Influence of Some Additives on State-of-Mix, Rheological, Tensile, and Dynamic Mechanical Properties in SBR Compounds

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ABSTRACT: The influence of some additives (Flexon processing oil, Struktol WB 16 slipping agent, and Struktol NS 60 homogenizing resin) on state-of-mix, rheological, tensile, and dynamic mechanical properties were investigated. It was found that extrudate swell of the rubber compounds with either processing oil or NS 60 is governed mainly by the state-of-mix, but by wall slip in the case of compounds with WB 16. As for the dynamic mechanical properties, the plasticizing effect is the major factor controlling the properties in the case of processing oil, while the degree of crosslink and dilution effect are the main factors in the case of NS 60. Both degree of crosslink and state-of-mix are responsible for the dynamic mechanical properties in the case of WB 16. In addition, it was found that the tensile properties are controlled mainly by the plasticizing effect in the case of processing oil, but by the degree of crosslink in the cases of WB 16 and NS 60. J Appl Polym Sci 80: 2474–2482, 2001

Key words: state-of-mix; effective filler volume fraction; tensile properties; dynamic mechanical properties; rheological properties

INTRODUCTION

It is known that in rubber compounding, some additional additives are used, apart from the conventional fillers and curatives. Some additives, including plasticizers and processing lubricants, are used to improve processability. In other words, such additives reduce compound viscosity, leading to a reduction in energy consumption and thus production cost.[1] Another group of additional chemicals is used to improve filler dispersion and extrudate surface quality, as well as physical properties of rubber compounds.[2–8] Examples of chemicals in this class are homogenizers (or dispersing agents) and slipping agents (or external lubricants). It has been reported that the state-of-mix (i.e., carbon black dispersion) plays a significant role in rheological properties of uncured rubber compounds, as well as in physical and dynamic mechanical properties in cured compounds.[9–11] Also, it has been reported that the addition of some additives influences the state-of-mix (i.e., carbon black dispersion), and thus rheological properties of the uncured rubber.[12]

The present study aims to further previous work[12] by investigating the influence of some ad-

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Table I Compounding Formulation Used in the Present Study

Ingredient	Amount Used (phr)
SBR 1502 (JSR, Japan)	100.0
ZnO (white seal, Chemmin Co. Ltd., Thailand)	5.0
Stearic acid (Polychem Co. Ltd., Thailand)	2.0
Carbon black N330 (Thai Carbon Product Co. Ltd., Thailand)	30.0
CBS (Santocure, Monsanto Co. Ltd.)	1.5
Sulphur (Chemmin Co. Ltd., Thailand)	2.5
Additives studied[a]	2.0, 4.0, 8.0, 16.0, and 20.0

[a] Flexon processing oil (Exxon Co. Ltd.), Struktol WB 16 (Struktol Co., USA), Struktol NS 60 (Struktol Co.).

ditives, Flexon processing oil, Struktol WB 16 slipping agent, and Struktol NS 60 homogenizer, on state-of-mix, rheological, tensile, and dynamic mechanical properties in SBR compounds.

EXPERIMENTAL

Materials

The compounding formulation used in the present study is given in Table I.

Mixing and Vulcanization

Mixing was carried out in a 1.2-l Banbury internal mixer with a fill factor of 0.5, a circulating water temperature of 40°C, and a rotor speed of 40 rpm. The mixing sequence is shown in Table II.

Curing time to be used for curing compounds was determined from the Oscillating Disk Rheometer (Monsanto model 100S) at the test temperature of 155°C. Then, rubber compounds were compression molded under a pressure of 15 MPa at 155°C using a hydraulic hot press.

Table II Mixing Sequence Used in the Study

Time (min)	Action
0	Add raw rubber
2	Add ZnO, stearic acid, and CBS
4	Add carbon black
9	Add additives studied
14	Add sulphur
16	Dump and sheet on the mill

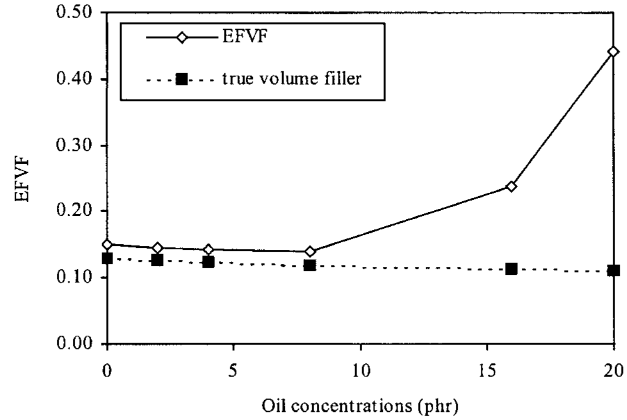

Figure 1 Influence of oil concentration on state-of-mix (as determined from EFVF).

State-of-Mix Determination

According to previous work,[7,9–12] the state-of-mix was determined from the values of effective filler volume fraction (EFVF or ϕ_e) that can be quantified using eq. (1), based on the release of immobilized rubber as the state-of-mix increases. The lower the EFVF, the higher the state-of-mix:

$$\phi_e = (\alpha \phi_a) + \phi_t \quad (1)$$

where α is the volume fraction of immobilised rubber in an agglomerate (0.647 for N330, from

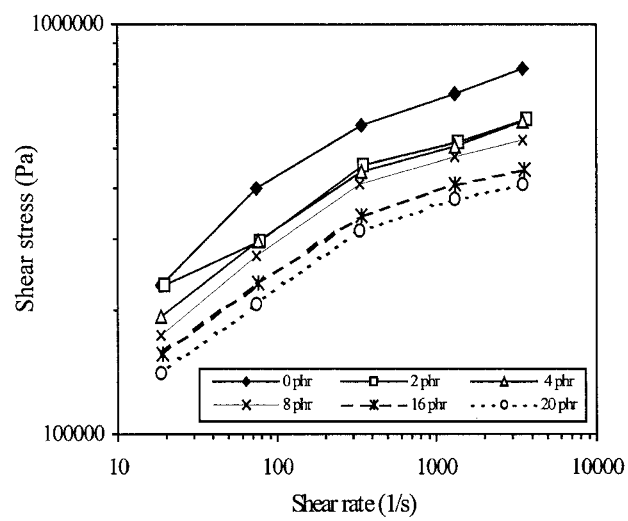

Figure 2 Influence of oil concentration on flow properties.

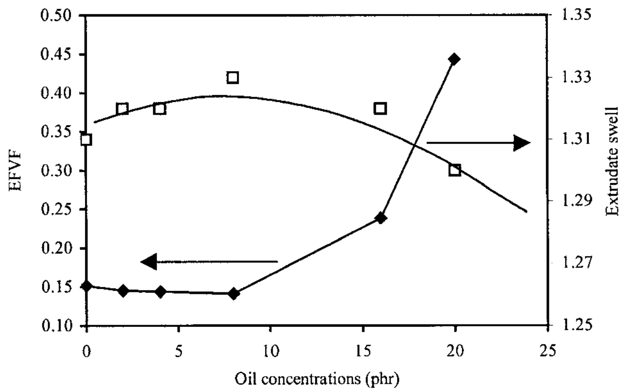

Figure 3 Influence of oil concentration on extrudate swell and EFVF.

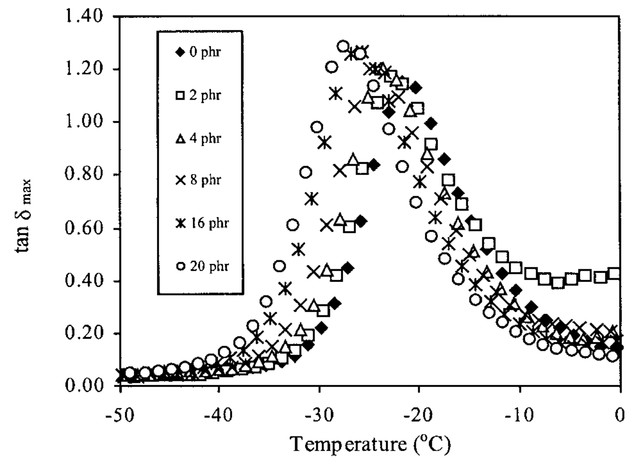

Figure 4 Influence of oil concentration on tan δ_{max}.

the DBP absorption value)[9]; ϕ_a is the volume fraction of agglomerates (equivalent to area fraction of agglomerates in thin section); and ϕ_t is the true volume fraction of carbon black (as calculated from the true density of carbon black, 1.8 g/cm^3).[9]

Determination of Rheological Properties

Rheological properties of the compounds were measured using a capillary rheometer (Rosand 612) with two dies of 2-mm diameter and L/D ratios of about zero (orifice die) as well as of 16 at the test temperature of 100°C. Extrudate swell was calculated from a ratio of extrudate to die diameters.

Degree of Crosslink Measurement

Approximately 0.2 g of vulcanized rubber was immersed in 30-mL toluene for 7 days at room temperature. The swollen specimens were blotted with filter paper and transferred quickly for weighing. Degree of crosslink was represented in terms of reciprocal swollen ratio, as shown in eq. (2):

$$\frac{1}{\text{swollen ratio}} = \frac{w}{w_s - w} \qquad (2)$$

where w is the weight of the unswollen rubber (g) and w_s is the weight of the swollen rubber (g).

Measurement of Dynamic Mechanical Properties

Dynamic mechanical properties of rubber vulcanisates were measured using the dynamic mechanical analyzer (Polymer Laboratories Mk II) in a bending mode with a peak to peak displacement of 64 μm. Measurements were carried out at

Table III tan δ_{max} and Glass Transition Temperatures of Compounds with Various Oil Concentrations

Levels of Oil (phr)	tan δ_{max}	T_g (°C)
0	1.15	−20.95
2	1.17	−22.68
4	1.20	−23.38
8	1.21	−24.10
16	1.26	−25.59
20	1.30	−26.66

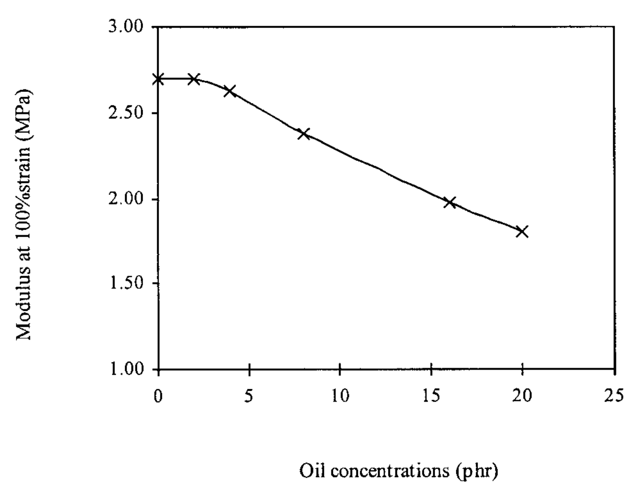

Figure 5 Influence of oil concentration on modulus at 100% strain.

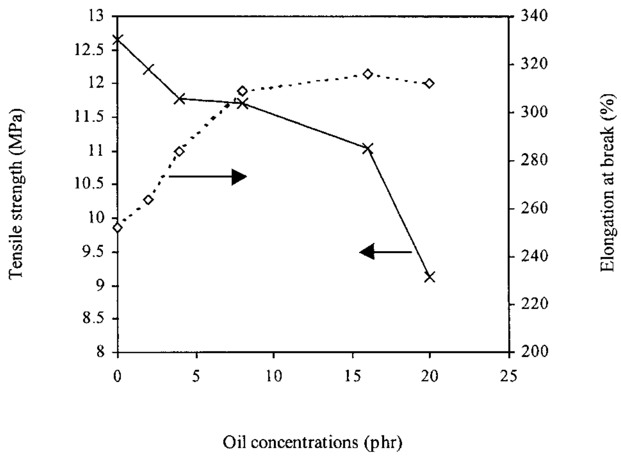

Figure 6 Influence of oil concentration on tensile properties.

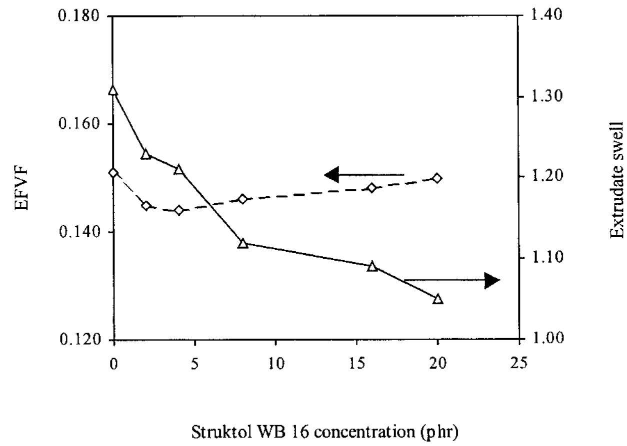

Figure 8 Influence of Struktol WB 16 concentration on extrudate swell and EFVF.

the temperature range of −100 to 50°C at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Influence of Flexon Processing Oil

State-of-Mix and Rheological Properties

It can be seen from Figure 1 that EFVF values are almost close to the true volume fraction of carbon black when the processing oil concentration is up to 8 phr, indicating the independence of oil loading on black dispersion. Above 8 phr of oil concentration, values of EFVF diverge from those of the true volume fraction of filler, indicating the reduction in carbon black dispersion with increasing oil concentration. The decrease in black dispersion can be caused by wall slip during mixing and/or by a reduction in viscosity, leading to a reduction in shear stress level for carbon black disagglomeration during mixing. Previous work[12] shows that the viscosity reduction caused by the plasticizing effect of oil, as shown in Figure 2, is responsible for a decrease in black dispersion.

From Figure 3, it can be seen that the extrudate swell increases with increasing oil concentrations up to 8 phr. Above this concentration, the extrudate swell decreases with further increasing oil concentration. The changes in extrudate swell can be explained by changes in effective filler volume fraction, i.e., the extrudate swell is controlled by a dilution effect at low oil concentra-

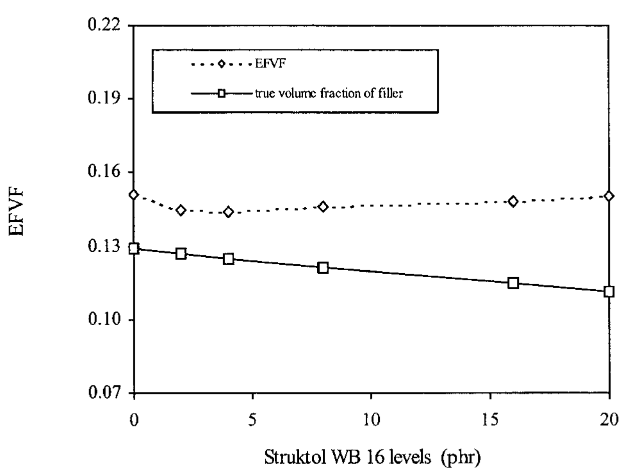

Figure 7 Influence of Struktol WB 16 concentration on state-of-mix (as determined from EFVF).

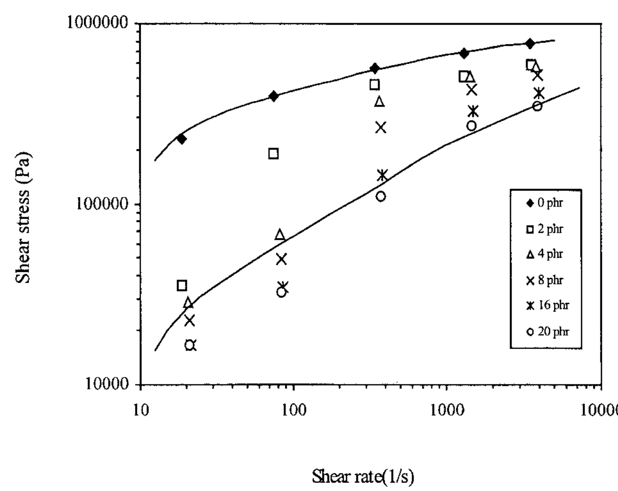

Figure 9 Influence of Struktol WB 16 concentration on flow properties.

Table IV tan δ_{max} and Glass Transition Temperature of Compounds with Various Struktol WB 16 Concentrations

Levels of Struktol WB 16 (phr)	tan δ_{max}	T_g (°C)
0	1.15	−20.95
2	1.15	−22.27
4	1.12	−22.21
8	1.01	−21.96
16	0.87	−22.24
20	0.85	−22.87

tions and by the state-of-mix at high processing oil concentrations. Details of the dependence of extrudate swell on EFVF have been reported previously.[9–10]

Dynamic Mechanical Properties

From Table III and Figure 4, it is evident that the position of the damping peak shifts toward the lower temperature and the peak height increases with increasing oil concentrations, indicating higher molecular mobility due to the plasticizing effect.[13]

Tensile Properties

Figures 5 and 6 reveal that modulus at 100% strain decreases with processing oil concentration. Elongation at break increases, whereas the tensile strength decreases with increasing oil concentration. The key factor responsible for the results obtained is the plasticizing effect caused by the addition of processing oil.[13]

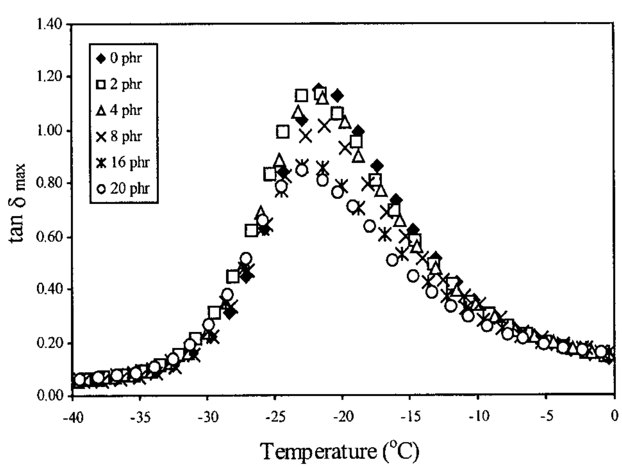

Figure 10 Effect of Struktol WB 16 concentration on tan δ_{max}.

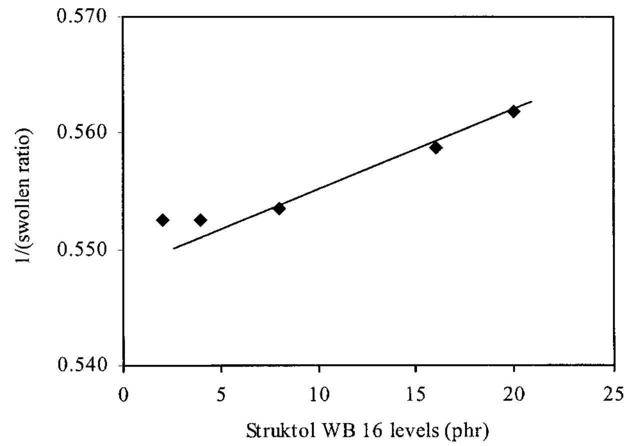

Figure 11 Effect of Struktol WB 16 concentration on degree of crosslink.

Influence of Struktol WB 16

State-of-Mix and Rheological Properties

From Figure 7, it can be seen that EFVF of compounds with Struktol WB 16 concentration up to 4 phr is close to the true volume fraction of carbon black, indicating no effect on black dispersion. Above the concentration of 4 phr, EFVF slightly diverges from the true volume fraction of filler due to the slippage produced by Struktol WB 16, yielding the reduction in stress levels for black disagglomeration during mixing. For the extrudate swell result illustrated in Figure 8, it can be seen that the extrudate swell decreases with an increase in Struktol WB 16 concentration. Therefore, the decrease in extrudate swell is mainly caused by wall slip, i.e., Struktol WB 16 acts as an external lubricant at the die wall. Wall slip leads

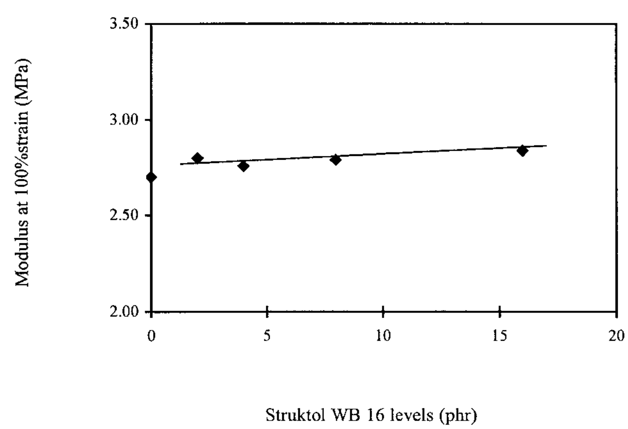

Figure 12 Effect of Struktol WB 16 concentration on modulus at 100% strain.

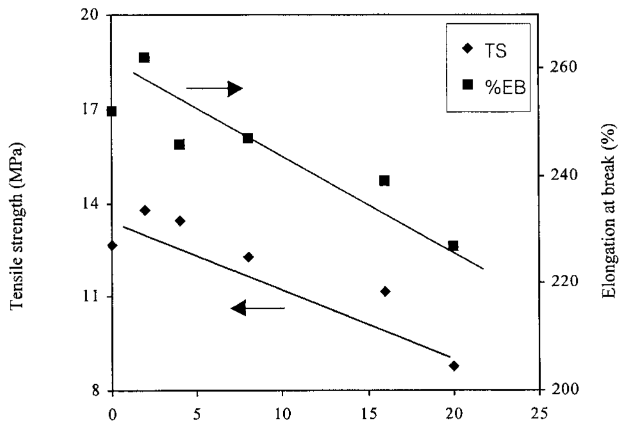

Figure 13 Effect of Struktol WB 16 concentration on tensile properties.

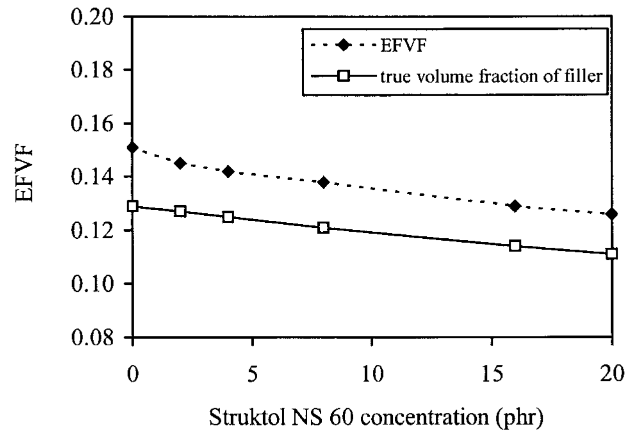

Figure 15 Influence of Struktol NS 60 concentration on state-of-mix (as determined from EFVF).

to a drastic reduction in shear stress of flow, as shown in Figure 9, and thus a decrease in energy applied to the rubber molecules. This result is in agreement with that of previous work.[12]

Dynamic Mechanical Properties

Table IV and Figure 10 reveal that the damping peak height decreases with an increase in Struktol WB 16 concentration, which can be explained by the increase in crosslink density, as shown in Figure 11, and/or an increase in EFVF.[10]

Tensile Properties

From Figures 12 and 13, it is obvious that the effect of Struktol WB 16 on the modulus at 100% strain is different from that of Flexon oil. Modulus slightly increases with increasing Struktol WB 16 concentration. Elongation at break appears to decrease with a progressive increase in Struktol WB16 concentration. Tensile strength is found to decrease with increasing Struktol WB16 concentration. The possible key responsible for the tensile results is the increase in degree of crosslink with increasing Struktol WB 16 concentration, as shown in Figure 11. According to Figure 14, with increasing degree of crosslink, modulus increases, while tensile strength increases and then decreases.[14–15] As a consequence, as Struktol WB 16 concentration increases, the relationship between tensile properties and degree of crosslink is in zone 3 of Figure 14.

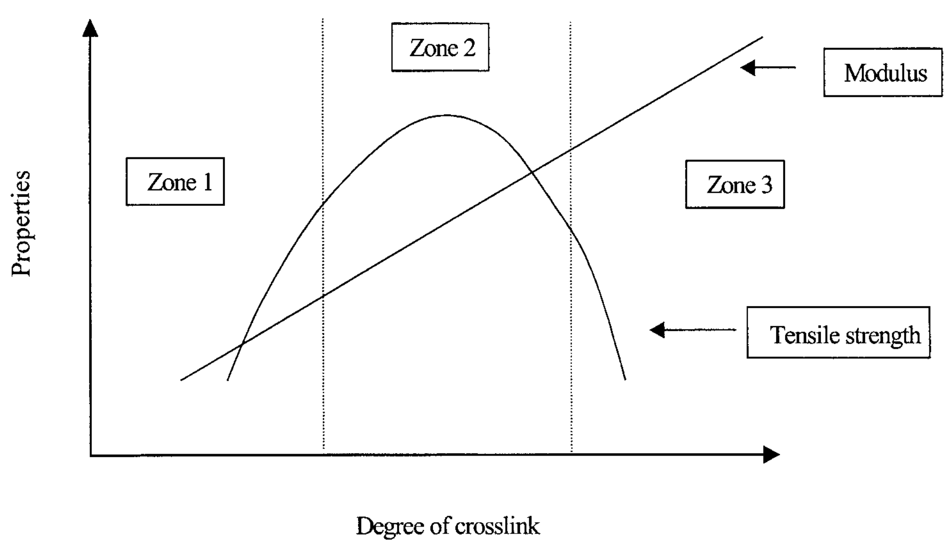

Figure 14 Relationship between degree of crosslink and tensile properties.

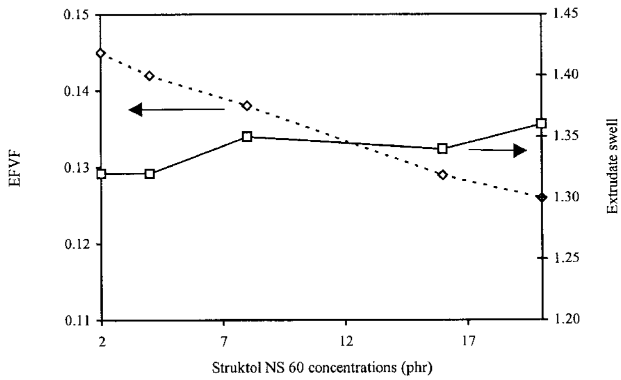

Figure 16 Influence of Struktol NS 60 concentration on extrudate swell and EFVF.

Influence of Struktol NS 60

State-of-Mix and Rheological Properties

It can be seen from Figure 15 that EFVF decreases with increasing Struktol NS 60 concentrations, with a trend similar to the true volume fraction of carbon black. In other words, the decrease in EFVF is due to the dilution effect. When higher Struktol NS 60 concentrations are added, the state-of-mix is not affected, which is opposite to the cases of oil and Struktol WB 16. The extrudate swell appears to increase with increasing Struktol NS 60 concentrations, as shown in Figure 16. It is clear that the extrudate swell result is agreement with the EFVF result, indicating that the change in state-of-mix caused by addition of Struktol NS 60 plays a significant role in extrudate swell.

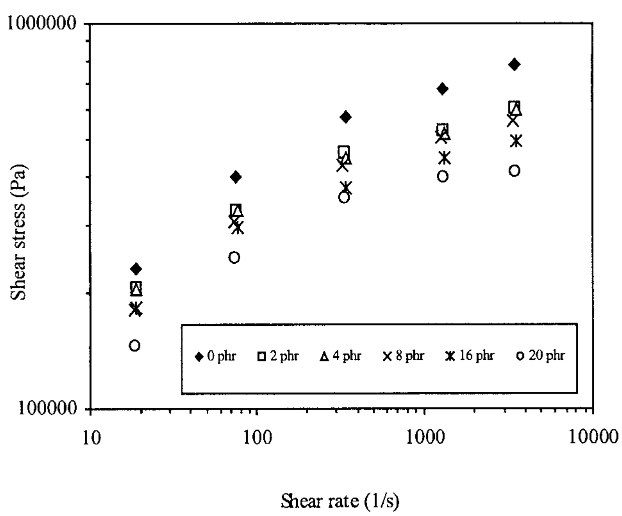

Figure 17 Effect of Struktol NS 60 concentration on flow properties.

Table V tan δ_{max} and Glass Transition Temperatures of Compounds with Various Struktol NS 60 Concentrations

Levels of Struktol NS 60 (phr)	tan δ_{max}	T_g (°C)
0	1.18	−22.82
2	1.21	−23.24
4	1.20	−22.65
8	1.17	−21.43
16	1.15	−20.55
20	1.16	−19.82

The reduction in shear stress with increasing Struktol NS 60 concentrations, as shown in Figure 17, is possibly caused by slippage and/or plasticizing effects.

Dynamic Mechanical Properties

It can be seen from Figure 18 and Table V that the tan δ_{max} seems to slightly increase as the Struktol NS 60 is added up to 4 phr, which could be explained by a decrease in degree of crosslink, as shown in Figure 19. Above this concentration, dilution effect is a key factor controlling a decrease in tan δ_{max} with increasing Struktol NS 60, because the excessive NS 60 resins could possibly act as undeformable reinforcing filler to compounds.

Determination of Tensile Properties

It can be seen from Figures 20 and 21 that modulus at 100% strain of compounds decreases with

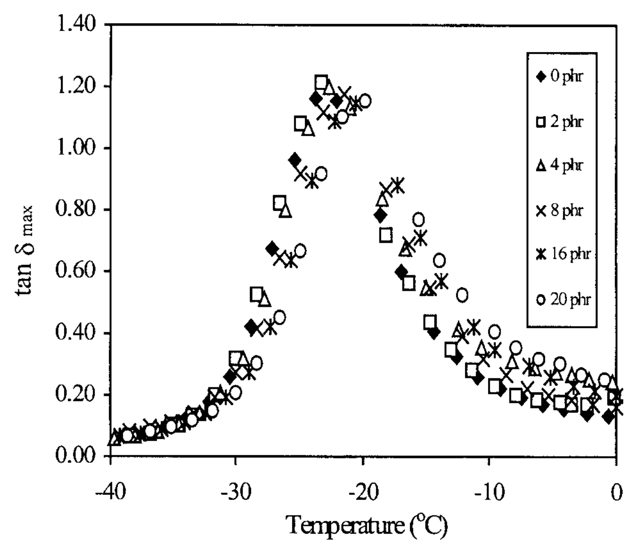

Figure 18 Effect of Struktol NS 60 concentration on tan δ_{max}.

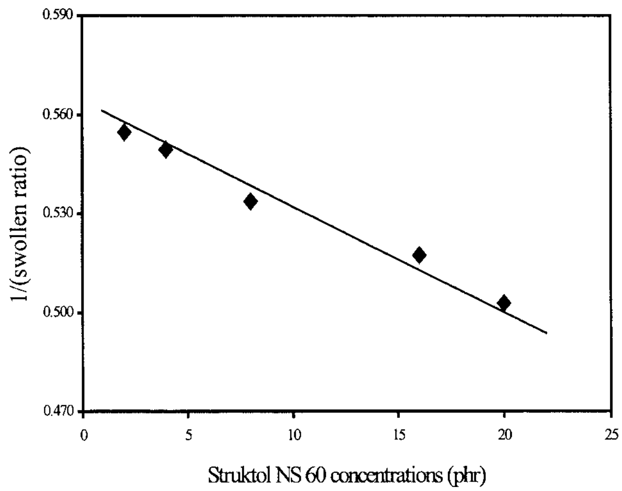

Figure 19 Relationship between degree of crosslink and Struktol NS 60 concentrations.

increasing Struktol NS 60 concentration. Percent elongation at break increases with Struktol NS 60 concentration, while the maximum tensile strength is observed at the Struktol NS 60 concentration of 4 phr. The decrease in degree of crosslink is responsible for the results obtained, i.e., the relationship between tensile properties and degree of crosslink is in zone 2 of Figure 14.

CONCLUSION

The influence of some additives (Flexon processing oil, Struktol WB 16 slipping agent, and Struktol NS 60 homogenizing resin) on state-of-mix, rheological, tensile, and dynamic mechanical

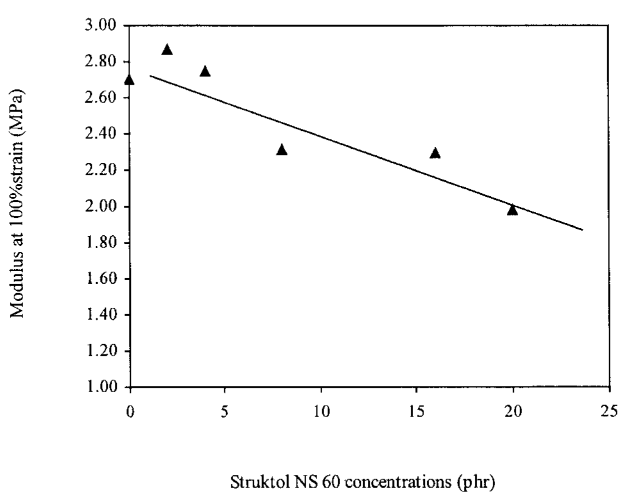

Figure 20 Effect of Struktol NS 60 concentration on modulus at 100% strain.

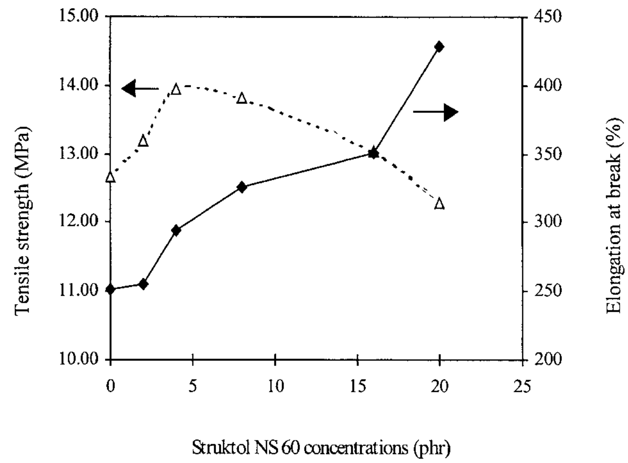

Figure 21 Effect of Struktol NS 60 concentration on tensile properties.

properties were investigated. The following conclusions can be drawn.

The extrudate swell results of the rubber compounds containing either processing oil or Struktol NS 60 are controlled mainly by the EFVF or state-of-mix. For compounds with Struktol WB 16, wall slip causes a significant decrease in extrudate swell.

As for the influence of some additives on dynamic mechanical properties of rubber compounds, it was found that: In the case of Flexon processing oil, the major factor governing the damping properties is the plasticizing effect; in the case of Struktol NS 60, degree of crosslink and dilution effect control the damping properties; and in the case of Struktol WB 16, both degree of crosslink and EFVF control the damping properties.

Regarding the effects of some additives on tensile properties, it was found that: In the case of processing oil, plasticizing effect controls tensile properties; and in the cases of Struktol WB 16 and NS 60, the major factor governing tensile properties is the degree of crosslink. Financial support from the National Metal and Materials Technology Center (MTEC) and from the Polymer Technology Research and Development Center, Institute of Science and Technology for Research and Development, is gratefully acknowledged.

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