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Starved Feeding for Improving the Mechanical Properties of Styrene-Butadiene Rubber Vulcanizates

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ABSTRACT

Gum and filled compounds of styrene-butadiene rubber are extruded through a laboratory extruder by varying the feeding rate at different temperatures and screw speed (rpm). The extruded compounds are vulcanized up-to their optimum cure times and the mechanical properties of the vulcanizates are determined. From the properties data obtained it is concluded that there is a specific feeding rate within the starved fed region, which results in maximum improved mechanical properties. The enhancement in properties is found to be due to better thermal and shear homogeneity.

Key Words: styrene-butadiene rubber, extrusion, feeding rate, starved feeding, mechanical properties

INTRODUCTION

Feeding of a polymer to a screw extruder can be carried out by adopting one of the following methods:
- starved feeding by using metering devices [1].
- flood feeding through a hopper [2].
- force feeding using a hopper compactor [3].

Among the above three approaches, starved feeding is commonly employed for improving the operation and versatility of single screw extruders [4]. For example, the same screw can handle a wide range of materials and performance requirements of utilizing horse power availability [5].

Furthermore, starved feeding requires lower torque [6] and achieves higher stock temperature and increased variability in output rate [7]. In starved extrusion, the effective metering depth of the screw is reduced and it results in better melting performance, due to the increase in rotational speed of the screw for the same screw rotation time [8]. Edwards et al. [9, 10] showed that the degree of mixing in the melting zone is more significant than that in the metering zone, as in starved extrusion. So starved feeding is likely to result in reduced mechanical breakdown due to uniform mixing, better thermal homogeneity and preferential orientation of the molecules due to comparative decrease in melt temperature [11] which may give rise to improved mechanical properties. This study is undertaken to determine the effect of feeding rate on the mechanical properties of gum and filled styrene-butadiene rubber (SBR) vulcanizates, since no work has been directed towards this angle.

EXPERIMENTAL

Materials

SBR: 23.5% styrene; Mooney viscosity, ML (1+4) at 100 °C, 49.2; supplied by Synthetic and Chemicals Ltd. Bareilly. Zinc oxide (ZnO), stearic acid Pilflex-13; [*N*-(1,3−dimethyl butyl)-*N*-phenyl-p-phenylene diamine], carbon black (HAF N330), aromatic oil, benzothiazyl disulphide (MBTS), tetramethylthiuram disulphide (TMTD), *N*-cyclohexyl 1-2 benzothiazyl sulphenamide (CBS) and sulphur used were of commercial grades.

Preparation of Test Samples

Tests were performed on a laboratory extruder attached to a Brabender Plasticoder model PL 2000 with an L/D ratio of 10 and a compression ratio of 1, equipped with a feeding roll, was used. The die used was a round capillary die with L/D ratio of 15. The formulations of the gum and filled compounds of SBR selected for the study are shown in Table 1.

Compounds were prepared on a laboratory two roll mill according to the ASTM D 3184 and 3189 (1973), and then sheeted out by passing through a 1mm nip of the mixing mill. The sheets were cut into 10mm strips for feeding into the extruder. Feeding rates were adjusted by placing different number of layers of the strips on the feeding roll, and it was measured by the rate of output of the extrudate. The compounds were extruded at varying feeding rates mainly in the starved fed regions at 20, 40, 60 and 80 rpm and at different temperatures. The cure curves of the SBR compounds after extrusion were taken on a Goettfert Elastograph model 67.85 according to the ASTM D 1646 (1981) at 150 °C. The extruded samples were vulcanized up-to their optimum cure times (90% of the time required for attaining maximum torque) in an electrically heated laboratory hydraulic press. The moulded samples were then cooled by immersing in water and dumb-bell specimens were cut out of the sheets for tensile testing. The tensile properties of vulcanizates were measured using a Zwick universal testing machine model 1445 at an extension rate of 500 mm/min according to the ASTM D 412 (1980).

Table 1. Formulations of the compounds.

Formulation	SBR-gum compound	SBR-filled compound
SBR	100	100
ZnO	4	4
Stearic acid	1.5	1.5
Anti-oxidant (Pilflex-13)	1.0	1.0
HAF Black (N 330)	–	45
Aromatic oil	–	6.0
MBTS	1.0	1.0
TMTD	0.25	0.25
CBS	0.8	0.8
Sulphur	2.0	2.0

The swelling index of the gum and filled vulcanizates were measured by equilibrium swelling in toluene [12] according to the following equation:

$$\text{Swelling index} = \frac{\text{final wt} - \text{deswollen wt}}{\text{initial wt}} \quad (1)$$

The viscosity values of a few samples of gum rubber extrudates were measured by using a Brookfield viscometer. The percent bound rubber content (filler gel) of a few samples was determined by immersing the samples in 25 mL of toluene for seven days at room temperature (solvent was renewed after three days). Then the sample was dried for one day in air at room temperature and then for 24 h in an oven at 105 °C. The percent bound rubber of the polymer (R_b) was then calculated according to the following equation [13].

$$R_b = \frac{W_{fg} - W[m_f/(m_f+m_p)] \times 100}{W[m_p/(m_f+m_p)]} \quad (2)$$

where: W_{fg} is the weight of carbon black and gel.

m_f is the weight of the filler in the compound.

m_p is the weight of the polymer in the compound.

W is the weight of the specimen.

The tensile fracture surfaces of a few typical samples were examined using a scanning electron microscope to study the mode of failure.

RESULTS AND DISCUSSION

Figure 1 shows the variation of tensile strength with feeding rate for SBR gum and filled vulcanizates for different rpm at 80 °C. The highest feeding rate for each rpm represents the feeding rate recommended by the manufacturer. It is found that irrespective of rpm, the tensile strength initially increases with feeding rate, reaches a maximum value and thereafter decreases. This shows that for a given shear rate and temperature, there is a particular feeding rate in the starved region which results in maximum tensile strength. This is possibly due to the improved uniformity in temperature of the compounds [14], as thick sections are not properly heated to uniform temperatures in the case of thermal insulators like rubber.

Furthermore, lower shear breakdown and preferential orientation of the molecules may be other reasons for the higher tensile strength at this feeding rate [15]. The preferential orientation effect is clearly seen, in this case, from the higher difference between the tensile strength measured along the longitudinal (extrusion) and transverse directions (Figures 1 and 2).

Figures 3 and 4 show the variation in elongation at break of SBR gum and filled vulcanizates with feeding rate in longitudinal (extrusion) and transverse directions at different rpms. As in the case of tensile strength, unimodal curves are obtained for each rpm. This further shows the efficiency of the starved extrusion in getting improved physical properties.

Figures 5 and 6 show the variation in tensile strength of SBR gum and filled vulcanizates with feeding rate at different temperatures at a fixed

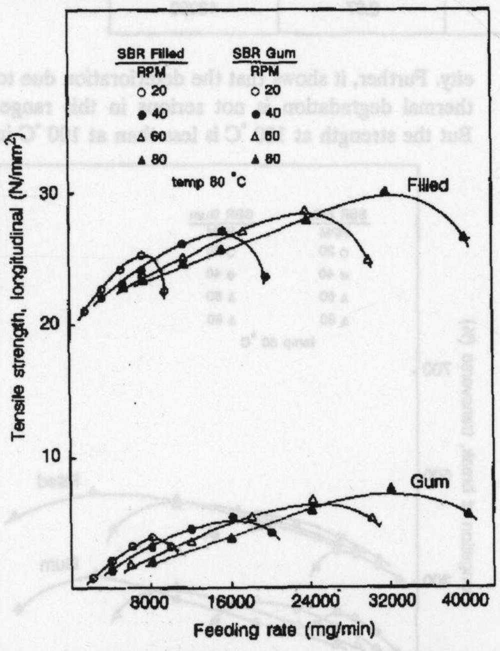

Figure 1. Effect of feeding rate on the tensile strength of gum and filled SBR vulcanizates at different rpm in longitudinal (extrusion) direction.

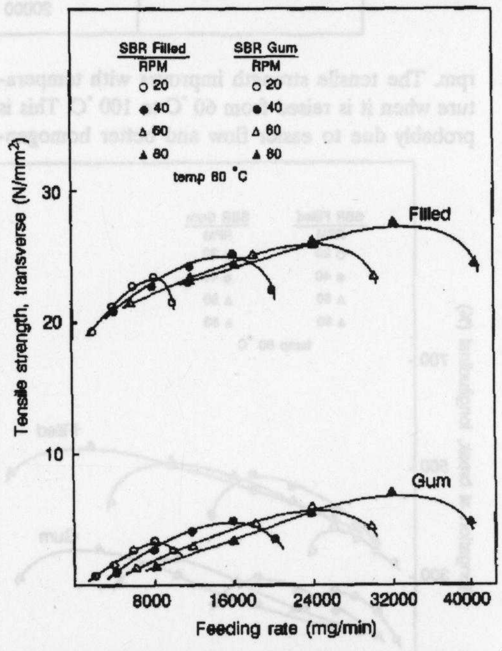

Figure 2. Effect of feeding rate on the tensile strength of gum and filled SBR vulcanizates at different rpm in transverse direction.

Table 2. The variation of swelling index and Brookfield viscosity values of gum SBR vulcanizates.

SBR sample	Feeding rate (mg/min)	Swelling index	Viscosity (cp)
Unextruded SBR	–	3.52	41200
SBR extruded at:	8000	3.51	43600
rpm=80; temp.=80 °C	16000	3.32	44400
	24000	2.96	45200
	32000	2.41	46400
	40000	2.75	44800
SBR extruded at:	4000	3.60	42000
rpm=40; temp.=100 °C	8000	3.42	42800
	12000	3.01	43600
	16000	2.62	44800
	20000	2.97	43200

rpm. The tensile strength improves with temperature when it is raised from 60 °C to 100 °C. This is probably due to easier flow and better homogeneity. Further, it shows that the deterioration due to thermal degradation is not serious in this range. But the strength at 120 °C is less than at 100 °C in

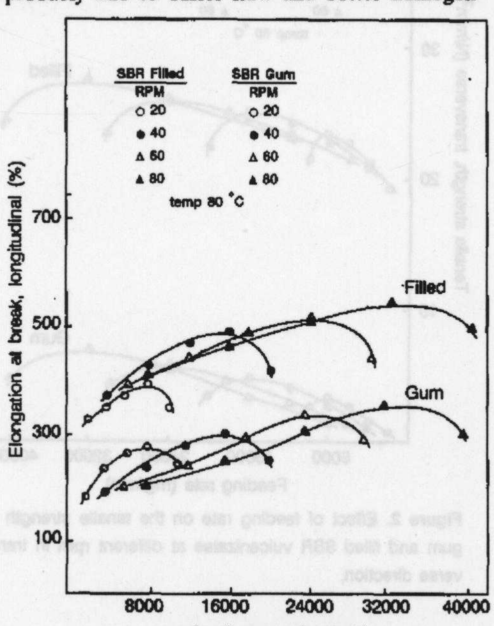

Figure 3. Effect of feeding rate on the elongation at break of gum and filled SBR vulcanizates at different rpm in longitudinal (extrusion) direction.

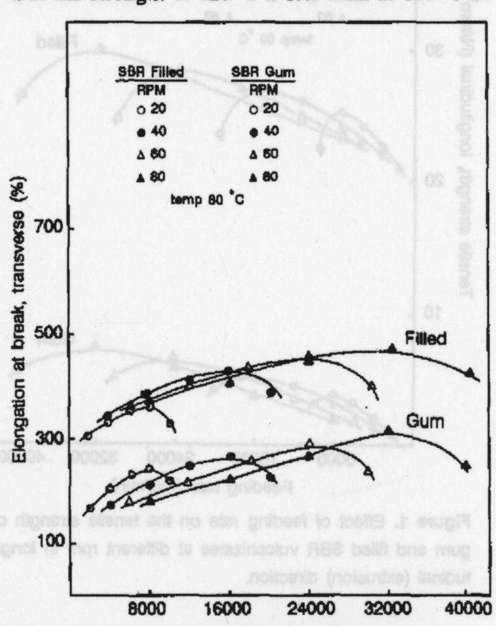

Figure 4. Effect of feeding rate on the elongation at break of gum and filled SBR vulcanizates at different rpm in transverse direction.

Table 3. The variation of swelling index and percentage bound rubber content of filled SBR vulcanizates.

SBR sample	Feeding rate (mg/min)	Swelling index	Bound rubber content, R_b (%)
Unextruded SBR	-	2.99	25
SBR extruded at: rpm=80; temp.=80 °C	8000	2.56	31
	16000	2.03	36
	24000	1.74	45
	32000	1.24	54
	40000	1.91	33
SBR extruded at: rpm=40; temp.=100 °C	4000	2.82	27
	8000	2.50	32
	12000	2.01	37
	16000	1.51	48
	20000	2.32	31

the case of gum and filled SBR vulcanizates showing the onset of degradation. At every temperature, the strength increases with feeding rate, reaches a maximum and decreases thereafter. As

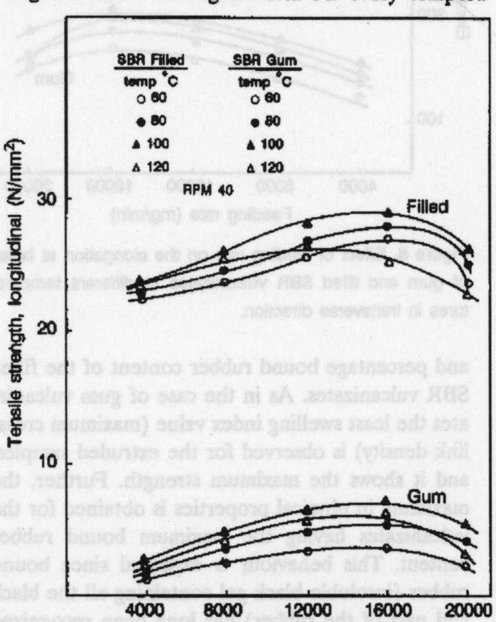

Figure 5. Effect of feeding rate on the tensile strength of gum and filled SBR vulcanizates at different temperatures in longitudinal (extrusion) direction.

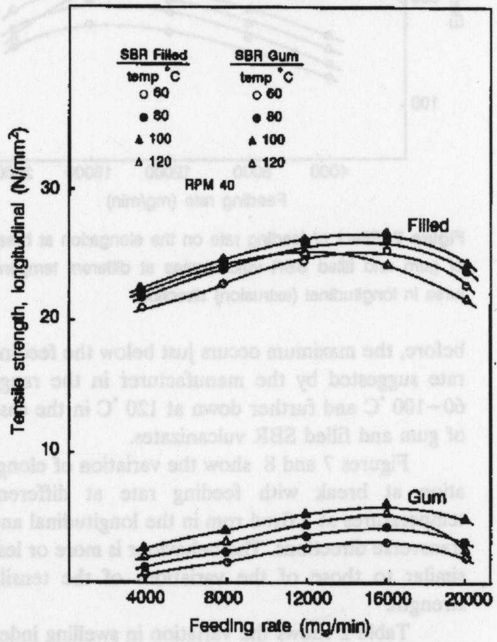

Figure 6. Effect of feeding rate on the tensile strength of gum and filled SBR vulcanizates at different temperatures in transverse direction.

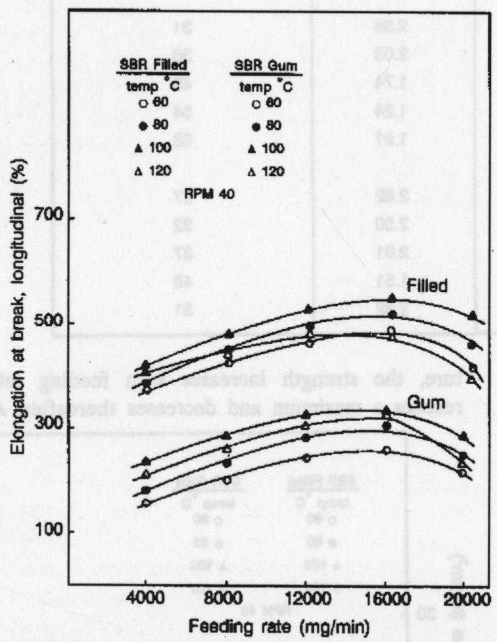

Figure 7. Effect of feeding rate on the elongation at break of gum and filled SBR vulcanizates at different temperatures in longitudinal (extrusion) direction.

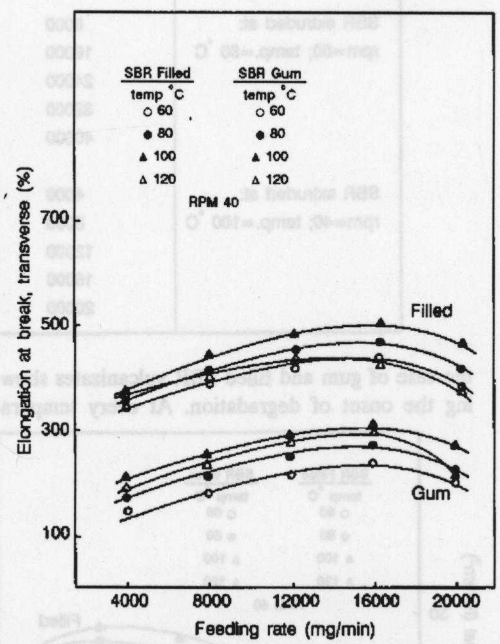

Figure 8. Effect of feeding rate on the elongation at break of gum and filled SBR vulcanizates at different temperatures in transverse direction.

before, the maximum occurs just below the feeding rate suggested by the manufacturer in the range 60–100 °C and further down at 120 °C in the case of gum and filled SBR vulcanizates.

Figures 7 and 8 show the variation of elongation at break with feeding rate at different temperatures at a fixed rpm in the longitudinal and transverse directions. The behaviour is more or less similar to those of the variations of the tensile strength.

Table 2 shows the variation in swelling index and Brookfield viscosity values of gum SBR vulcanizates and extrudates, respectively. It may be observed that the samples which give maximum physical properties show the least swelling index or maximum cross-link density. Moreover, starved extrusion results in higher viscosity values of the solutions due to lower mechanical breakdown.

Table 3 shows the variation of swelling index and percentage bound rubber content of the filled SBR vulcanizates. As in the case of gum vulcanizates the least swelling index value (maximum cross-link density) is observed for the extruded samples, and it shows the maximum strength. Further, the maximum in physical properties is obtained for the vulcanizates having the maximum bound rubber content. This behaviour is expected since bound rubber (insoluble black gel containing all the black and part of the rubber) has long been recognized as an important factor in the proper rubber-filler interaction and hence in rubber properties [16]. The tensile fracture surface of the starved fed vulcanizate is compared with those of the normal fed and unextruded samples in Figures 9(a)–(c). The starved fed sample shows a continuous orientation pattern arranged in regular order, while such regularity is not observed in the case of unextruded or normally fed samples.

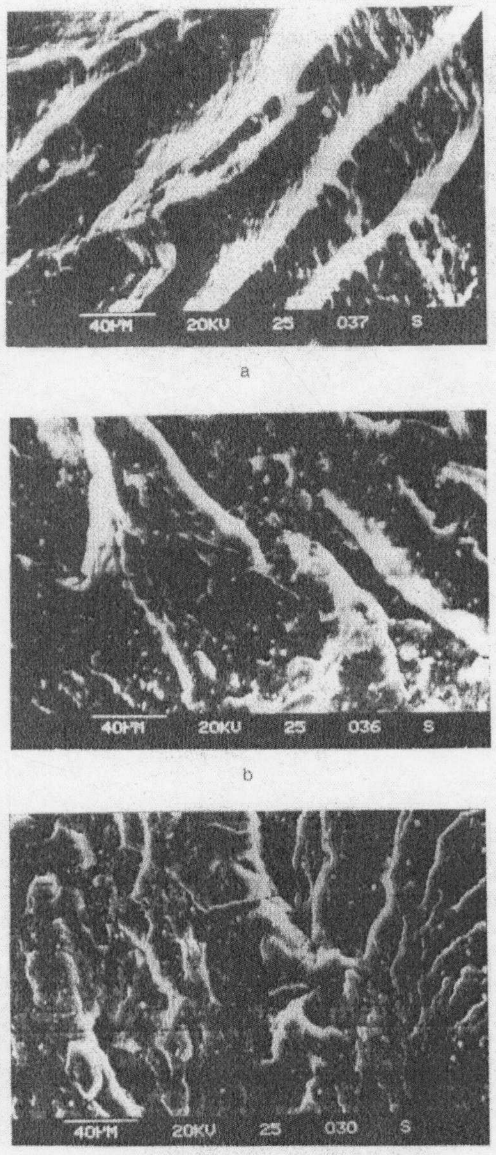

Figure 9. SBR extruded starved fed sample (a); SBR extruded normally fed sample (b); SBR unextruded sample (c).

CONCLUSION

Starved feeding in extrusion results in better heat transfer characteristics, proper preferential orientation, less mechanical breakdown and hence in a more uniform cross-link density and rubber-filler interaction. For a given screw, there is an optimum feeding rate in the starved fed region which results in maximum physical properties. So running an extruder at a slightly starved condition is an attractive means of improving the physical properties in addition to running the extruder at a lower torque.

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