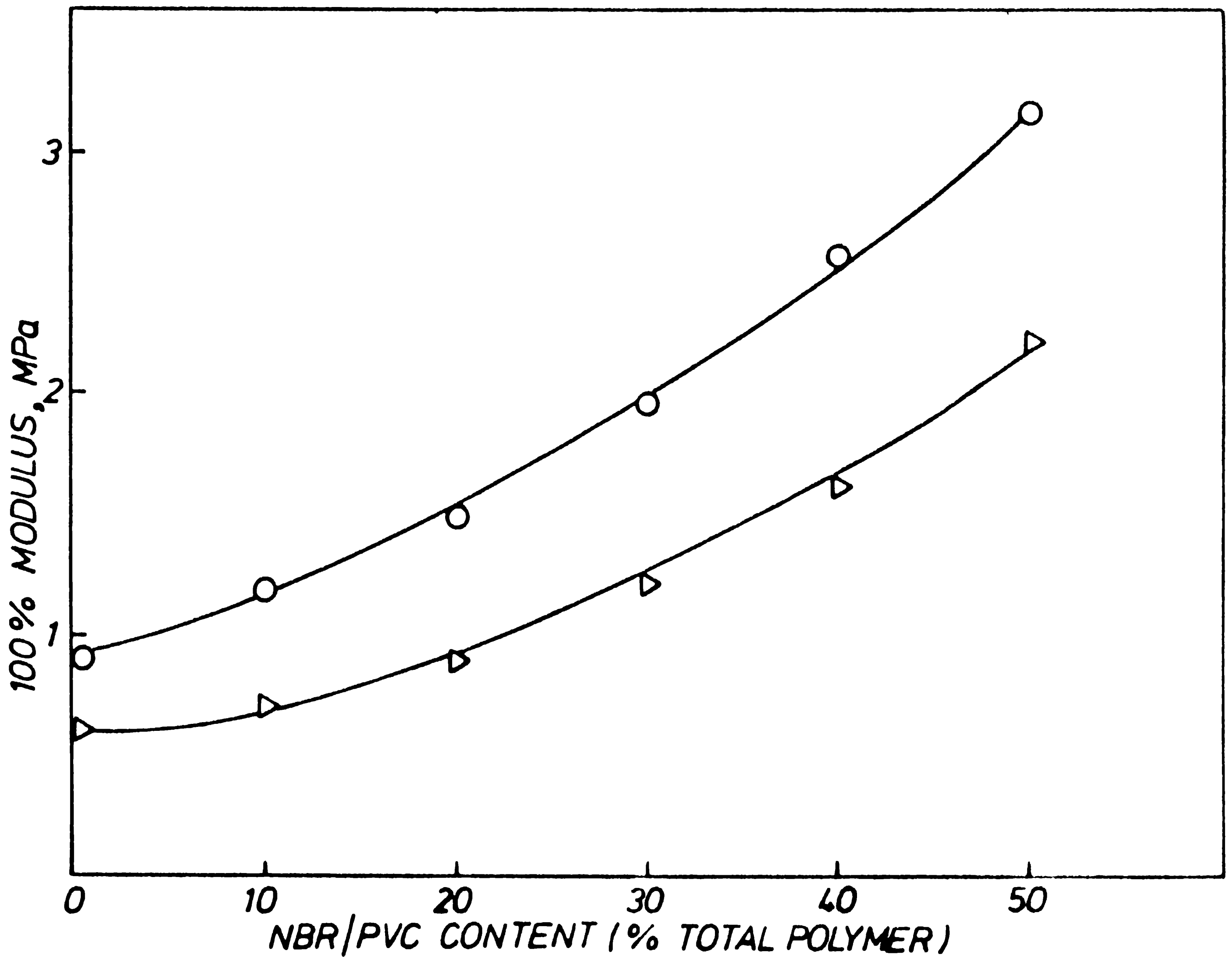


Fig. 5.7 Variation of 100% modulus of polysulphide/NBR/PVC blend with NBR/PVC content: (△) before ageing, (○) after ageing.

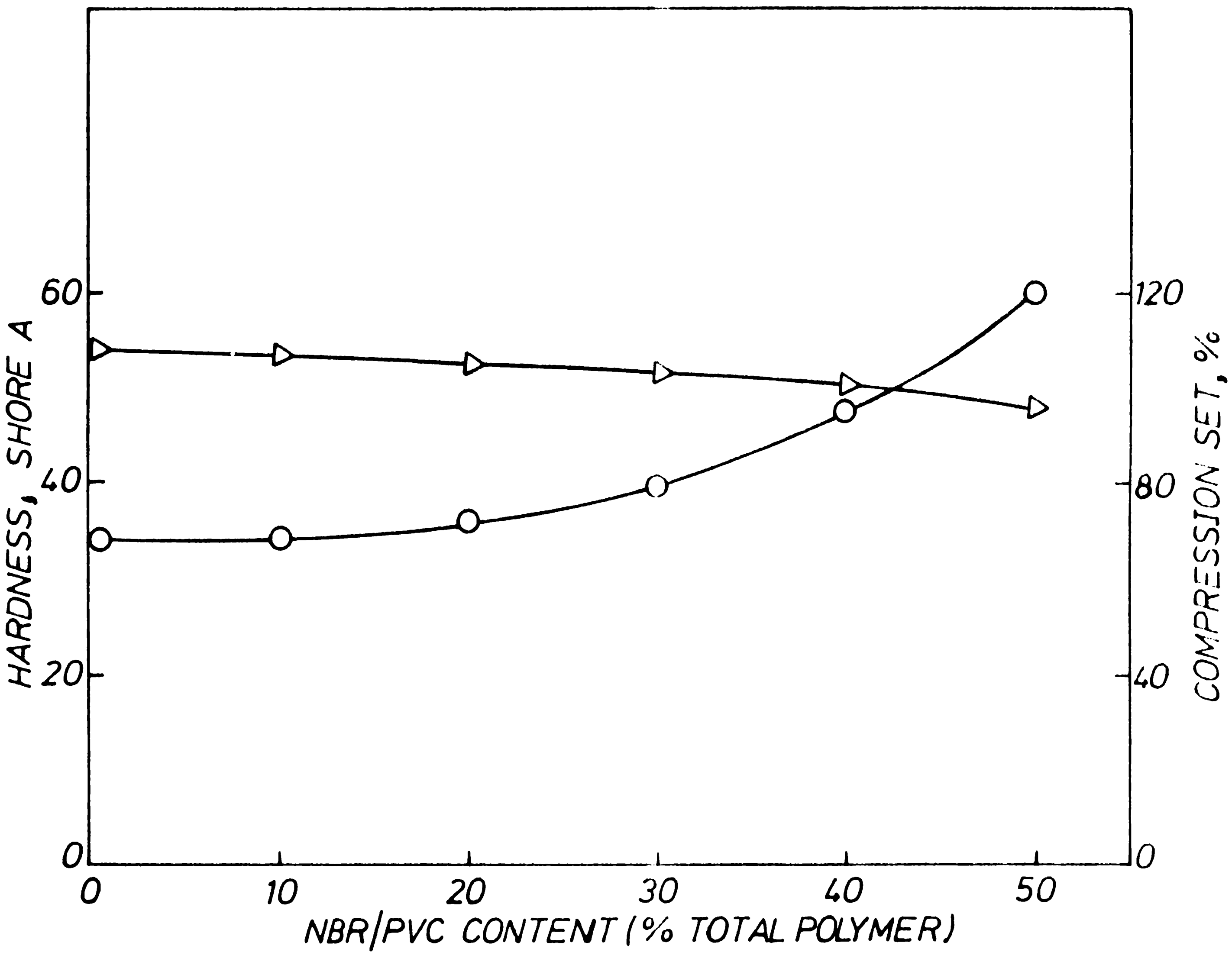


Fig. 5.8 Variation of hardness and compression set of polysulphide/NBR/PVC blend with NBR/PVC content: (△) compression set, (○) hardness.

and NBR both deteriorate with ageing, this abnormal behaviour might be due to the small amounts of crosslinks induced in the PVC phase during ageing in presence of ZnO and TMTD[23]. The increase in the modulus values with ageing is expected, since there is a considerable reduction in elongation with ageing.

The solvent resistance of the blends (Table 5.9) is not so outstanding as that of pure polysulphide rubber. However, the values are within reasonable limits for practical applications. The resistance of the polysulphide rubber against ketones seems to be the most affected by blending with NBR/PVC. This may be due to the severe swelling of NBR in polar solvents such as ketones and esters[18].

Summary

The following conclusions could be drawn from this study on NBR/PVC blends.

1. An optimum value exists for a blending parameter such as temperature (when other parameters are fixed) for the preparation of an NBR/PVC blend of a particular composition and this optimum value could be determined using a Brabender Plasticorder.

Table 5.9

Solvent resistance of polysulphide/NBR/PVC blends
(% increase in weight in 30 days)

Vulcanizate	A	B	C	D	E	F
Solvent						
Toluene	77.86	97.85	107.56	111.51	112.32	113.25
Methanol	1.64	4.82	5.43	6.52	7.25	7.54
Acetic acid	39.58	42.34	43.12	43.84	44.52	45.13
Methyl ethyl ketone	28.34	85.22	133.09	229.16	285.96	330.20
Water	4.19	4.35	4.46	4.68	4.72	4.82

2. NBR/PVC blends could be extended using general purpose rubbers like NR, SBR or BR by replacing part of NBR. The resulting ternary blends also possess some improved mechanical properties when the modification is limited to small quantities. SBR could be added in larger amounts than NR or BR without much deterioration in the mechanical properties of NBR/PVC blends. The compatibility of PVC with rubbers could be estimated using a Brabender Plasticorder.

3. Polysulphide rubber could be modified with NBR/PVC blends to generate high performance ternery blends with good solvent resistance and mechanical properties.

4. MgO/ZnO/Stearic acid system could be used to stabilize the PVC phase in blends of PVC with rubber(s). MgO, ZnO and stearic acid are conventional ingredients used in rubber compounding and hence they may not adversely affect the rubber(s). Further this stabilizer system does not impair colour, is non-sulphide staining and nontoxic. Hence PVC blends stabilized with this system are found to possess good mechanical properties and colour flexibility and they could be used in food contact applications.

References

1. J.A.Manson in "Encyclopedia of PVC", L.I.Nass and C.A.Heiberger (Eds.), Vol.I, Chap.10, Marcel Dekker, New York (1986).

2. G.H.Hofmann in "Polymer Blends and Mixtures", D.J.Walsh, J.S.Higgins and A.Maconnachie (Eds.), Chap.7, Martinus Nijhoff Publishers, Dordrecht (1985).

3. J.A.Manson, Pure.Appl.Chem., 53, 471 (1981).

4. R.A.Emnatt, Ind.Eng.Chem., 36, 730 (1944).

5. O.Olabisi, L.Robeson and M.T.Shaw, "Polymer-Polymer Miscibility", Academic Press, New York (1979).

6. M.Matsuo et al, Polym.Eng.Sci., 9,197 (1969).

7. J.E.Pittenger and G.F.Cohan, Mod.Plast., 25, 81 (1947).

8. J.R.Dunn, Rubber Chem.Technol., 49, 978 (1976).

9. P.J.Corish and B.D.W.Powell, Rubber Chem.Technol., 47, 481 (1974).

10. A.H.Mazumdar and M.S.Majmudar, "Chemaprene Rubber Handbook", Chap.7, Synthetics & Chemicals Ltd., Bombay (1983).

11. M.T.Shaw in "Polymer Blends and Mixtures", D.J.Walsh, J.S.Higgins and A.Maconnachie (Eds.), Chap.3, Martinus Nijhoff Publishers, Dordrecht (1985).

12. C. Roja Rao and K.Ramamurthy, Popular Plast., 12, 15 (1977).

13. L.A.Utracki, Polym.Plast.Tech.Eng., 22, 49 (1984).

14. P.J.Cornish in "Polymer Blends and Mixtures", D.J.Walsh, J.S.Higgins and A.Maconnachie, (Eds.), Chap.12, Martinus Nijhoff Publishers, Dordrecht (1985).

15. S.Krause in "Polymer Blends", D.R.Paul and S.Newmann (Eds.), Vol.1, Chap.2, Academic Press, New York (1978).

16. R.J.Crawford, "Plastics and Rubbers Engineering Design and Applications", Mechanical Engineering Publishers Ltd., London (1985).

17. K.E.George, R.Joseph and D.J.Francis, J.Appl.Polym.Sci., 32, 2867 (1986).

18. H.H.Bertram in "Development in Rubber Technology-2", A.Whelan and K.S.Lee (Eds.), Chap.3, Applied Science Publishers Ltd., London (1981).

19. W.Cooper and G.M.Doyle, in "Rubber Technology and Manufacture", C.M.Blow and C.Hepburn (Eds.), p.163, Butterworths, London (1985).

20. D.C.Blackly, "Synthetic Rubbers", p.300, Applied Science Publishers, London (1983).

21. J.R.Panek in "Rubber Technology", M.Morton (Ed.), pp.349-367, Van Nostrand Reinhold Company, New York (1973).

22. R.A.Garipova et al, Int.Polym.Sci.Technol., 10, No.1, 4 (1983).

23. V.Duchacek and A.Kuta, J.Appl.Polym.Sci., 27, 1549 (1982).

CHAPTER - 6

MODIFICATION OF POLYCHLOROPRENE WITH POLY(VINYL CHLORIDE)

MODIFICATION OF POLYCHLOROPRENE WITH POLY(VINYL CHLORIDE)

Polymer blends have been the subject of major investigations over the last ten years and are continuing with an ever greater intensity. The great variety of commercially available elastomers and thermoplastics offers a myriad of opportunities for blending. Blends of acrylonitrile-butadiene rubber (NBR) and poly(vinyl chloride) (PVC) are perhaps the earliest commercial example of miscible polymer-polymer systems[1]. Because of the miscibility of the components in all proportions, both PVC-rich and NBR-rich blends have been prepared[1,2]. Usually plasticized PVC is added for preparing NBR-rich blends. These blends have better resistance to ultraviolet rays and ozone,better resistance to tearing, flexure, ageing, solvents etc. compared to NBR[3]. At higher concentrations of PVC, NBR acts as a permanent plasticizer for PVC. It was this success story of NBR/PVC blends that prompted the preparation of polychloroprene/ poly(vinyl chloride) blends.

Polychloroprene (CR) provides a very useful all-round balance of properties. It has good oil resistance, chemical resistance, weather resistance and nonflammability[4-6]. It also shows good resistance to heat ageing, to oxidation and in particular, to attack by ozone. However, chloroprene rubber is still regarded as a special purpose synthetic rubber because it is considerably more expensive than the general purpose hydrocarbon rubbers. Hence attempts have already been made to blend CR with other polymers like carboxylated polyethylene[7]. Properties of poly(vinyl chloride) (PVC) are in many cases similar to those of polychloroprene. Properly stabilized PVC would show higher resistance to heat ageing, oxidation, ozone attack etc. because of its saturated structure. PVC has also higher strength, modulus and hardness compared to CR. PVC is a cheap plastics material and hence it would be advantageous to produce CR rich blends of CR and PVC as substitutes for CR. On the other hand CR could be tried as permanent plasticizer for PVC in PVC rich blends of CR and PVC. This would impart softness to the PVC matrix without losing its nonflammability, chemical resistance, weather resistance, oil resistance etc. CR and PVC are also likely to be compatible[8] (solubility parameters:[9] CR = 9.2-9.4 $(\mathrm{cal/cm^3})^{\frac{1}{2}}$, PVC = 9.5 $(\mathrm{cal/cm^3})^{\frac{1}{2}}$) which is another favourable pointer towards the preparation of CR/PVC blends. Also, good adhesion between the CR phase and PVC phase is possible because of the similarity in structure[10]. It has been shown in this study that MgO/ZnO combination, conventional curative for CR, in presence of stearic acid could act as an efficient stabilizer for plasticized PVC (Chapter 3) and that tribasic lead sulphate (TBLS), conventional heat stabilizer for PVC, could be an efficient curative for CR (Chapter 4) These additives were hence used in a dual role in this study.

BLENDS OF POLYCHLOROPRENE AND PLASTICIZED POLY(VINYL CHLORIDE)

Experimental

1. Modification of CR with PVC

When the amount of CR was generally in excess of PVC, the blend was vulcanized similar to that of pure CR. MgO/ZnO combination in presence of stearic acid was used both as the curative for CR and stabilizer for PVC. Blending of CR and plasticized PVC was done on the Brabender Plasticorder at 150°C for two minutes using roller type rotors at a speed of 30 rpm. MgO, ZnO and stearic acid required for stabilizing PVC were added at this stage. However, MgO, ZnO, stearic acid and ethylene thiourea (NA-22) required for the vulcanization of CR were added later on a laboratory mixing mill at near ambient temperature. The cure curves of the mixes were then taken on the Monsanto Rheometer. The mixes were then vulcanized upto the respective optimum cure times on a laboratory press at 150°C. The formulations of the mixes are shown in Table 6.1 and the cure curves in Figs.6.1 and 6.2.

Table 6.1

Modification of CR with PVC - Formulations of the mixes

Mix	A	B	C	D	E	F	G
CR (W type)*	100	90	80	70	60	50	40
PVC	--	10	20	30	40	50	60
Dioctyl phthalate (50 phr PVC)	--	5	10	15	20	25	30
MgO (4 phr CR + 4 phr PVC)	4	4	4	4	4	4	4
ZnO (5 phr CR + 4 phr PVC)	5.0	4.9	4.8	4.7	4.6	4.5	4.4
Stearic acid (2 phr CR + 3 phr PVC)	2.0	2.1	2.2	2.3	2.4	2.5	2.6
NA-22 (0.5 phr CR)	0.5	0.45	0.4	0.35	0.3	0.25	0.2

* Type 2 (Chapter 2).

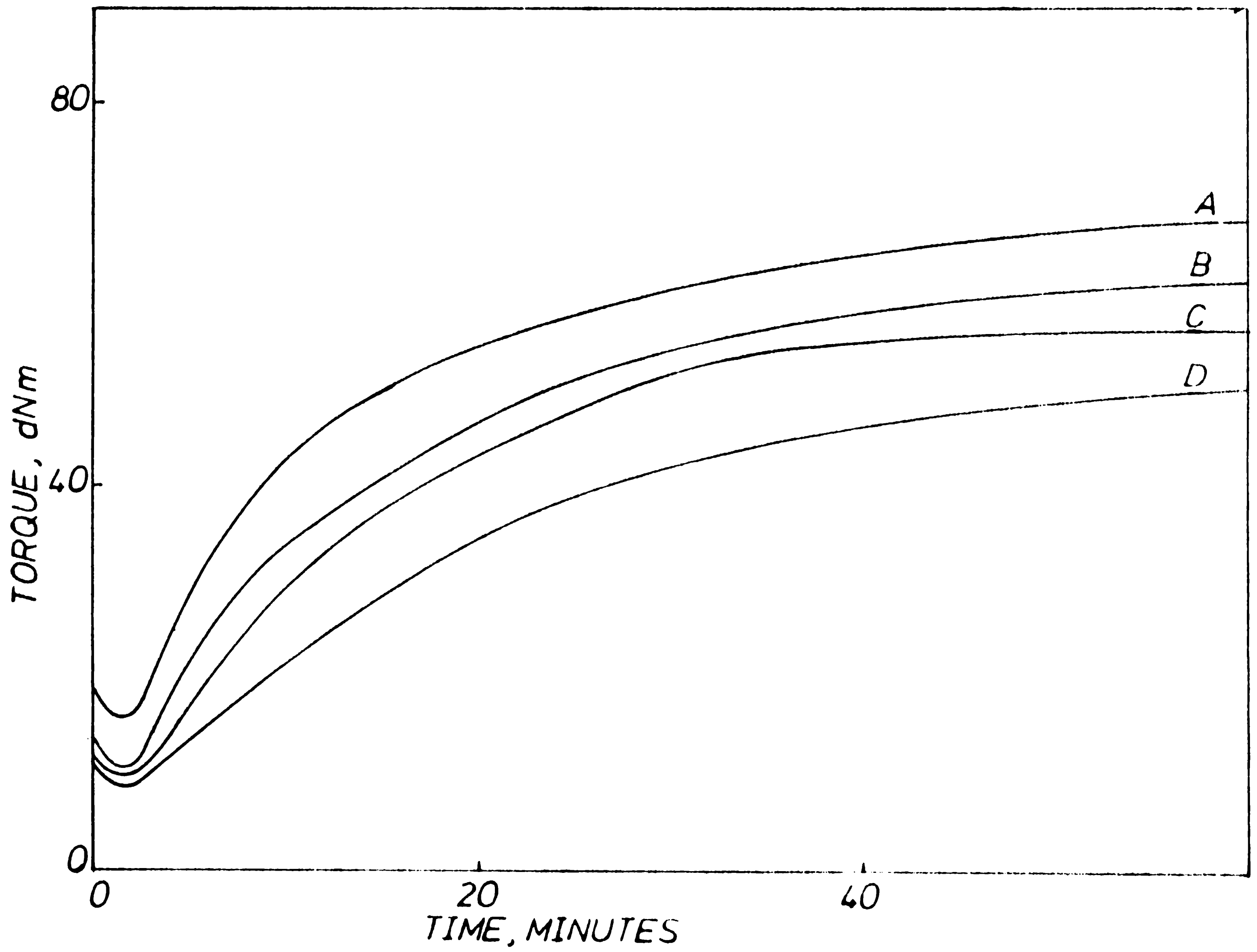


Fig. 6.1 Cure curves of CR/PVC mixes (Ref. Table 6.1)

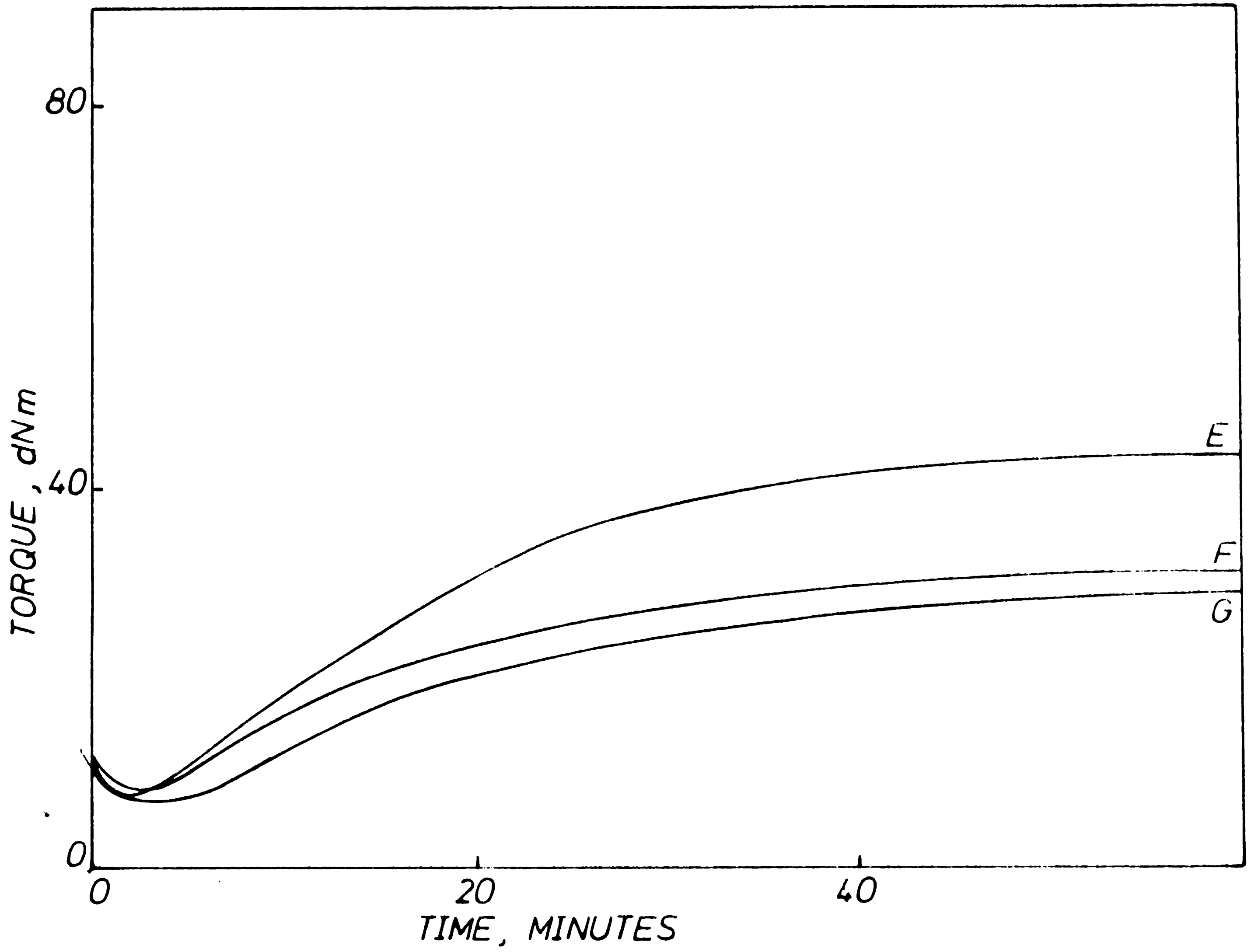


Fig. 6.2 Cure curves of CR/PVC mixes (Ref.Table 6.1)

Tensile properties of the blends were determined as per ASTM D412 (1980) test method on a Zwick Universal Testing Machine. Hardness of the vulcanizates was determined according to ASTM D2240 (1981) and expressed in Shore A units. Compression set was determined according to ASTM D395 (1982). The resistance to swelling of the vulcanizates was determined by allowing circular specimens to stand in excess chloroform for 48 hours and then measuring the percentage change in weight. The ageing resistance was determined by keeping the vulcanizates at 100°C for 48 hours in an air oven and then measuring the retention in these properties. SEM observations of the tensile failure surfaces were made using a Phillips 500 model scanning electron microscope.

2. Modification of PVC with CR

When the amount of PVC was generally in excess of CR, the CR phase was dynamically crosslinked[11-13] at the time of blending and then the blend was sheeted out similar to that of pure PVC. TBLS was used both as the curative for CR and stabilizer for PVC since this procedure involved higher temperatures. Blending of CR and plasticized PVC was done on the Brabender Plasticorder employing the same mixing parameters as before, but at 190°C. The blending was continued till the dynamic crosslinking of the CR phase was over as observed from the torque - time curve of the Brabender Plasticorder. Then the blend was sheeted out by pressing for two minutes at 190°C on a laboratory hydraulic press. An antioxidant, phenyl-β-naphthylamine (PBN), was also added for this study because the blending and moulding were done at 190°C. The formulations used for the study are shown in Table 6.2

The tensile properties of the blends were determined as per ASTM D412 (1980) test method.

Results and discussion

1. Modification of CR with PVC

The cure curves (Figs.6.1 and 6.2) of the mixes show that the presence of PVC does not affect the curing of CR. The scorch safety improves with increase in PVC content. The maximum torque decreases with increasing amounts of PVC, obviously due to the lower melt viscosity of plasticized PVC compared to that of CR. The cure curves further show that there is no scorching of the mixes during blending.

The tensile strength of the blends (Fig.6.3) decreases with increase in PVC content, eventhough the tensile strength of plasticized PVC is higher than that of CR. The tensile strength goes to a minimum and then starts increasing only

Table 6.2

Modification of PVC with CR - Formulations of the mixes

Mix	F'	G'	H	I	J	K
PVC	50	60	70	80	90	100
CR (W type)*	50	40	30	20	10	--
Dioctyl phthalate (50 phr PVC)	25	30	35	40	45	50
TBLS (same as the loading of MgO and ZnO in Table 6.1)	8.5	8.4	8.3	8.2	8.1	8.0
Stearic acid (2 phr CR + 3 phr PVC)	2.5	2.6	2.7	2.8	2.9	3.0
NA-22 (0.5 phr CR)	0.25	0.20	0.15	0.10	0.05	--
PBN (1 phr CR + 1 phr PVC)	1	1	1	1	1	1

* Type 2 (Chapter 2).

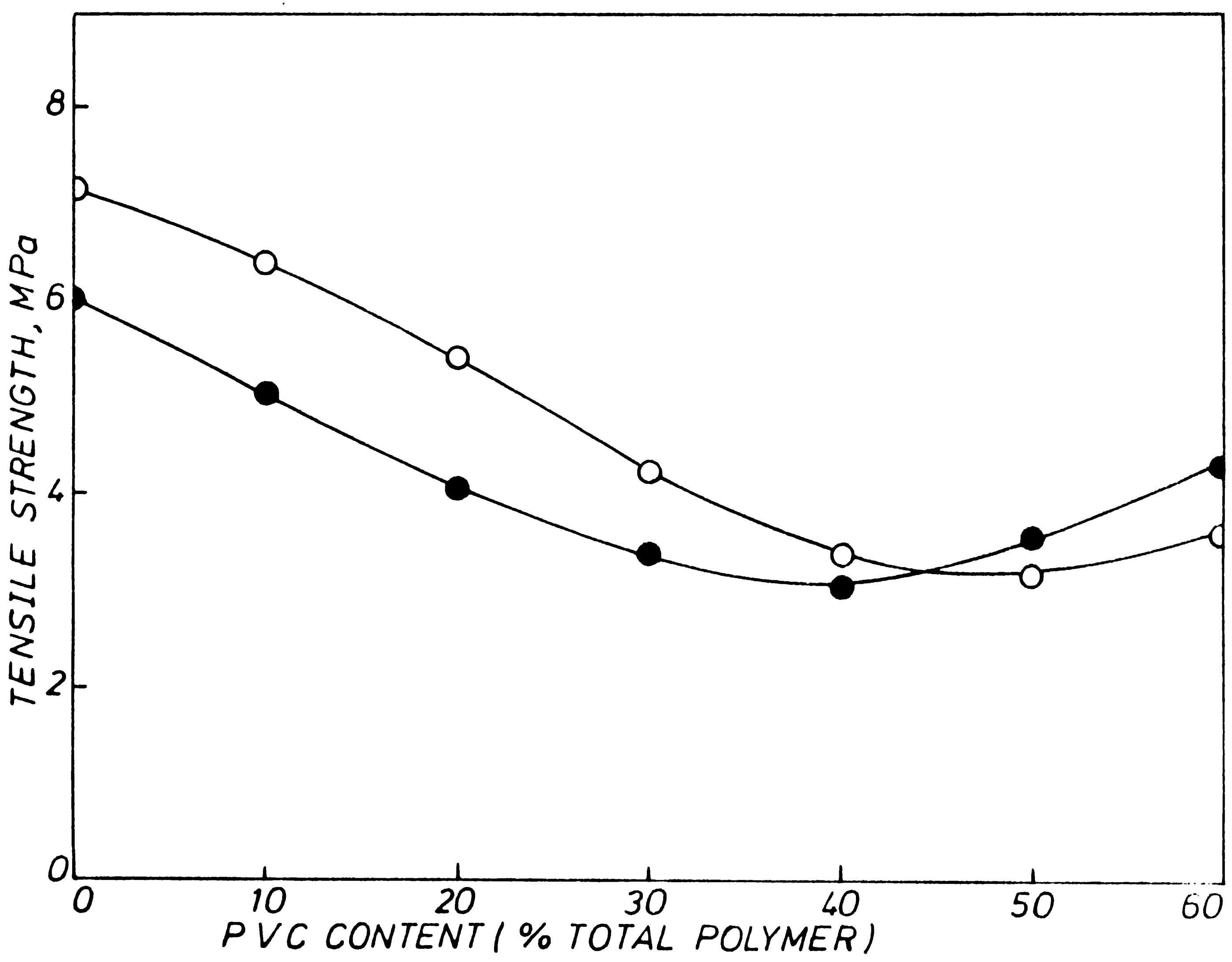


Fig. 6.3 Variation of tensile strength of CR/PVC blend with PVC content: (○) before ageing, (●) after ageing.

after the PVC content is about 50% of the total polymer. To understand this phenomenon the SEM photographs of the tensile fracture surface of pure CR, 30% PVC blend and 60% PVC blend were taken (Figs.6.4, 6.5, 6.6 and 6.7). These figures suggest that the PVC phase becomes continuous only when the PVC content is fairly high. This might imply that the composition at which tensile strength of the blends starts increasing is the one at which PVC phase becomes continuous.

The variation in tensile strength of the blends with ageing (Fig.6.3) is interesting. The retention in tensile strength improves with increase in PVC content and finally the aged samples take over the values of the original samples when the PVC content is above 50%. This behaviour shows that the PVC phase is comparatively unaffected by the ageing conducted at 100°C. Eventhough there was no intention of crosslinking the PVC phase in this study, there could occur a low degree of crosslinking in the PVC phase in the presence of ZnO[14]. The increase in tensile strength with ageing of the samples with higher PVC content might be due to a slight increase in this crosslink density occurring in the PVC phase.

The variation of elongation at break with PVC content (Fig.6.8) is more or less similar to that of the

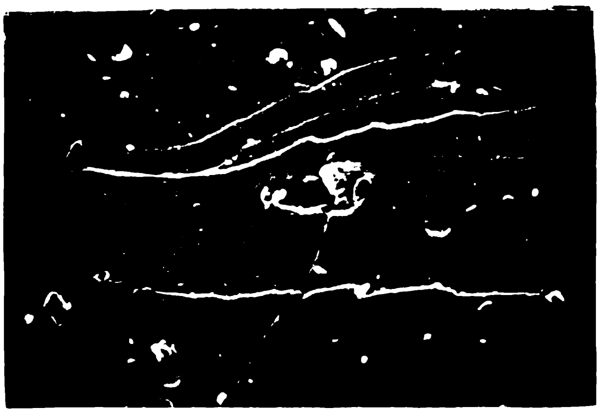


Fig. 6.4 SEM photograph of the tensile fracture surface of CR (X200)

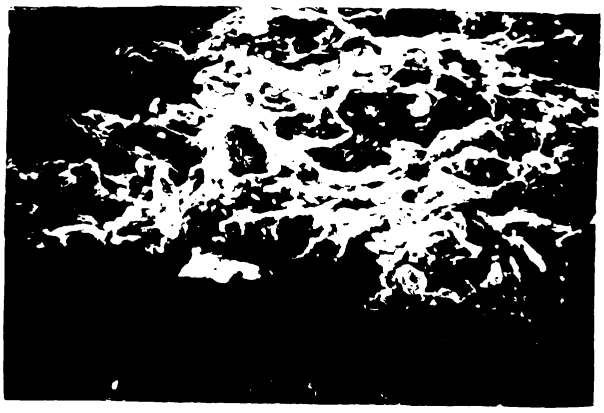


Fig. 6.5 SEM photograph of the tensile fracture surface of 30% PVC blend (X200)

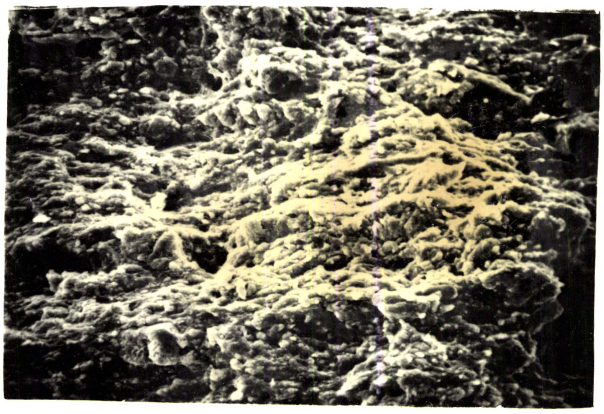


Fig. 6.6 SEM photograph of the tensile fracture surface of 60% PVC blend (X200)

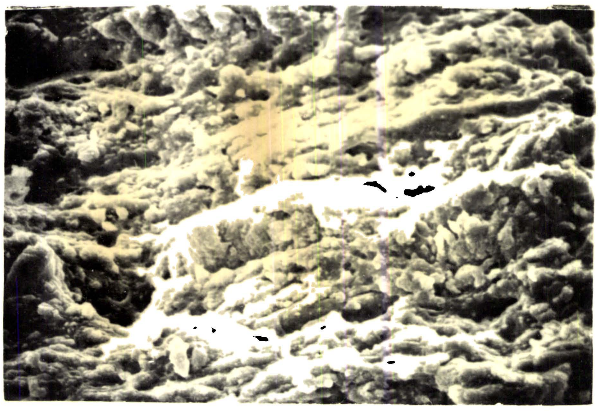


Fig. 6.7 SEM photograph of the tensile fracture surface of 60% PVC blend (X400)

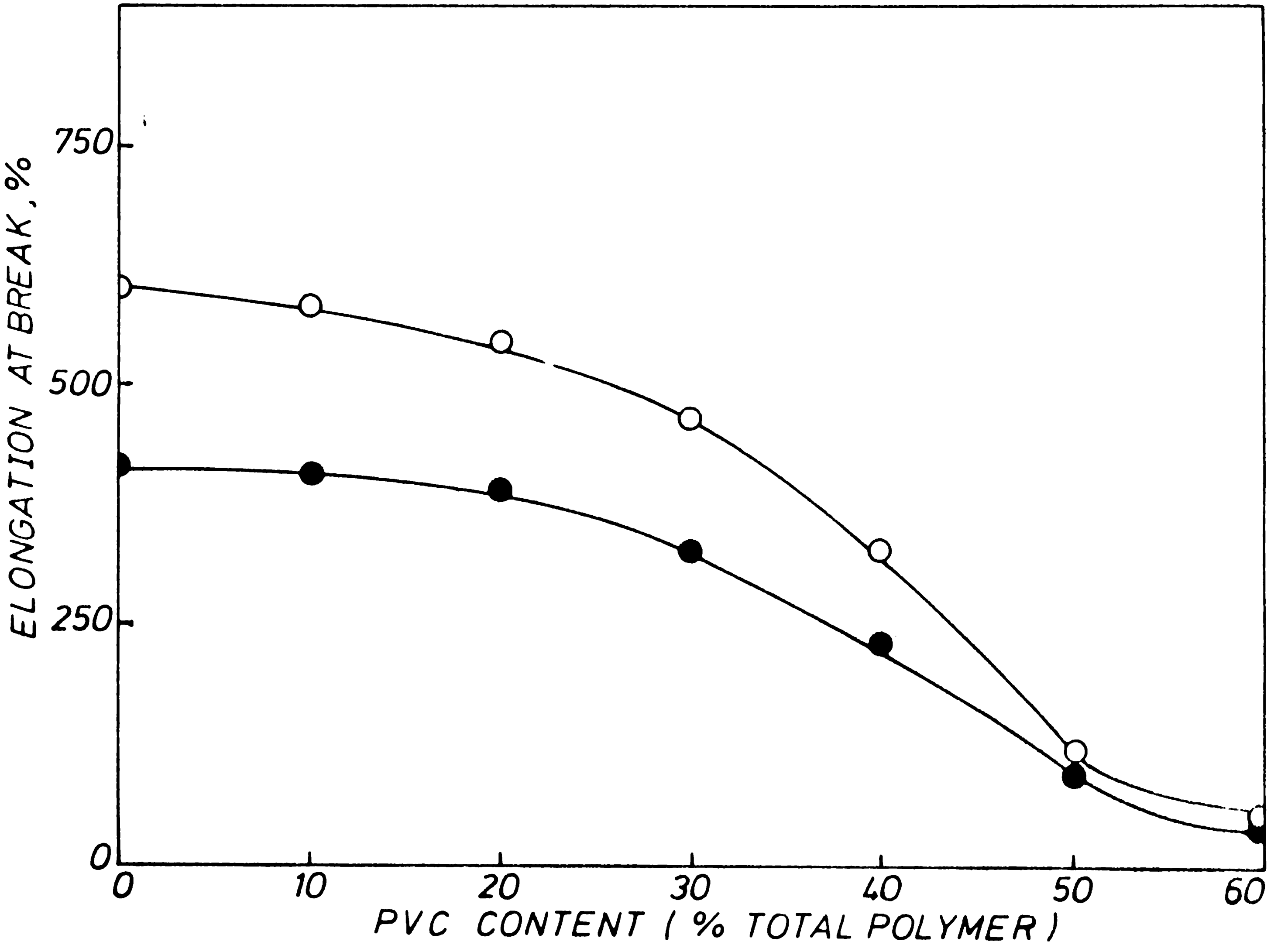


Fig. 6.8 Variation of elongation at break of CR/PVC blend with PVC content: (○) before ageing, (●) after ageing.

tensile strength. The retention of this property with ageing is also found to improve with increase in PVC content. The modulus and hardness of the blends improve with PVC content (Figs.6.9 and 6.10). This is due to the higher modulus and hardness of PVC compared to CR and is expected. These values further increase with ageing due to the increase in crosslink density of the matrix with ageing.

The deterioration of the set property with PVC content (Fig.6.11) is also expected due to the decrease in rubbery properties with increase in PVC content. However, there is a marked improvement in the values with ageing. The resistance to swelling seems to improve with PVC content as seen by the swelling behaviour of the blends in chloroform (Fig.6.12). The resistance improves further with ageing due to the increase in the crosslink density. However, the blends are not suitable for prolonged contact with solvents since there is a chance of the plasticizer getting extracted.

2. Modification of PVC with CR

Blends F' and G' with the same polymer compositions of blends F and G are found to show more or less similar physical properties. This suggests that this method of preparing CR/PVC blend could actually supplement the previous method and could be employed when the amount of PVC is higher.

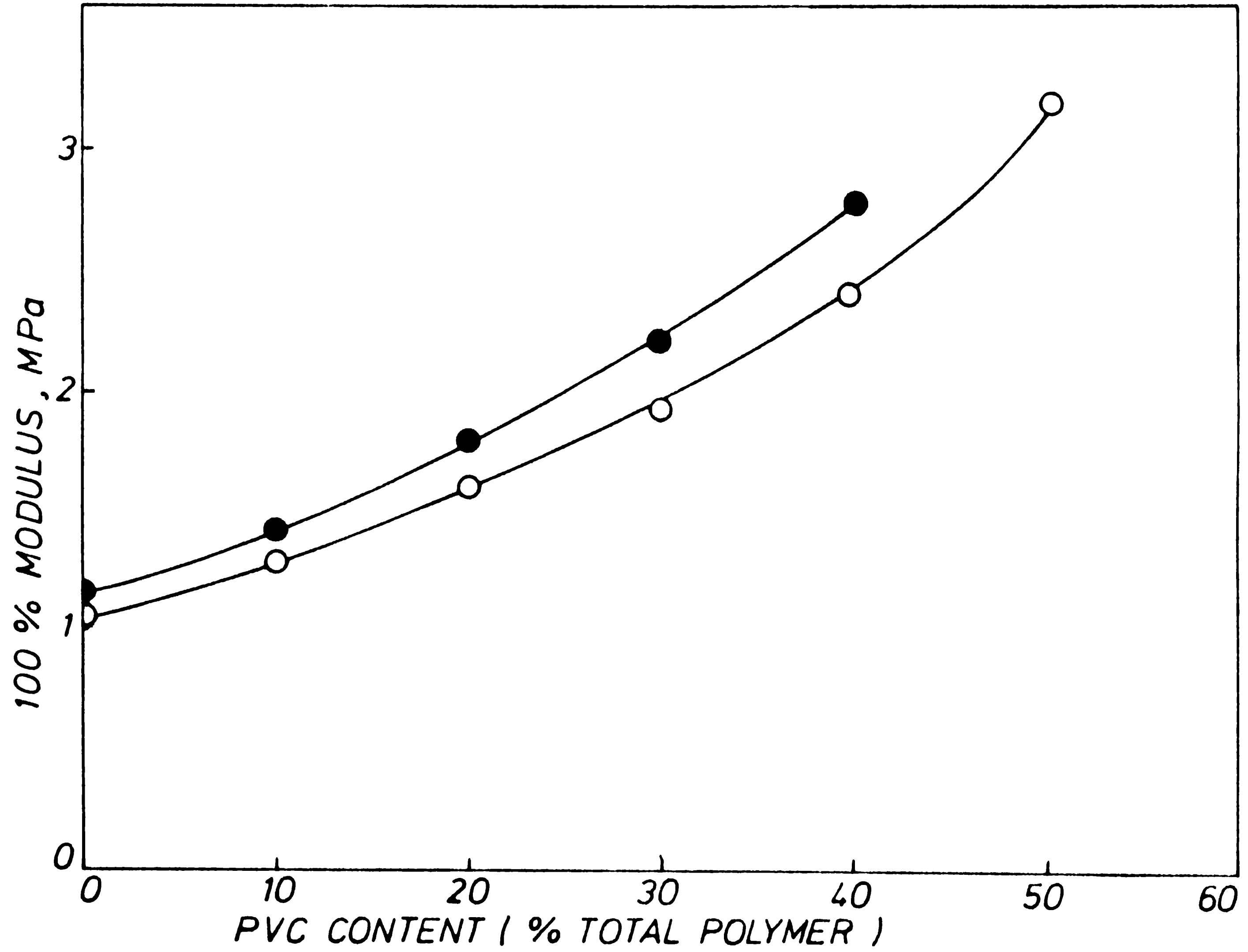


Fig. 6.9 Variation of 100% modulus of CR/PVC blend with PVC content: (○) before ageing, (●) after ageing.

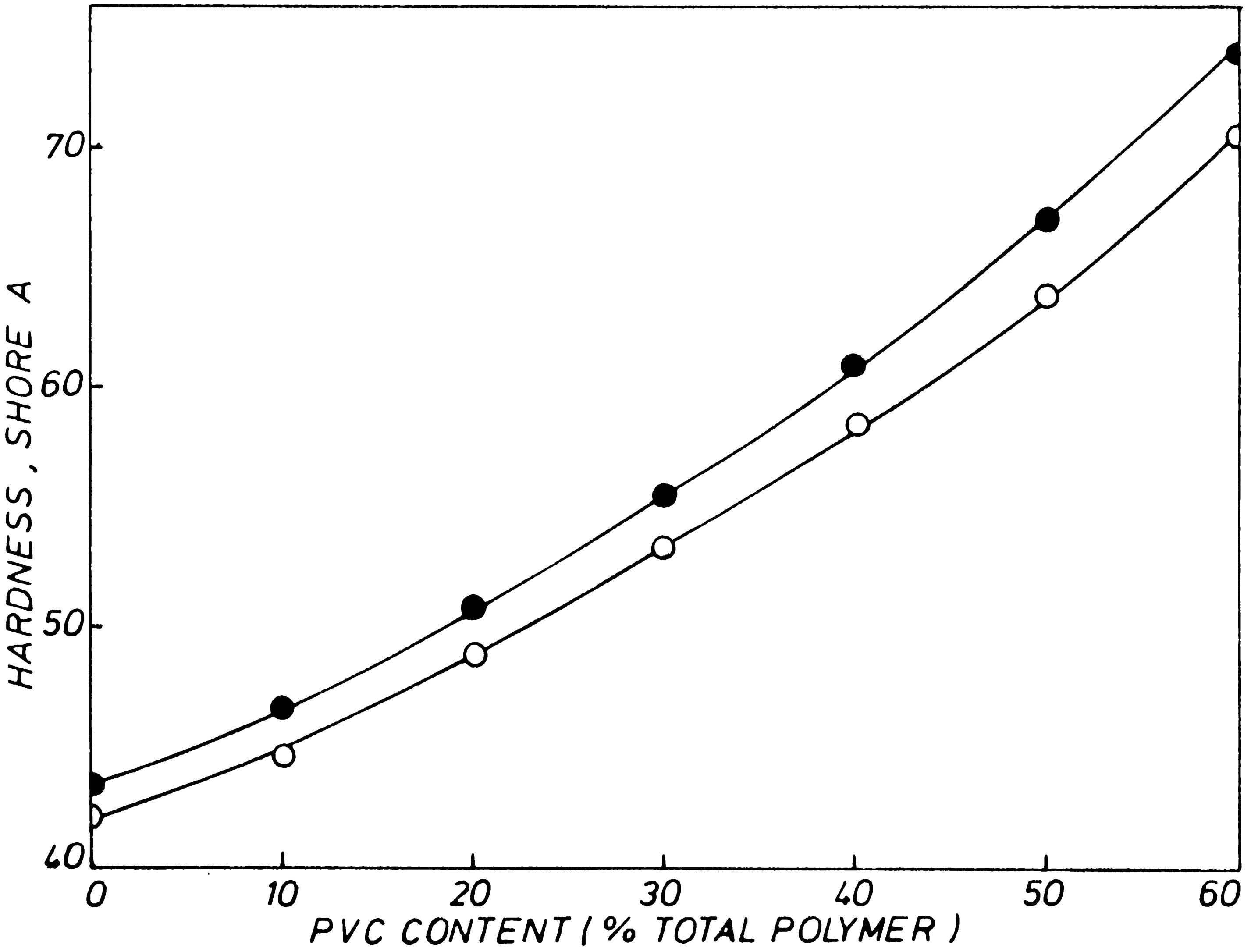


Fig. 6.10 Variation of hardness of CR/PVC blend with PVC content: (○) before ageing, (●) after ageing.

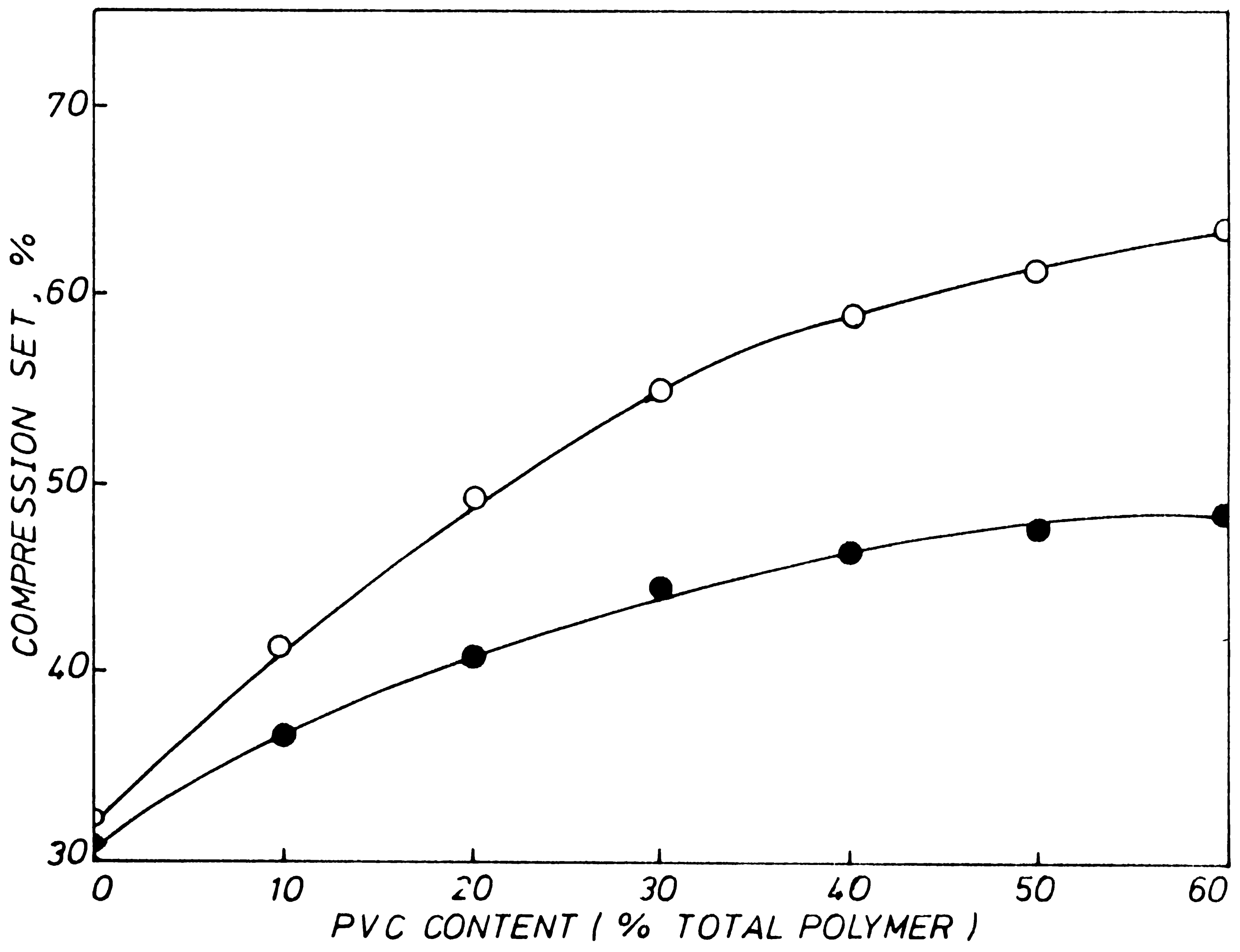


Fig. 6.11 Variation of compression set of CR/PVC blend with PVC content: (○) before ageing, (●) after ageing.

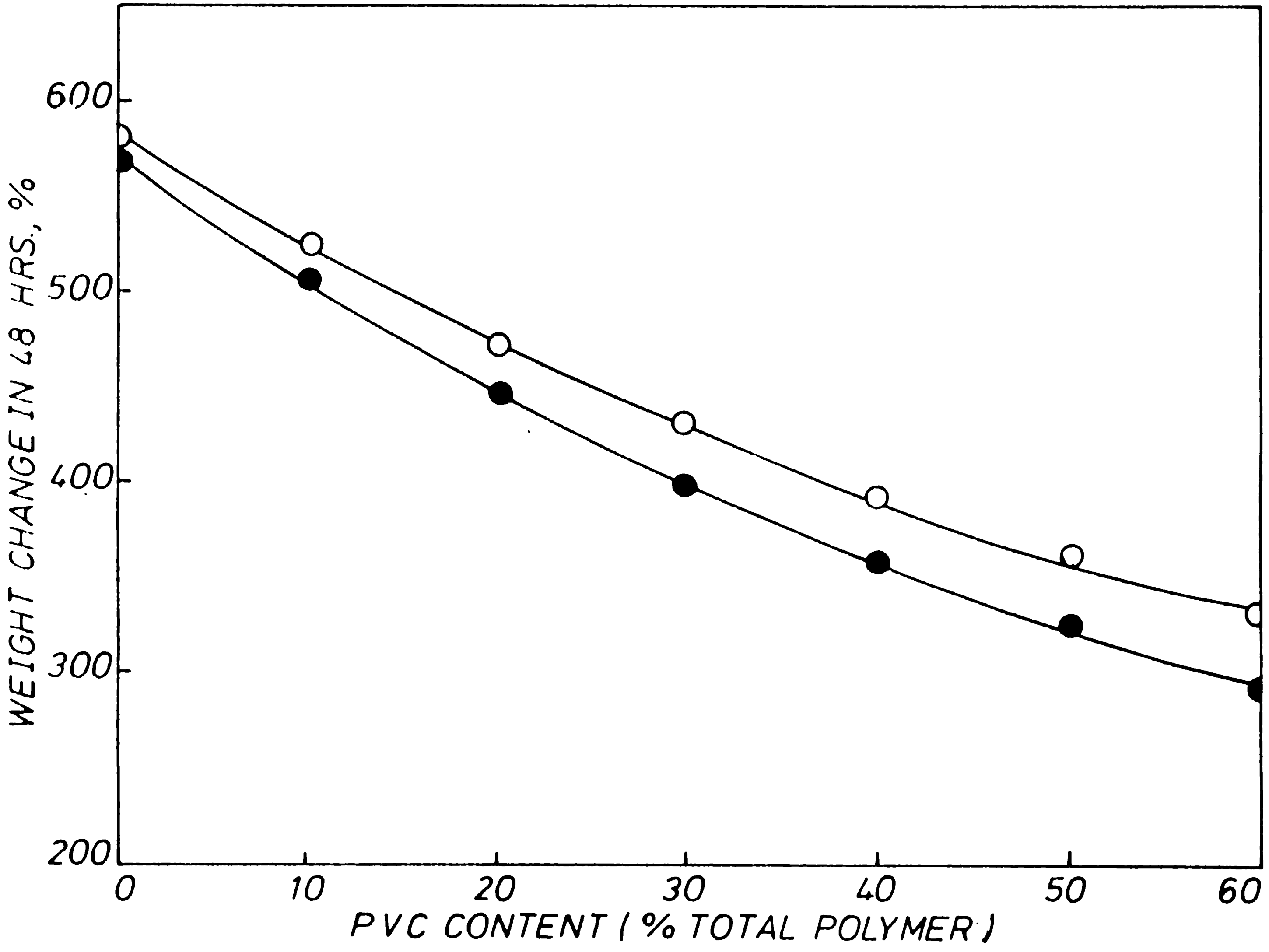


Fig. 6.12 Variation of resistance to swelling in chloroform of CR/PVC blend with PVC content: (○) before ageing, (●) after ageing.

The tensile strengths of the blends prepared through the two different routes were combined in Fig.6.13. The large deviation in tensile strengths from the linear relationship might indicate that the polymers are not fully compatible. Fig.6.14 which is a combined curve of the elongation at break also shows a similar trend.

MODIFICATION OF POLYCHLOROPRENE WITH UNPLASTICIZED PVC

1. Using MgO/ZnO system as the curative and stabilizer

Experimental

The formulations used for the preparation of polychloroprene (CR)/unplasticized PVC (UPVC) blends are shown in Table 6.3. The ingredients were mixed on a Brabender Plasticorder model PL3S using a roller type rotor employing a speed of 30 rpm at a temperature of 110±2°C for six minutes. All the ingredients, except the accelerator were added initially and the accelerator was added only after four minutes to prevent premature vulcanization. Cure curves of the various compounds were taken at 150°C on the Monsanto Rheometer. Three typical cure curves are shown in Fig.6.15. Optimum cure times of all the compounds are shown in Table 6.4. Samples for evaluating the various physical properties of the blends were vulcanized upto the respective optimum cure

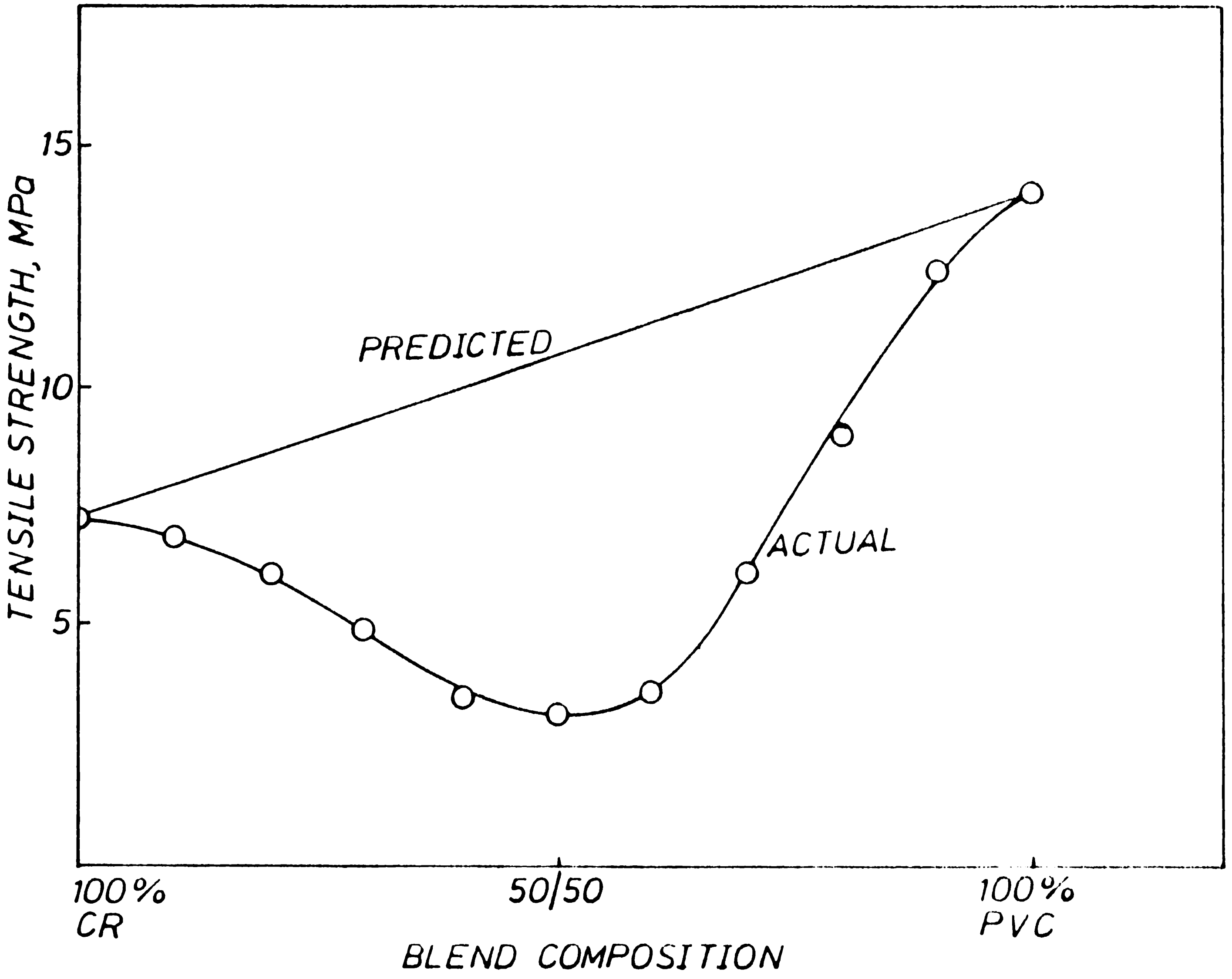


Fig. 6.13 Variation of tensile strength of CR/PVC blend over the entire blend composition.

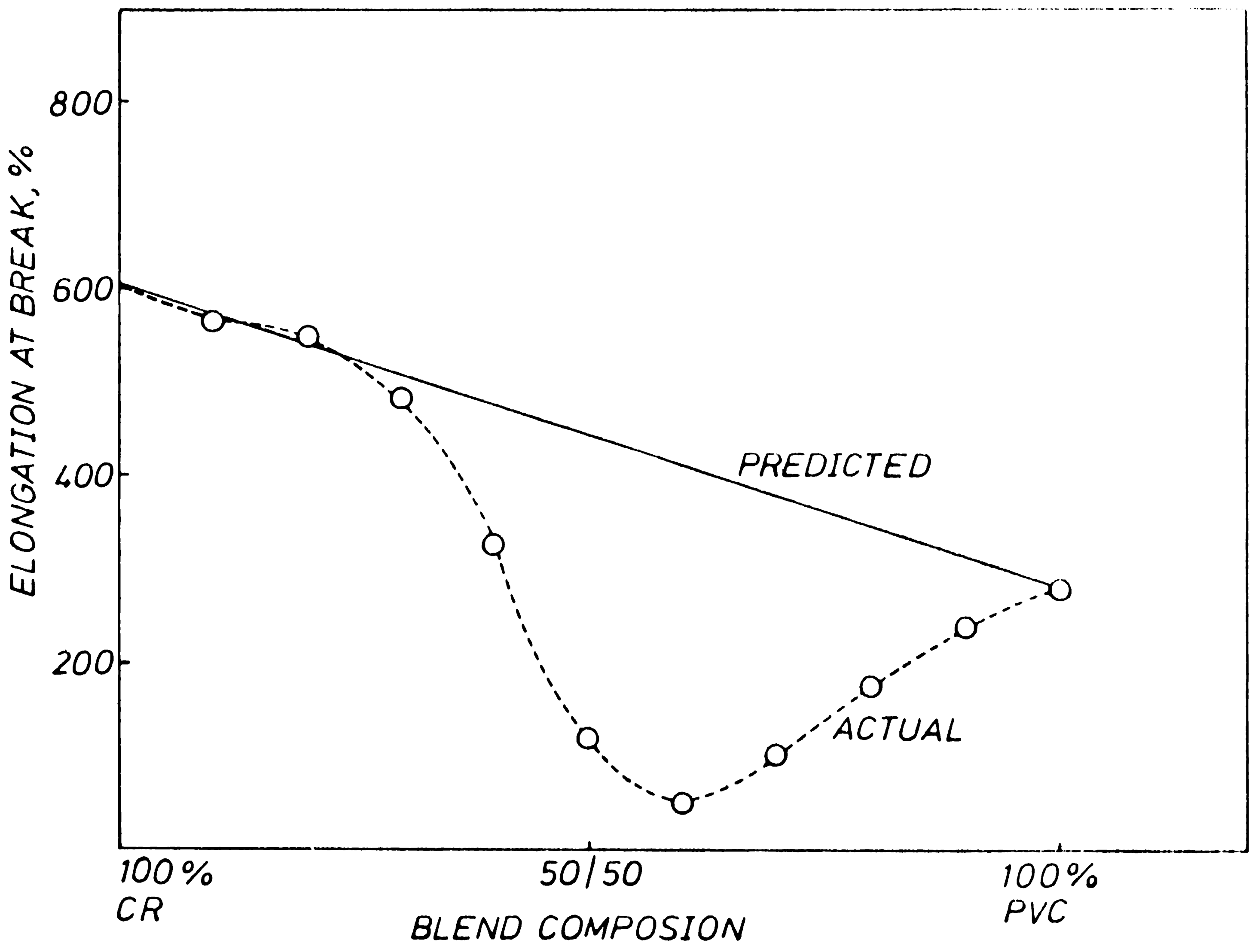


Fig. 6.14 Variation of elongation at break of CR/PVC blend over the entire blend composition.

Table 6.3

Modification of CR with UPVC - Formulations of the mixes

Mix	A	B	C	D	E	F	G	H
CR (W type)*	100	95	90	85	80	75	70	60
PVC	--	5	10	15	20	25	30	40
MgO (4 phr CR + 4 phr PVC)	4	4	4	4	4	4	4	4
ZnO (5 phr CR + 5 phr PVC)	5	5	5	5	5	5	5	5
Stearic acid (3 phr CR + 3 phr PVC)	3	3	3	3	3	3	3	3
NA-22 (0.5 phr CR)	0.5	0.475	0.45	0.425	0.40	0.375	0.35	0.30

* Type 3 (Chapter 2).

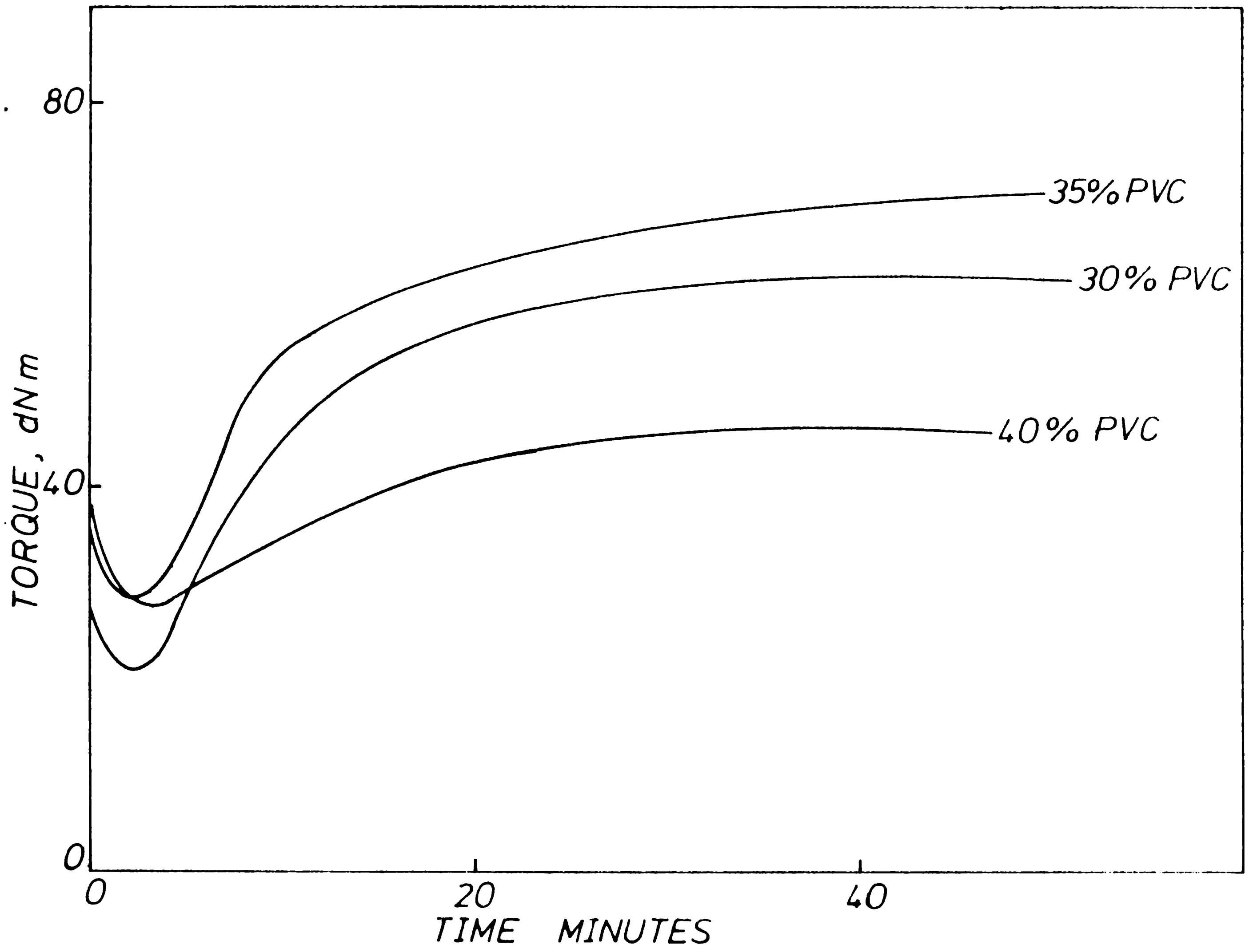


Fig. 6.15 Cure curves of typical CR/UPVC mixes.

Table 6.4

Variation of curetime, hardness, resistance to swelling and ozone resistance of CR/UPVC blends with PVC content

PVC content	Optimum curetime (mins.)	Hardness (Shore-A)	Resistance to swelling (% increase in wt. in 24 hrs)	Ozone resistance	
				Quality retention in 10 hrs (%)	Quality retention in 20 hrs (%)
0	20	44.0	6.97	100	95
5	20	47.5	6.77	100	90
10	23	48.0	6.70	100	90
15	20	50.5	6.65	95	80
20	20	52.0	6.49	90	75
25	25	57.5	6.38	85	65
30	23	59.0	5.89	85	65
40	20	67.0	5.54	Sample broken in 6 hrs	--

times at 150°C. The tensile properties of the blends were determined as per ASTM D412 (1980) on a Zwick Universal Testing Machine. The ageing resistance of the vulcanizates was determined by keeping the samples at 100°C for 96 hours in an ageing oven and then measuring the retention in tensile properties. The ozone resistance was determined according to ASTM D1171 (1974) using a Mast ozone chamber. Shore-A type durometer was used for determining the hardness of the vulcanizates as per ASTM D2240 (1981). The resistance to swelling of the vulcanizates was determined in ASTM reference oil No.3 by allowing circular specimens to stand in excess oil for 24 hours and then measuring the percentage change in weight.

Results and discussion

Fig.6.15 shows the cure curves of three typical CR/UPVC blends. The PVC phase does not seem to affect the crosslinking of the CR phase. The maximum torques attained by the blends is interesting. When the PVC content increases from 30% to 35% the maximum torque increases due to the increase in melt viscosity. However, when the PVC content increases from 35% to 40% the maximum torque decreases. This indicates that the plasticizing action of the CR phase present in this case is not sufficient to cause the fusion of the same amount of PVC as in the previous case. This further shows that the plasticizing action of CR on PVC is inferior to that of NBR.

The variation of tensile strength with PVC content is given in Fig.6.16. The tensile strength increases initially, reaches a maximum and then decreases. The initial improvement in tensile strength is expected since PVC has a higher tensile strength than CR. The decrease in tensile strength at higher loadings of PVC might be due to the lack of complete fusion of the PVC phase in turn due to low plasticizing action of the CR phase. This may also indicate a lack of compatibility of the constituents. The variation of elongation at break with PVC content (Fig.6.17) also shows a similar trend as that of the tensile strength. The hardness and the resistance to swelling of the blends improve with increase in PVC content as expected (Table 6.4). PVC, being a saturated polymer, is likely to exhibit better ozone resistance compared to that of CR. However, there is no clear cut improvement in ozone resistance with increase in PVC content. This behaviour, again, might be due to lack of complete fusion of the PVC phase and miscibility between the phases. This reasoning is exemplified by the fact that a sample containing 40% PVC broke in the ozone chamber in just six hours.

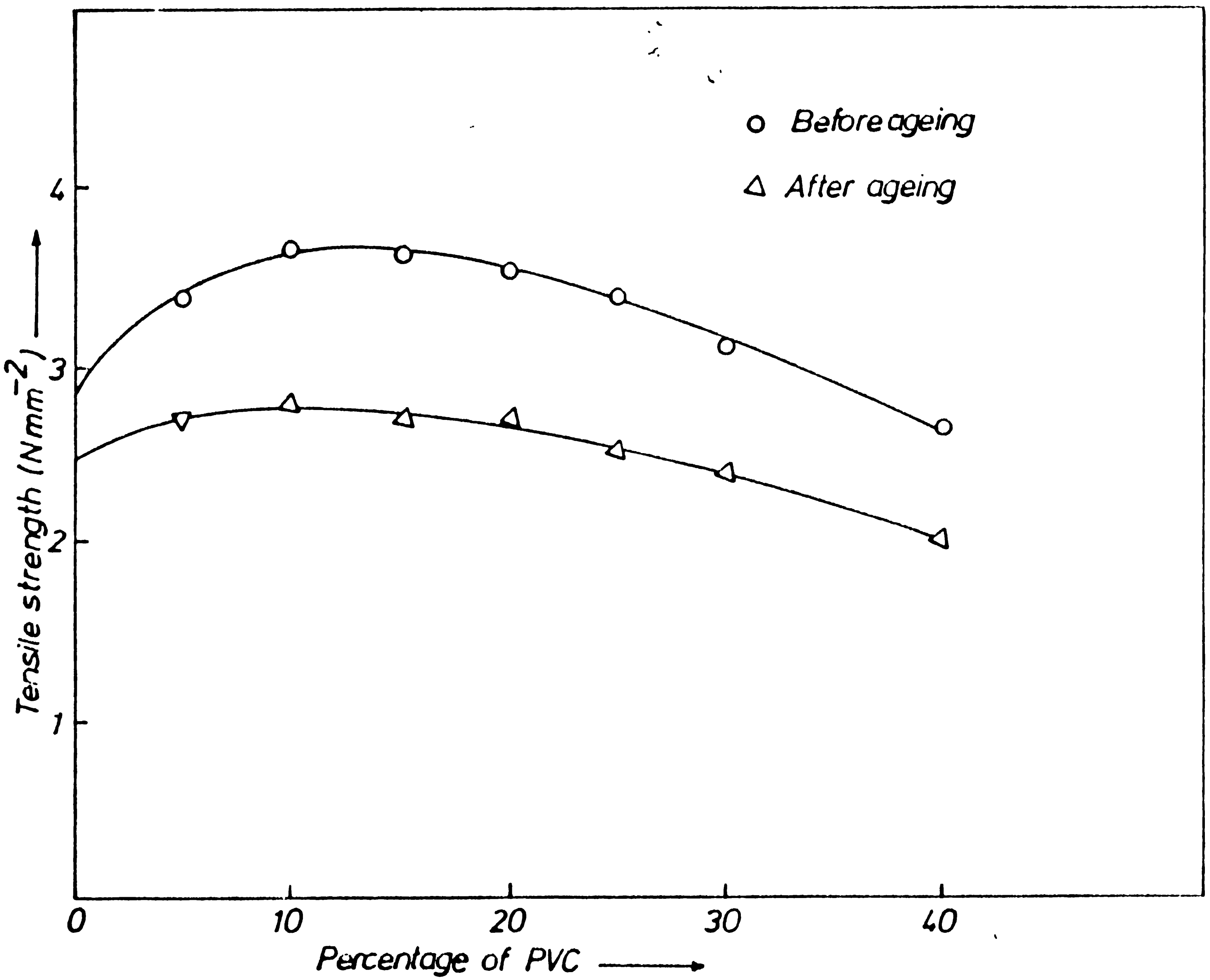


Fig. 6.16 Variation of tensile strength of CR/UPVC blend with PVC content.

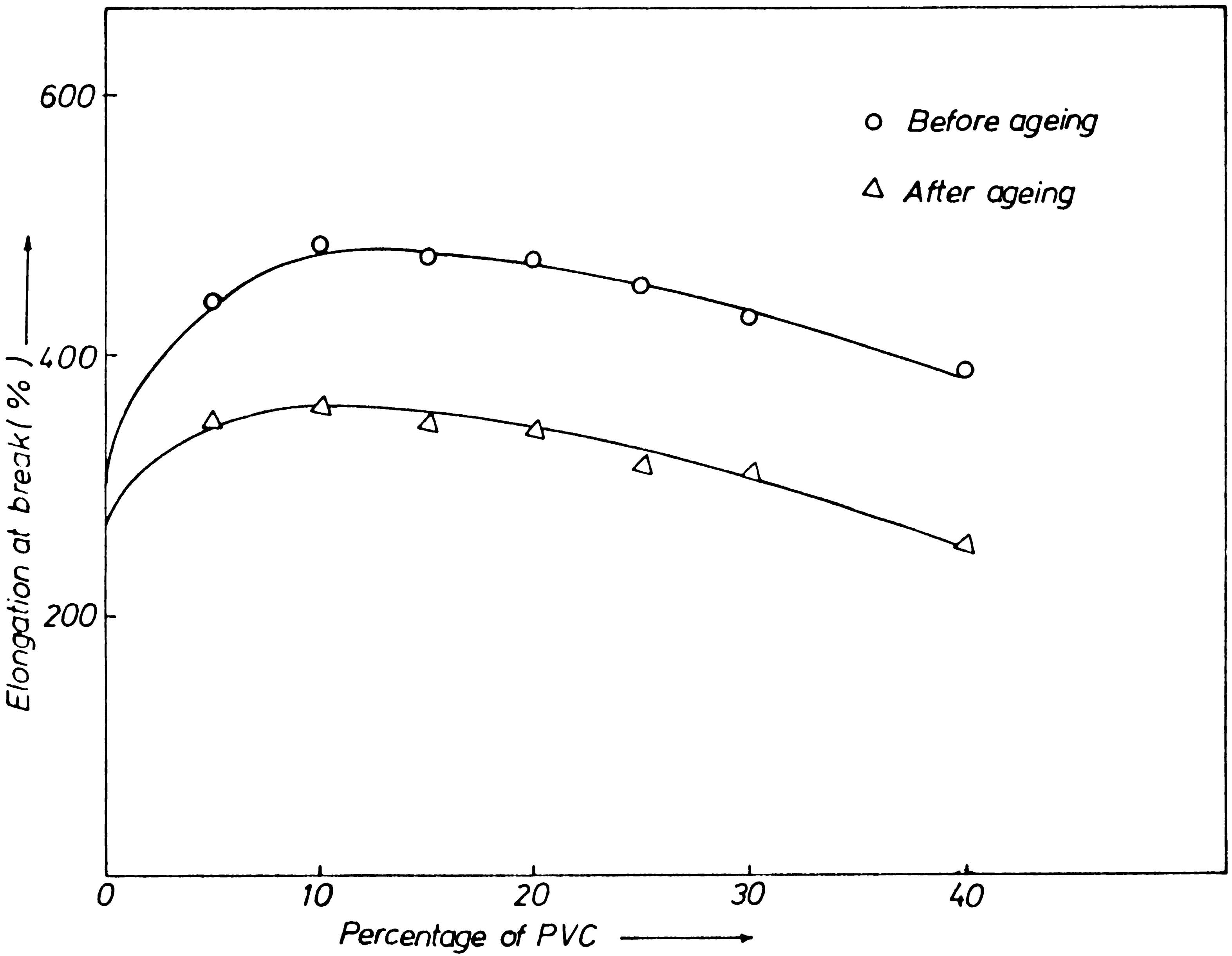


Fig. 6.17 Variation of elongation at break of CR/UPVC blend with PVC content.

2. Using tribasic lead sulphate (TBLS) as the curative and stabilizer

Experimental

The formulations used for the preparation of the blends are shown in Table 6.5. CR, PVC and other ingredients were blended together on a warm laboratory mill. The blends were then compression moulded at 190°C for 3 minutes when the curing of the CR phase and the melting of the PVC phase could occur. The mould was water cooled immediately after it was taken out of the hydraulic press, keeping the sample still under compression. The tensile properties of the blends were determined as per ASTM D412 (1980) test method and are shown in Figs.6.18, 6.19 and 6.20. Hardness of the blends was determined according to ASTM D2240 (1981) and expressed in Shore A units (Fig.6.21).

Results and discussion

The tensile properties of these blends are also more or less similar to those of the CR/UPVC blends employing the MgO/ZnO system as the curative and stabilizer. However, the tensile strength improves only a little in this case with PVC content (Fig.6.18) and then starts decreasing. This indicates that the PVC phase is not fully homogenized even at high concentrations of CR unlike the previous study in which MgO/ZnO system was used. This suggests that the lubricant action of

Table 6.5

Modification of CR with UPVC - Formulations of the mixes

Mix	A	B	C	D	E
CR (W type)*	100	90	80	70	60
PVC	--	10	20	30	40
TBLS	10.0	10.0	10.0	10.0	10.0
Stearic acid	3.0	3.0	3.0	3.0	3.0
NA-22	0.5	0.45	0.40	0.35	0.30
PBN	1.0	1.0	1.0	1.0	1.0

*Type 2 (Chapter 2)

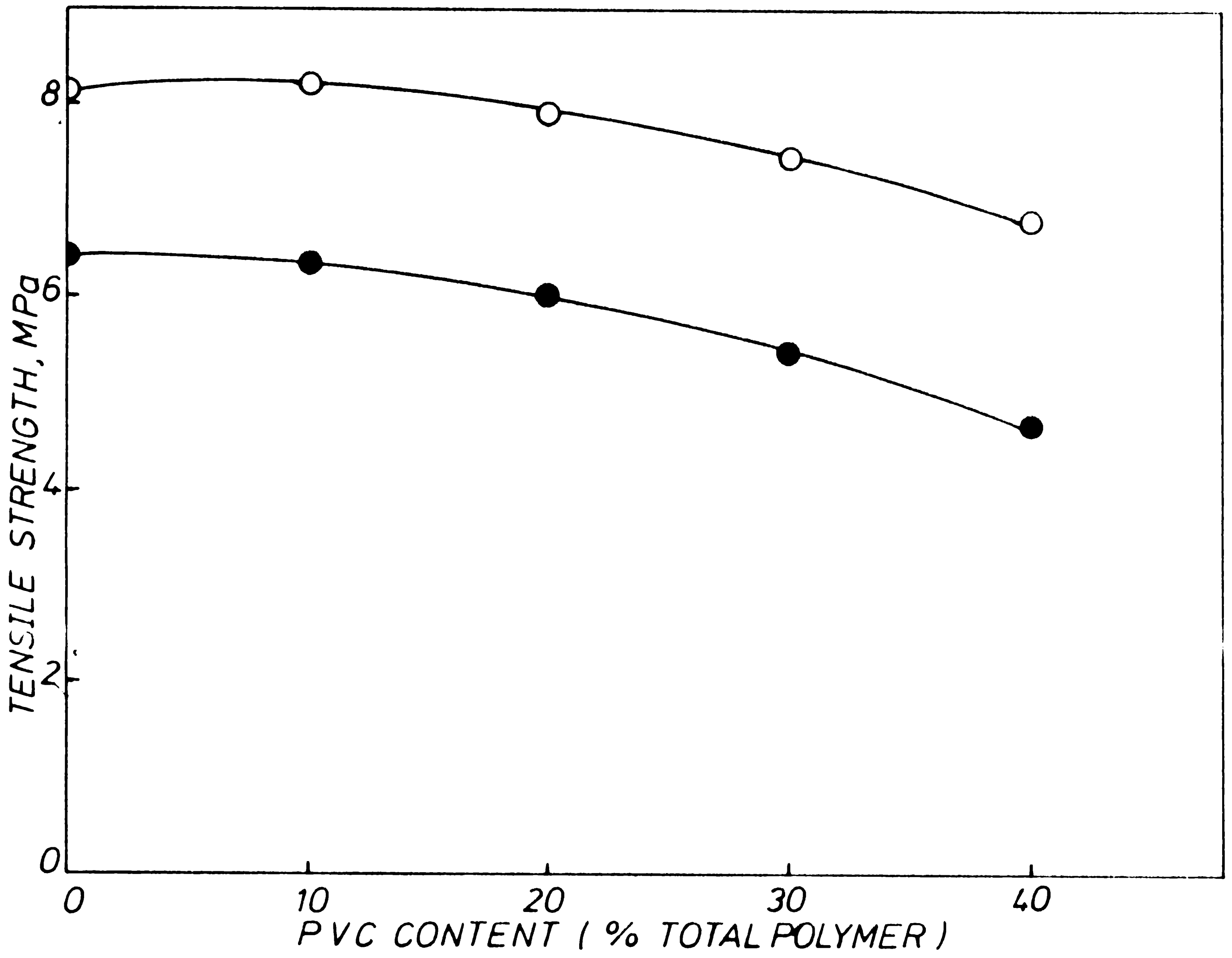


Fig. 6.18 Variation of tensile strength of CR/UPVC blend with PVC content: (○) before ageing, (●) after ageing.

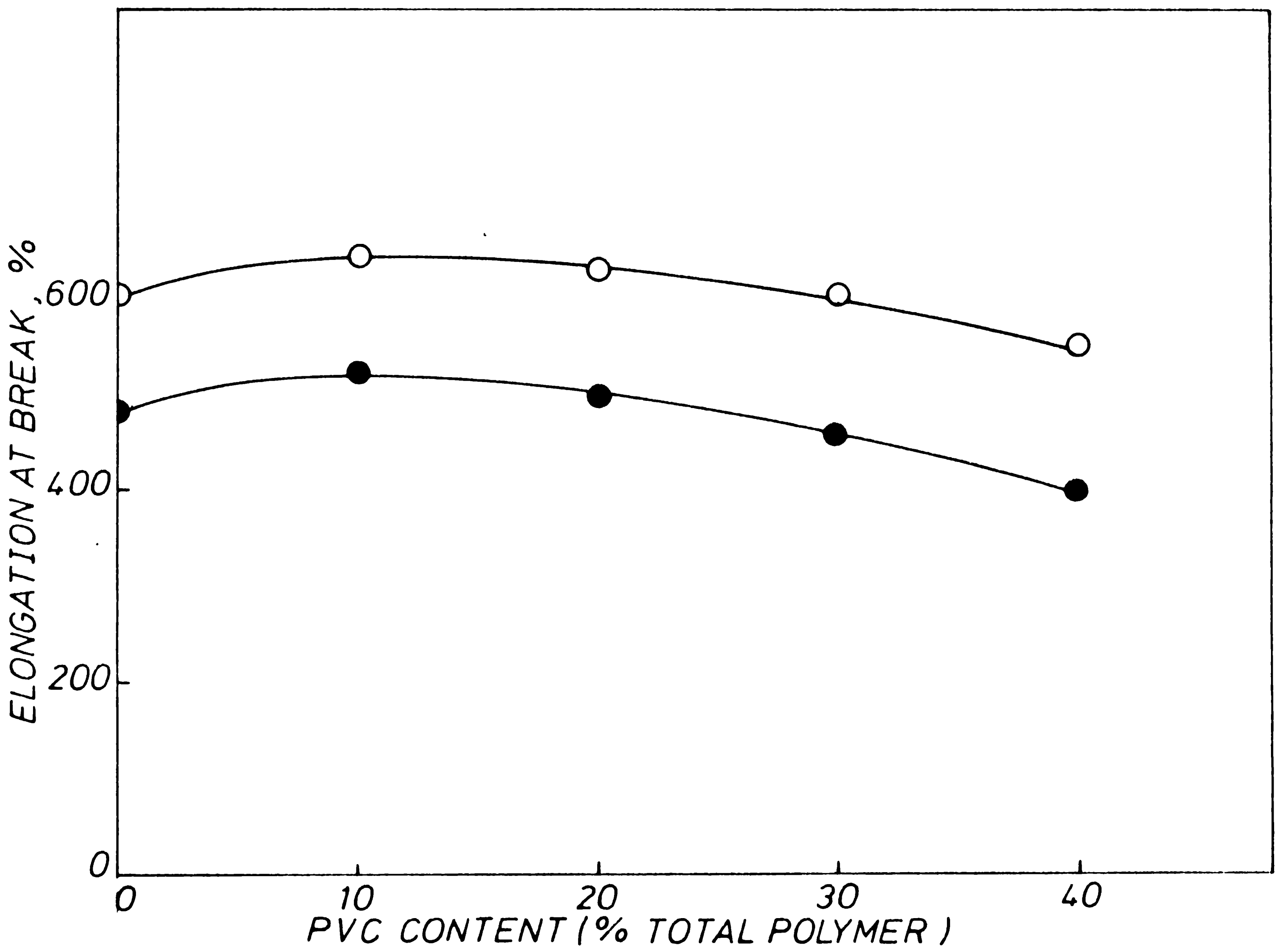


Fig. 6.19 Variation of elongation at break of CR/UPVC blend with PVC content: (○) before ageing, (●) after ageing.

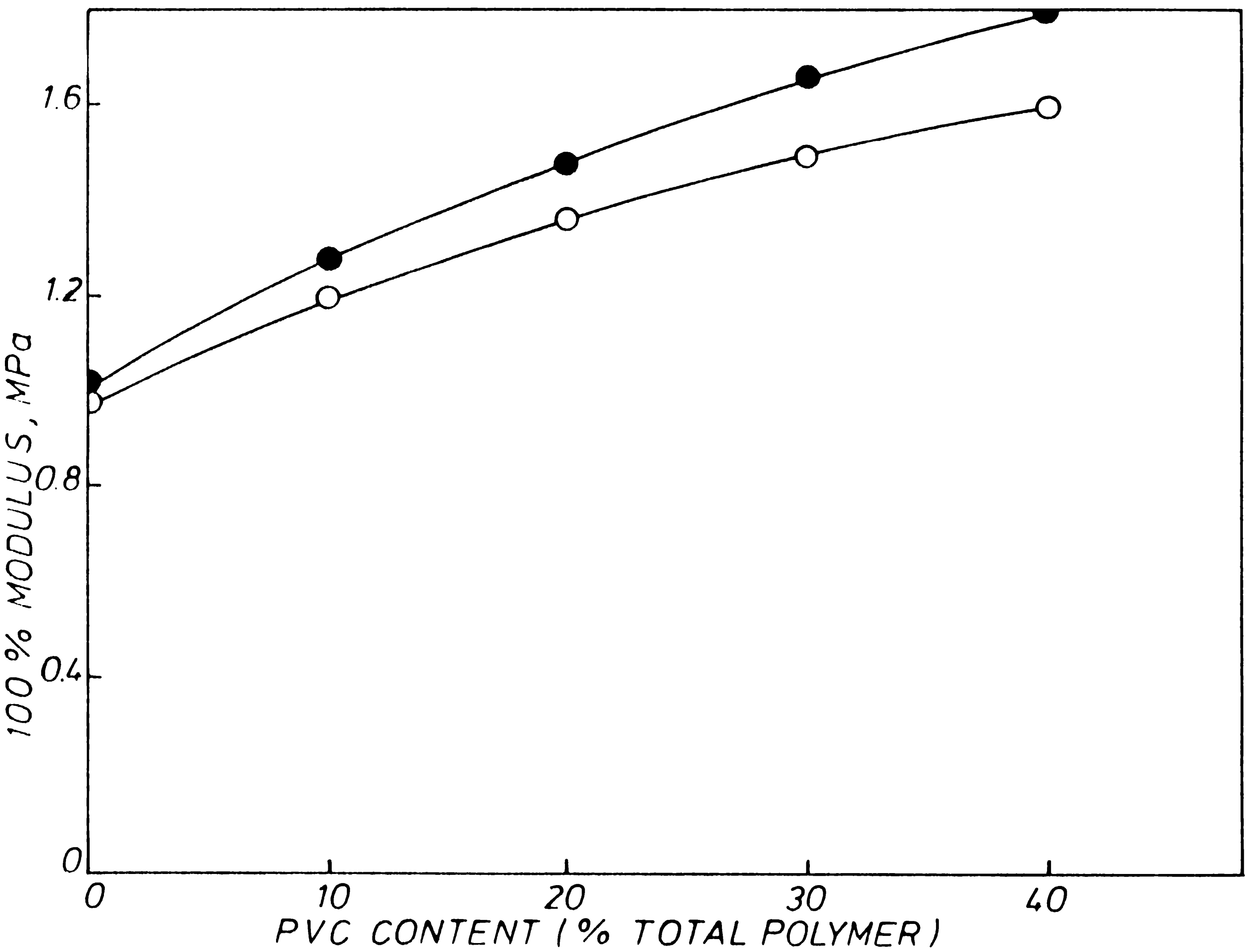


Fig. 6.20 Variation of 100% modulus of CR/UPVC blend with PVC content: (○) before ageing, (●) after ageing.

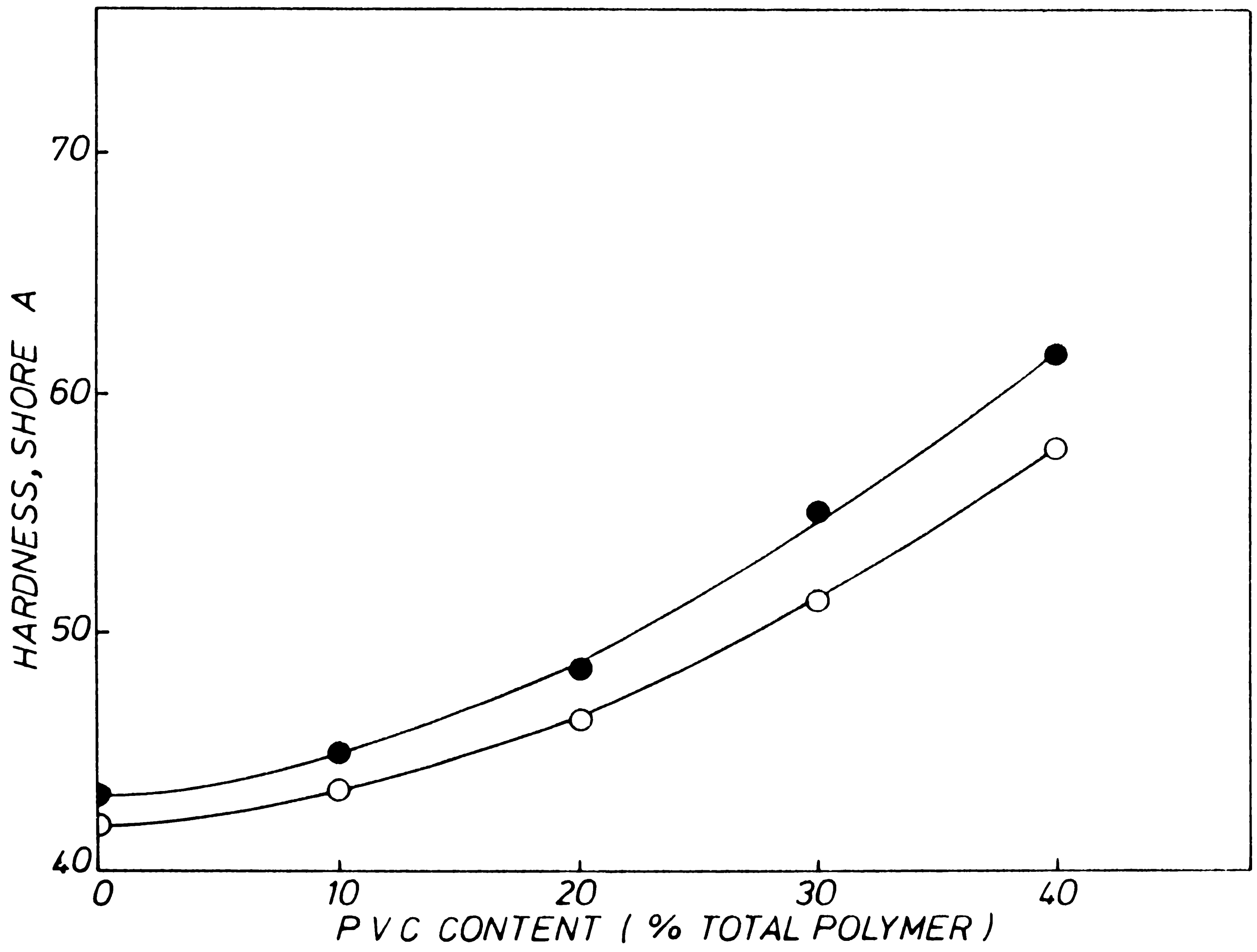


Fig.6.21 Variation of hardness of CR/UPVC blend with PVC content: (○) before ageing, (●) after ageing.

TBLS is low, compared to that of MgO and ZnO. The variation of elongation at break also shows a similar trend (Fig.6.19). The modulus (Fig.6.20) and hardness (Fig.6.21) improve with PVC content as expected. The ageing resistance of the blends is more or less similar to that of CR alone which further shows lack of fusion and homogenization of the PVC phase.

Summary

The blends of polychloroprene and plasticized poly (vinyl chloride) do not obey the linear rule of mixtures in physical properties. However, these blends are found to be a new class of potential polyblends, with very good ageing resistance, high modulus and hardness, which could advantageously replace CR in many applications. Blends of polychloroprene and unplasticized PVC display very good physical properties even at low concentrations of PVC. However, the plasticizing action of CR is found to be less than that of NBR, and hence blending of CR and UPVC requires high temperatures. MgO/ZnO/stearic acid system is effective both as curative and stabilizer in low temperature blending of CR and plasticized PVC or CR and low concentrations of UPVC. Tribasic lead sulphate could be used both as curative and stabilizer in high temperature blending of CR and PVC.

References

1. J.R.Dunn, Rubber Chem.Technol., 49, 978 (1976).

2. O.Olabisi, L.M.Robeson and M.T.Shaw, "Polymer-Polymer Miscibility", Academic Press, New York (1979).

3. P.J.Corish and B.D.W.Powell, Rubber Chem.Technol., 47, 481 (1974).

4. M.L.Ural'skii et al, Int.Polym.Sci.Technol., 7, No.6, 1 (1980).

5. D.C.Blackley, "Synthetic Rubbers", Applied Science Publishers, London (1983).

6. W.P.Fletcher in "Rubber Technology and Manufacture", C.M.Blow and C.Hepburn (Eds.), pp.118-125, Butterworths, London (1985).

7. I.M.Piroeva et al, Int.Polym.Sci. Technol., 12,No.7,30(1985).

8. S.Krause in "Polymer Blends", D.R.Paul and S.Newmann (Eds.), Vol.1, Chap.2, Academic Press, New York (1978).

9. J.A.Brydson, "Plastics Materials", Chap.4, Butterworth Scientific, London (1982).

10. K.Mori and Y.Nokamura, Plast. & Rub. Proc. & Appl., 3, 17 (1983).

11. W.K.Fischer, Rubber World, 167, 49 (1973).

12. B.Kuriakose and S.K.De, Polym.Eng.Sci., 25, 630 (1985).

13. A.Y.Coran and R.P.Patel, Rubber Chem.Technol., 54, 892 (1981).

14. V.Duchacek and A.Kuta, J.Appl.Polym.Sci., 27, 1549 (1982).

CHAPTER - 7

SUMMARY AND CONCLUSIONS

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MgO/ZnO/Stearic acid combination has been shown to be an efficient stabilizer system for PVC[1] for the first time. The full potential of this discovery may not be obvious immediately. This stabilizer system is superior to most of the conventional stabilizers of PVC in non-toxic applications and in retaining the colour flexibility of the polymer. All the three ingredients are conventional materials in rubber compounding[2] and hence the system was found to be useful in blends of PVC with other elastomers. On the debit side, the system is not very efficient in high temperature applications, especially for rigid PVC processing. However, for most PVC-rubber blends, the processing could be done at lower temperatures due to the plasticizing action of the rubbers. Another disadvantage of the system is the comparatively higher levels of loading required for efficient stabilization.

Another significant finding of the study is that tribasic lead sulphate (TBLS) could be an efficient curative for polychloroprene rubber[3]. TBLS has many advantages over the conventional curative of CR, viz., MgO/ZnO combination.

TBLS is a more efficient curative and the total loading required is less than that of the MgO/ZnO combination. Further, the vulcanizates cured with TBLS are found to display better mechanical properties than those cured with MgO and ZnO. The TBLS cured vulcanizates are also found to exhibit good solvent resistance comparable to the lead oxide cured vulcanizates of polychloroprene. Thus tribasic lead sulphate seems to be a good compromise between the MgO/ZnO combination and the lead oxide as the curative for CR. On the debit side, the toxicological hazards of TBLS would have to be fully assessed before putting it into critical applications.

Several methods have been suggested for improving the properties and performance of NBR/PVC blends. In all the studies conducted, MgO/ZnO/stearic acid system was used as the stabilizer for the PVC phase and was found to be efficient. The importance of optimizing the blending parameters in the preparation of NBR/PVC blends has been reported prior to this study[4,5]. However, the present study has shown that for getting the best out of NBR/PVC blends, the blending parameters have to be optimized for every composition of NBR/PVC blends[6]. It was also shown that conventional equipments like the Brabender Plasticorder could be used for determination of these optimum parameters. Modification of

NBR/PVC blends using general purpose rubbers like natural rubber, styrene-butadiene rubber and polybutadiene rubber was done mainly for economic advantage. However, the ternary blends were also found to possess some improved mechanical properties[7]. The discovery that a measure of the compatibility of PVC with other elastomer(s) could be estimated from studies conducted on a Brabender Plasticorder is also noteworthy. The modification of NBR/PVC blends with polysulphide rubber was aimed at generating ternary blends for critical applications. The product was found to display a well balanced compromise between the outstanding solvent resistance of polysulphide rubber and the good mechanical and processing properties of NBR/PVC blends[8].

The blends of CR and PVC have been developed as replacement of CR in critical applications, especially for high temperature resistance. Modification of CR with rigid PVC improves the strength of CR[9] even at low concentrations of PVC. But for generating a new class of temperature resistant elastomeric substance, it is the retention of strength which is more important than the original strength. Hence, extensive studies were done on the blends of plasticized PVC and CR, eventhough the mechanical properties of the blends were found to be generally inferior to those of pure CR.

The ageing resistance of these blends were found to be very good. Coupled with this high heat resistance, the blends possess the high modulus and hardness of PVC[10,11], which could be advantageously made use of.

References

1. K.E.George, R.Joseph and D.J.Francis, Plast. & Rub. Proc. & Appl., 5, 179 (1985).

2. A.F.Nasnikov, A.A.Nosnikov and G.A.Blokh, Int.Polym.Sci. Technol., 10, No.10, 54 (1983).

3. R.Joseph, K.E.George and D.J.Francis, Angew.Makromol. Chem., 148, 19 (1987).

4. L.A.Ultracki, Polym.Plast.Technol.Eng., 22, 27 (1984).

5. C.C.Lee et al, J.Appl.Polym.Sci., 9, 2047 (1965).

6. K.E.George, R.Joseph and D.J.Francis, J.Appl.Polym.Sci., 32, 2867 (1986).

7. K.E.George et al, Polym.Eng.Sci., in press.

8. K.E.George et al, J.Mater.Sci.Lett., 5, 1221 (1986).

9. R.Joseph, K.E.George and D.J.Francis, Intern.J.Polymeric Mater. 11, 95 (1986).

10. K.E.George, R.Joseph and D.J.Francis, Paper presented at the International Conference in Rubber and Rubber Like Materials, November 6-8, (1986), Jamshedpur.

11. K.E.George, R.Joseph and D.J.Francis, Angew.Makromol.Chem., in press.

PUBLICATIONS FROM THIS WORK

1. Magnesium oxide/zinc oxide combination--Efficient stabilizer for PVC
   Plast. & Rubb.Proc. & Appl., 5, 179 (1985).

2. Tribasic lead sulphate as efficient curing agent for polychloroprene
   Angew.Makromol.Chem., 148, 19 (1987).

3. Studies on NBR/PVC blends
   J.Appl.Polym.Sci., 32, 2867 (1986).

4. Modification of acrylonitrile-butadiene rubber/poly(vinyl chloride) blends using natural rubber, styrene-butadiene rubber and polybutadiene rubber
   Polym.Eng.Sci., in press.

5. Modification of polysulphide rubber using butadiene-acrylonitrile copolymer/poly(vinyl chloride) blend
   J.Mater.Sci.Lett., 5, 1221 (1986).

6. Modification of polychloroprene with poly(vinyl chloride)
   Intern.J.Polymeric Mater., 11, 95 (1986).

7. Studies on polychloroprene/poly(vinyl chloride)
   Presented at the International Conference on rubber and rubber like materials, November 6-8, (1986), Jamshedpur.

8. Blends of polychloroprene and poly(vinyl chloride)
   Angew.Makromol.Chem., in press.