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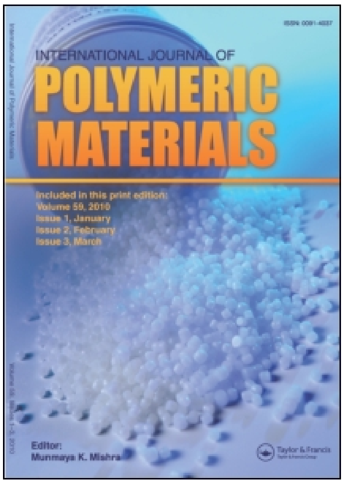

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Rheological Study of Filled SBR Compounds with Trans-Polyoctenylene (TOR) and their Interaction Mechanism

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To cite this Article Chattaraj, P. P. , Kalidaha, A. K. , Mukhopadhyay, R. , Bhattacharya, A. K. and Tripathy, D. K.(1996) 'Rheological Study of Filled SBR Compounds with Trans-Polyoctenylene (TOR) and their Interaction Mechanism', International Journal of Polymeric Materials, 33: 1, 73 — 87

To link to this Article: DOI: 10.1080/00914039608028609

URL: http://dx.doi.org/10.1080/00914039608028609

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Intern. J. Polymeric Mater., 1996, Vol. 33, pp. 73–87
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Rheological Study of Filled SBR Compounds with Trans-Polyoctenylene (TOR) and their Interaction Mechanism

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(Received October 18, 1995)

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The purpose of this study is to find the suitability of a crosslinkable processing aid, trans-polyoctenylene (TOR) on general purpose rubber based filled compounds for application in thick rubber products. Objective is to have better processability as well as improvement in vulcanizate properties using TOR. Thus to investigate its effect as processing aid, rheological behaviour of TOR filled Styrene butadiene rubber (SBR) compounds has been studied in a capillary rheometer. Two types of carbon black were used. All compounds show pseudoplastic behaviour and obey Power-law equation in the shear rate range studied. True viscosity decreases marginally at 60°C and increases little at 100°C with addition of TOR. Die swell (index) decreases with incorporation of TOR, a probable mechanism has been suggested. Maximum recoverable deformation (ν_m) has been correlated with die swell (α). Principal normal stress difference (N_1) decreases with increase in TOR which is explained through mechanistic theory of particle-particle interaction. Incorporation of TOR in the system lowers activation energy of flow. Study concludes with selection of TOR dose.

KEY WORDS: Pseudoplastic behaviour, die swell (index), pseudostructure, principal normal stress difference, activation energy, entanglements, rheology, SBR, filled compounds, polyoctenylene.

1. INTRODUCTION

Manufacturing of rubber product is a complex process involving two important steps i.e. mixing and processing of unvulcanized compounds. Behaviour of polymer and polymeric compound during these unit operations depends upon how they respond to applied stress and deformation. This is known as rheological properties. Study on flow property of elastomers and its compound dates back to 1820's. There are many review papers on processability and rheological properties[1–2] of rubber. Reports on

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processing and rheological analysis of carbon black filled SBR are also available in recent literature.[3] Nevertheless, use of processing aids (generally 1–10 phr) is well established in the rubber industry[4] which are mostly petroleum oils. Effect of aromatic, napthanic and other petroleum oils on rheological behaviour of rubber compounds has been investigated by many scientists.[5–7]

However, the new class of processing aids that has been developed gives trouble free processing of the rubber compound and better long term properties. They are different from conventional processing aids (oil) as they do not leach out,[8] have minimum diffusion/migration property[8] from surface to bulk and also do not affect the vulcanizate properties[8] of a product. They are solid in nature unlike oils thus making handling easier and reducing spillage hazards in the working area. TOR, mixture of hydrocarbon resins (aromatic and aliphatic), fatty acid derivatives are few of this new class. Present work is confined to TOR only with a view to understand the suitability of this new polymer[9,10] as a processing aid in general purpose rubbers for application in thick rubber article, sacrificing even little in cost. However, available literature[11] on TOR is less particularly with respect to rheological studies. Thus, considering various applications of carbon black reinforced SBR compounds (in suitable areas of tyre, hose, conveyor belt, etc.) initial attempt has been made to present results on rheological properties of filled SBR compounds (with curatives) in presence of TOR using single capillary rheometric measurement. Very low shear rates[12] were used in the study to understand basic rheological response of the compounds. Besides viscous and elastic effect, a theoretical model has been developed to calculate ν_m from experimentally measurable parameter like α. Activation energy of flow was calculated to examine the effect of TOR on energy conservation during processing. 10–20 parts of TOR has been found as optimum dose for processing in a typical SBR filled (HAF and ISAF) compound.

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2. EXPERIMENTAL

Details of the material used are given in Table I. Mixing (formulation in Table II) was done in two steps (masterbatch and final) in a laboratory Banbury as reported previously.[13]

Rheological measurements were carried out in a Monsanto processability tester (MPT). The test was conducted using different capillary having *l/d* ratios of 20, 10, 5 and 1 (for Bagley correction) at different apparent shear rates viz. 36.5, 91, 182, 455 $\sec^{-1}$. Extrusion temperatures were 60, 80, 100, 120, 140°C. However to avoid repetition, the test results of the compounds concerning all *l/d* ratios, shear rates and temperatures have not been reported in this paper, rather a representative combination of each of these variables has been given. The die swell (at the exit of the die as soon as the extrudate comes out) was directly recorded from the laser scanning system attached with the instrument. The detailed procedure of MPT is discussed in literature.[14]

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TABLE I

Details of materials used

Material	Characteristics	Source
Styrene-butadiene rubber	1502 grade, ML_{1+4} at 100°C = 49	Nippon Zeon Co. Tokyo, Japan
Trans-polyoctenylene (TOR)	8012 grade, m.p.=54°C Tg = -65°C Cis:20%, Trans:80%	HÜLS, Germany
High abrasion furnace black (HAF)	N 330, Surface area =80 m^2g^{-1}	Thai Carbon Ltd., Thailand
Intermediate super abrasion furnace Black (ISAF)	N 220, Surface area =120 m^2g^{-1}	---Do---
N-Cyclohexyl benzothiazyl sulfenamide (CBS)	Rubber grade	Bayer (I) Ltd. India
Sulfur, ZnO, Stearic acid etc.	Rubber grade	Standard suppliers of India.

TABLE II

Compound formulation*

Ingredients	A	C	E	G	A1	C1	E1	G1
HAF(N330)	70	70	70	70	-	-	-	-
ISAF(N220)	-	-	-	-	60	60	60	60
TOR	0	5	10	20	0	5	10	20

*All compounds contain; SBR-1502:100, ZnO:4, Stearic Acid:3, S:1.75, CBS:1

3. CALCULATION OF RHEOLOGICAL PARAMETERS

The apparent shear stress (τ_a), apparent shear rate ($\dot{\gamma}_a$), and apparent viscosity (η_a) were calculated using the following equations[15]

$$\tau_a = d\Delta P/41 \ldots \tag{1}$$

$$\dot{\gamma}_a = 32Q/\pi d^3 \ldots \tag{2}$$

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TABLE III

Non-Newtonian index (n') and consistency index (K) of filled SBR compounds

Temp. (°C)	Compounds	l/d ratio							
		20 : 1		10 : 1		5 : 1		1 : 1	
		n'	K X 10^{-4} (Pa.$S^{n'}$)	n'	K X 10^{-4} (Pa.$S^{n'}$)	n'	K X 10^{-4} (Pa.$S^{n'}$)	n'	K X 10^{-4} (Pa.$S^{n'}$)
60	A	0.307	19.2	0.308	20.3	0.310	20.3	0.308	21.2
	C	0.300	19.8	0.297	19.9	0.300	19.5	0.304	19.6
	E	0.269	24.1	0.270	23.7	0.271	24.2	0.270	24.0
	G	0.239	30.4	0.242	30.0	0.245	30.5	0.235	30.1
	A1	0.308	18.3	0.310	18.5	0.310	20.0	0.305	19.0
	C1	0.286	21.5	0.285	21.1	0.282	21.8	0.285	21.0
	E1	0.251	26.8	0.255	26.9	0.250	25.7	0.251	27.0
	G1	0.204	36.4	0.206	36.5	0.206	36.0	0.207	35.7
100	A	0.167	17.1	0.170	17.2	0.168	17.0	0.170	17.1
	C	0.172	17.5	0.174	17.8	0.172	18.0	0.172	17.3
	E	0.191	17.8	0.191	17.8	0.195	17.6	0.192	17.5
	G	0.216	17.8	0.215	17.6	0.218	17.6	0.220	17.5
	A1	0.204	19.7	0.205	20.6	0.207	20.0	0.203	19.5
	C1	0.160	23.2	0.161	23.3	0.165	23.5	0.160	23.0
	E1	0.245	24.4	0.240	24.9	0.242	23.8	0.245	23.3
	G1	0.251	24.3	0.251	24.8	0.245	23.2	0.252	23.6

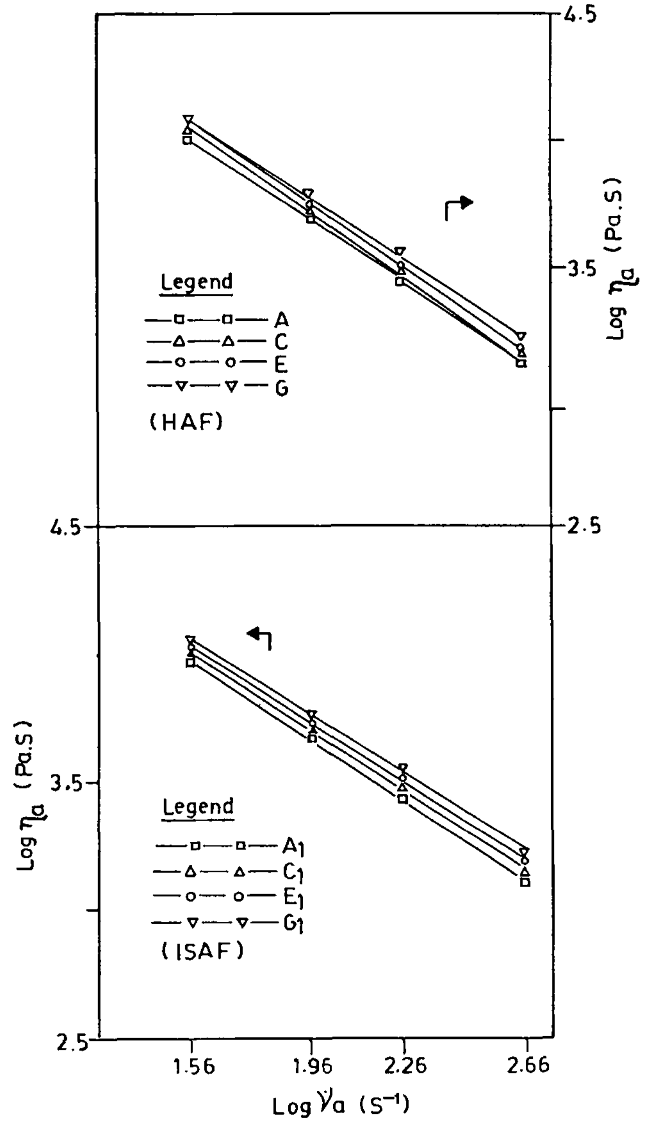

FIGURE 1 Apparent viscosity with apparent Shear rate at 100°C.

$$\eta_a = \tau_a/\dot{\gamma}_a \ldots \tag{3}$$

Within the shear rate range investigated log-log plots of τ_a vs $\dot{\gamma}_a$ showed linear relationship for all the compounds at different temperature and *l/d* ratios. The equations to those lines were obtained by linear regression using software. All the systems obeyed Power-law equation as follows

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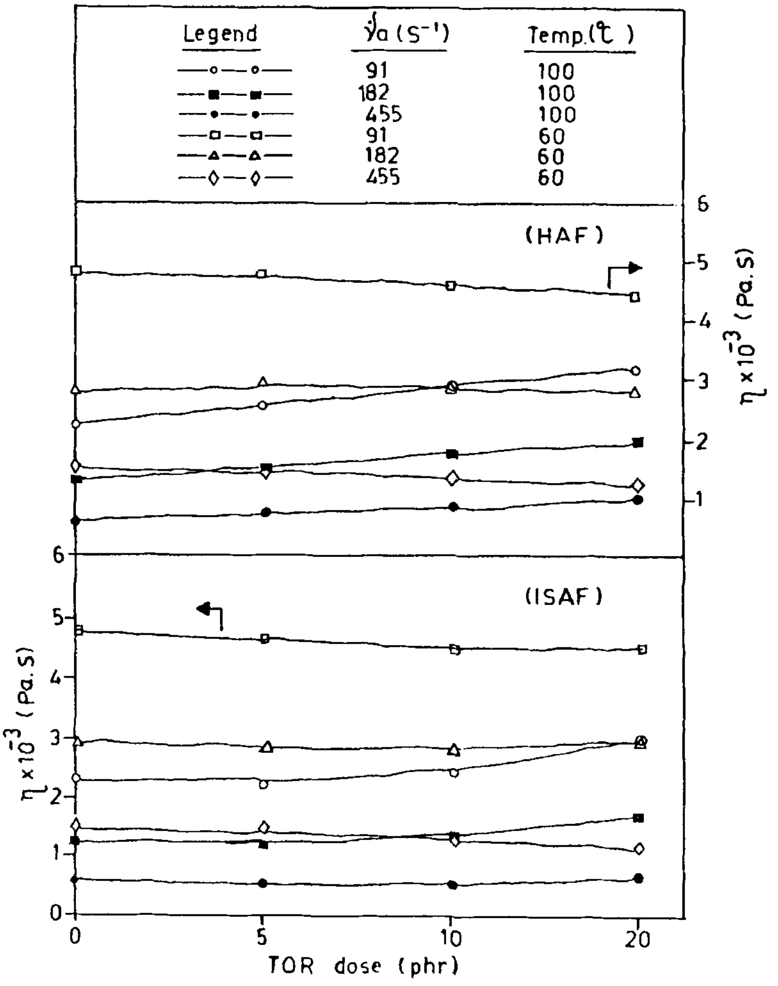

FIGURE 2 True viscosity with TOR dose at 100°C and 60°C.

$$\tau_a = K(\dot{\nu}_a)^{n'} \ldots \tag{4}$$

where n' is the slope and K is obtained from the intercept of the line.

True shear stress (τ_t), true shear rate ($\dot{\nu}_t$) and true viscosity (η) were calculated applying the correction factors as below[16]

$$\tau_t = \Delta P/4(l/d + l/d \text{ correction}) \ldots \tag{5}$$

$$\dot{\nu}_t = [(3n' + 1)/4n']\dot{\nu}_a \ldots \tag{6}$$

$$\eta = \tau_t/\dot{\nu}_t \ldots \tag{7}$$

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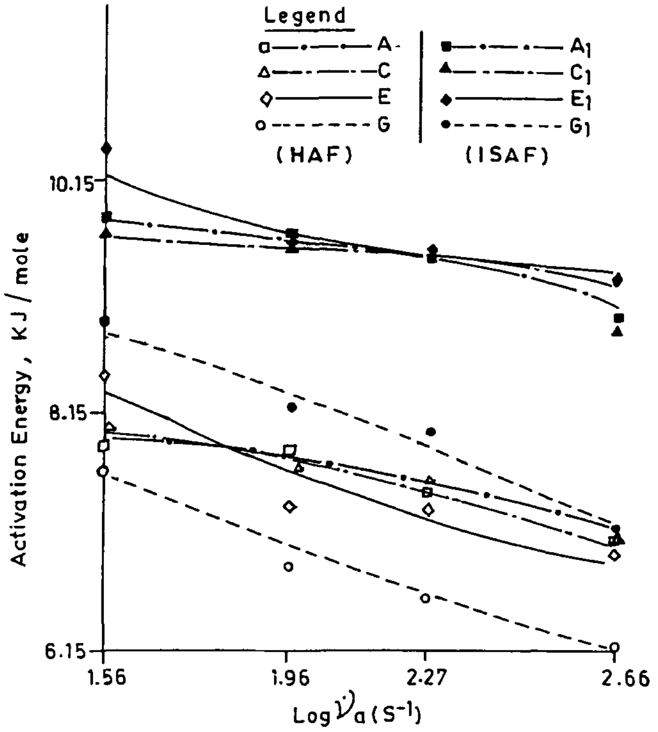

FIGURE 3 Activation energy with shear rate, $l/d = 20:1$.

where ΔP = pressure drop across the length of the capillary, d and l = diameter and length of the capillary respectively, Q = volumetric flow rate, n' = non-Newtonian index, K = consistency index [i.e. the viscosity (Pa·S$^{n'}$) at unit shear rate], $[(3n' + 1)/4n']$ = Rabinowitsch correction factor. Bagley correction[16] (Equation 5) and Rabinowitsch correction (Equation 6) were made in order to take care of the entrance pressure loss and rate of shear at the wall respectively.[15]

Activation energy (E_ν) of compound flow at a constant rate of shear was determined by using Arrhenius-Frenkel-Eyring formula.[17]

$$\eta_\nu = B \exp(E_\nu/RT) \ldots \tag{8}$$

where η_ν is the viscosity at a particular shear rate, B is a constant, R is gas constant and T is the absolute temperature.

ν_m has been calculated using the following equation[17]

$$\nu_m = [1/2C(\alpha^{-4} + 2\alpha^2 - 3)]^{0.5} \ldots \tag{9}$$

where C is a constant and is given by the relation

$$C = (3n' + 1)/4(n' + 1) \ldots \tag{10}$$

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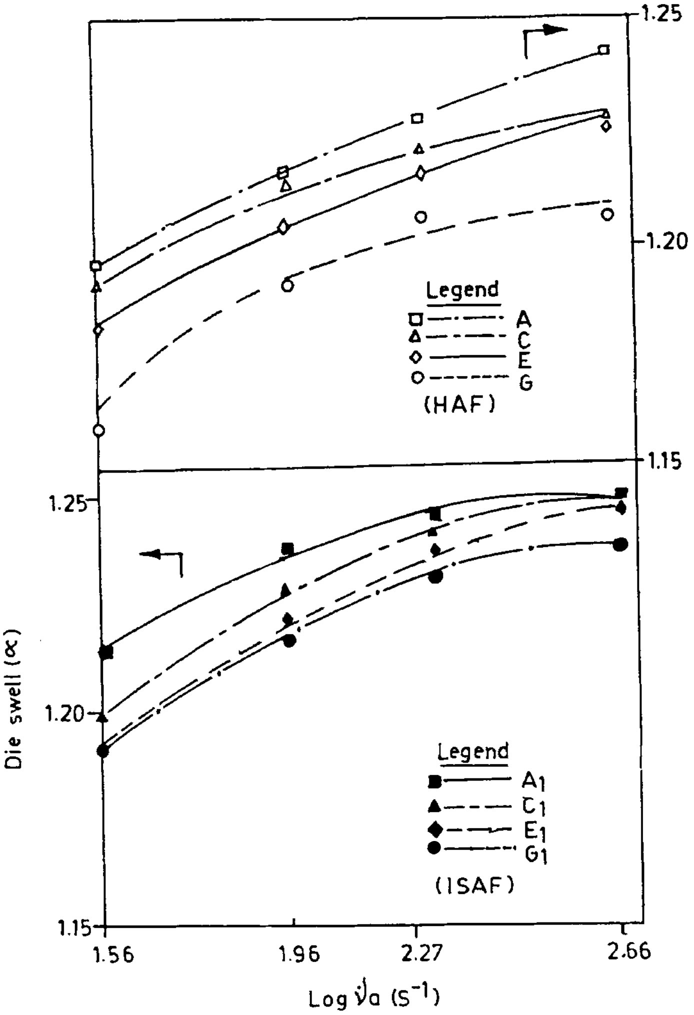

FIGURE 3a Die swell (α) with shear rate at 120°C, *l/d* = 20:1.

α, the swelling index[18] is the ratio of the extrudate diameter (d_e) to capillary diameter (d_c) as reported by Graessley *et al.*[19]

N_1 is calculated using the equation[17]

$$N_1 = [(2 + \nu_m)\nu_m/2(1 + \nu_m)]\tau_a \ldots \tag{11}$$

where τ_a is the apparent shear stress at a particular *l/d* ratio, temperature and apparent shear rate.

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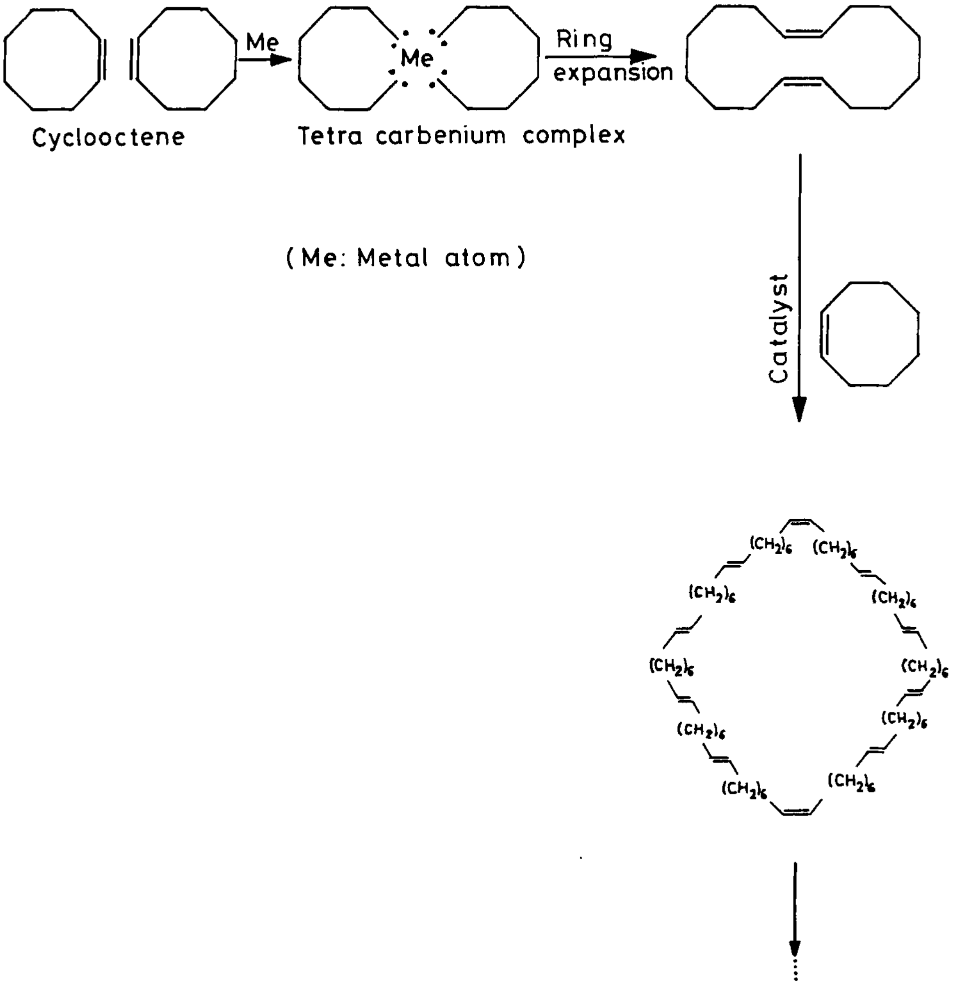

FIGURE 3b Metathesis polymerisation of cyclooctene and formation of macro-rings.

4. RESULTS AND DISCUSSION

4.1 Viscous Effect

Table III shows that non-Newtonian index (*n*′) at 60°C decreases with incorporation of TOR (minimum with 20 parts TOR) for all compounds and in all *l*/*d* ratios. At 100°C, *n*′ increases with incorporation of TOR (maximum with 20 parts TOR) for all compounds and in all *l*/*d* ratios. Consistency index (*K*) in all *l*/*d* ratios increases with addition of TOR at 60 and 100°C (comparatively more at 60°C). *n*′ and *K* values do not virtually change with *l*/*d* ratio of capillary for all compounds.

Figure 1 shows that at 100°C, apparent viscosity decreases with the apparent shear rate. Same is the trend at all temperature and in all *l*/*d* ratios (hence not re-

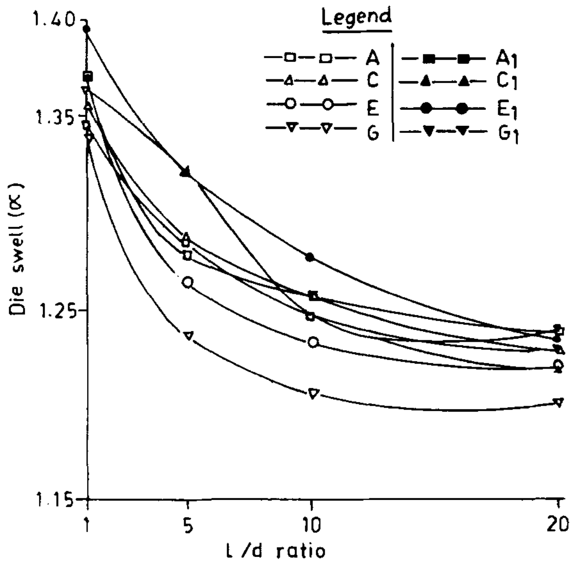

FIGURE 4 Die swell (α) with *l/d* ratio at 100°C.

ported)—showing the pseudoplastic behaviour of the compounds. At 60°C, true viscosity shows slight decreasing trend for TOR filled compounds at all shear rates as the melt viscosity of TOR is low at this temperature. However at 100°C, true viscosity (Figure 2) tends to increase marginally with TOR at all shear rates under study though m.p. of TOR is 55°C and its ML_{1+4} value at 100°C is approx. 5.[11] This seems anomalous and may be because of some thermally induced three dimensional pseudostructure[20] which are probably formed in compounds with TOR at 100°C. Marginal increase of viscosity with addition of TOR has also been seen in Figure 1. Since the viscosity of TOR filled compounds does not increase at lower temperature (60°C) it may be helpful for compound safety during processing at lower temperature. This shows that temperature has an effect on ways how TOR works as a processing aid. TOR is known to be a polymeric processing aid[11] which normally acts as a plasticizer.[21] However its polymeric nature is responsible for formation of pseudostructure at 100°C whereas its plasticizing effect reduces compound viscosity at 60°C.

4.1.1 Activation energy. Activation energy of flow at different shear rate has been determined from equation 8 for all compounds. At a particular shear rate activation energy marginally decreases (Figure 3) with addition of TOR which may be because of plasticizing effect of TOR.[21] TOR melts and dissolves easily during mixing and increases free volume in polymer chains which overall gives a plasticized mass.[22] It is also seen that energy decreases in general with increase in shear rate both for HAF and ISAF filled compounds.

4.2 Elastic Effect

Figure 3a shows that both in HAF and ISAF filled system die swell in all shear rate decreases marginally with incorporation of TOR. Polyoctenylenes contain 15% of

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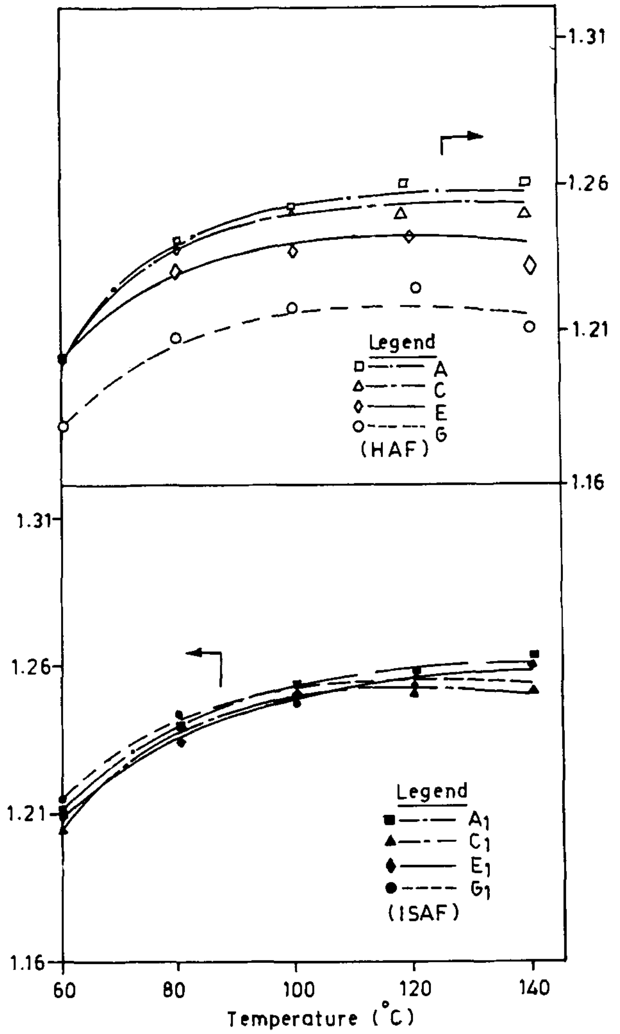

FIGURE 5 Die swell (α) with temperature at $\dot{\gamma}_a$ = 455 s^{-1}, l/d = 20:1.

cyclic oligomers having molecular weight up to 500 and 85% of acyclic polymers.[11] They do also have cyclic portions beyond the oligomer fraction.[11] Moreover they are metathesis polymer of cyclooctene (Figure 3b). It has been reported that during polymerisation of cyclooctene macro-rings of TOR (Figure 3b) form catena units. Thus a structure induced interaction[11] takes place between the long chain molecules of polymer and larger rings and perhaps catena units of TOR in the form of loose entanglements. These entanglements restrict the movement of polymeric chain just after they exit from the die which might account for thermal stability of the extrudate.[11] Such entanglements may be shown as follows:

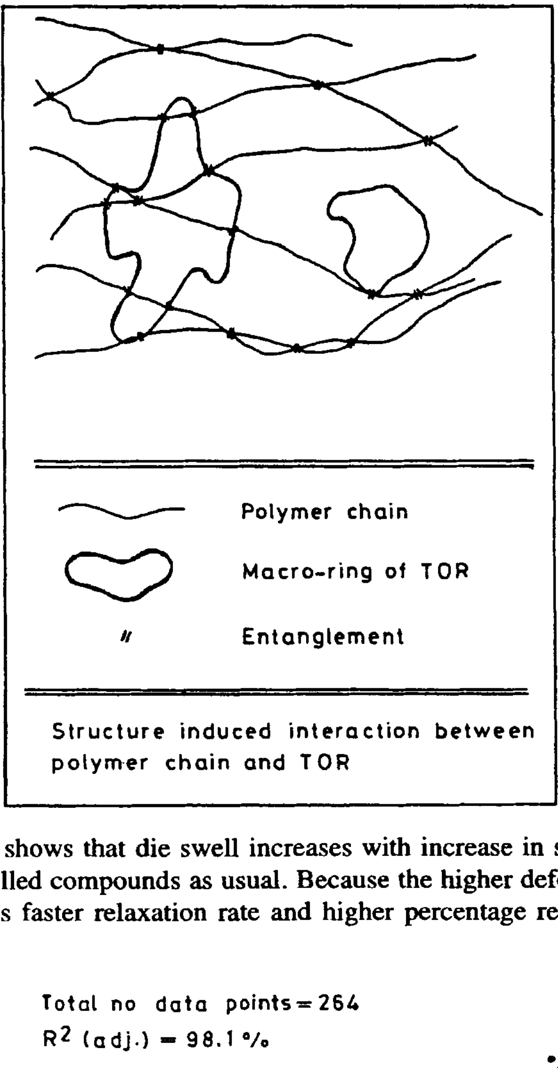

Figure 3a also shows that die swell increases with increase in shear rate for both HAF and ISAF filled compounds as usual. Because the higher deformation at higher shear rate induces faster relaxation rate and higher percentage recovery of original

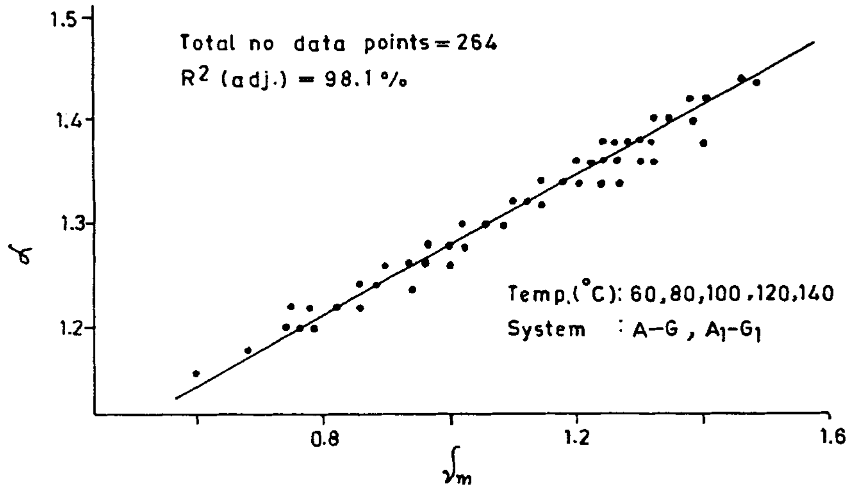

FIGURE 6 Correlation between die swell (α) with maximum recoverable deformation (ν_m).

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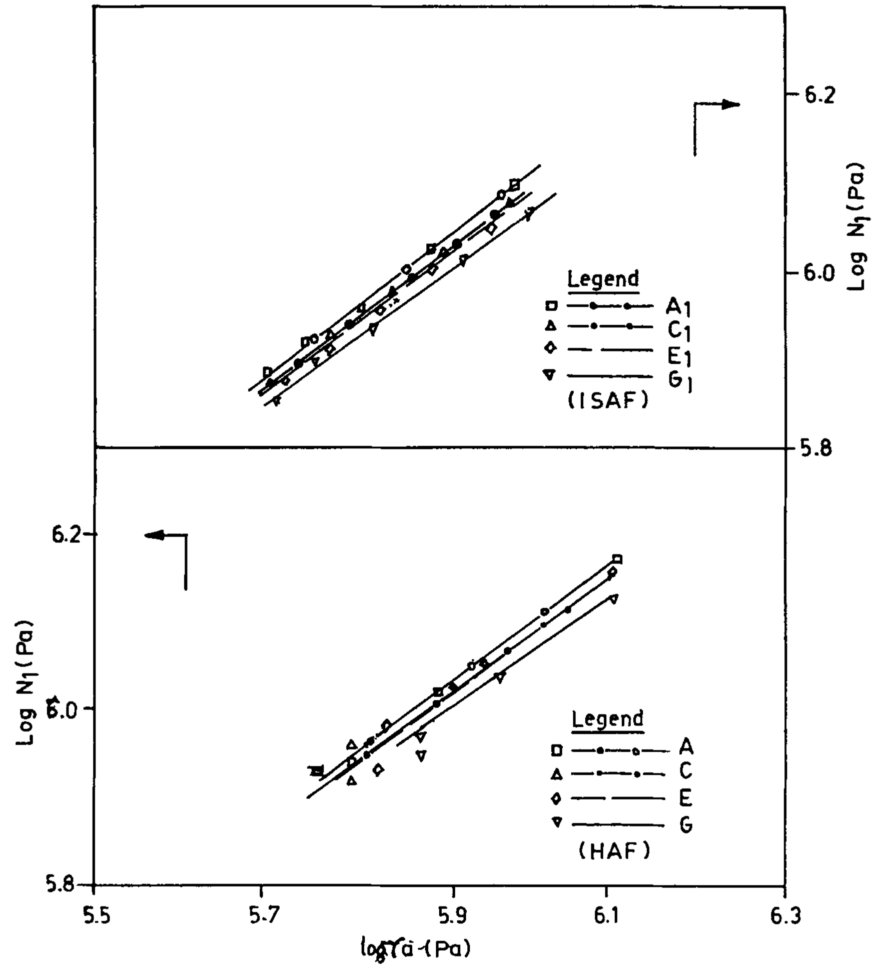

FIGURE 7 Principal normal stress difference with shear stress, *l/d* = 20:1, $\dot{\gamma}_a = 455\ s^{-1}$.

elastic stress.[23] Die swell decreases with increase in *l/d* ratio of the capillary for all compounds (Figure 4). This is probably because of the higher residence time of the compounds in the capillary of high *l/d*'s. As a result, a greater part of the elastic stress decreases within the capillary and die swell diminishes.[23] Die swell of compounds increases with increase in temperature till 100°C (Figure 5). It is known, as the temperature increases mobility of the polymer chain increases resulting increase of die swell which occurs in case of a gum compound. Probably the same theory works for filled system.

ν_m has been calculated (Equation 9) assuming the viscous response of rubber which obeys Power-law model and the elastic behaviour that obeys Hooke's law. Die swell is a qualitative manifestation of the recoverable deformation of the mix after the deformation force is withdrawn.[23] More and more is recoverable deformation, more is the die swell.[23] An attempt has been made to correlate ν_m with α and TOR dose for filled system. ν_m has been calculated for different system and plotted with die swell (Figure 6) which gives a straight line. Equation to this line is

$$\alpha = 0.36\nu_m + 0.94 \ldots \quad (12)$$

This relation is independent of filler type and TOR dose, temperature, shear rate and *l/d* ratio which has been obtained by single variable linear regression analysis using Linpack routines (total no. of points are 264, but all the points are not shown in figure as they will overlap). The equation can be applied for any other similar system to correlate recoverable deformation with die swell.

4.3 Mechanistic Theory of Suspension

Equation 11 has been used to calculate the principal normal stress difference (N_1) for the systems studied. Log-log plot of N_1 vs τ_a (Figure 7) shows a linear relationship with all the compounds and is independent of temperature. It is found that N_1 decreases with increasing TOR doses. White *et al.*[12] reported that large quantities of solid particles (filler) in polymers has good influence on both rheology and processability of the mix. He also reported that there are systems which have strong particle-particle (filler) interaction and hence exhibits yield values. Particle-particle interaction of filler is also known as inter-particle association which creates particle-polymer gel. This gel is responsible for origin of yield value in the system. Due to the formation of loose entanglements (as shown earlier) between polymer chain and TOR, more particle-polymer gel is probably formed in the compound containing TOR. Thus, yield value probably increases with TOR filled compounds which depress N_1. Change in temperature (80–140°C) has no effect on N_1 as the points for different temperatures lie on the same line. Figure 7 shows a set of parallel lines where slope value decreases slightly with incorporation of TOR in HAF as well as in ISAF filled compounds.

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5. CONCLUSIONS

1. All the systems under study show pseudoplastic flow. Temperature has an effect on working principle of TOR as a processing aid. At 60°C, it acts more as a plasticizer and hence true viscosity decreases with addition of TOR. At 100°C, it acts more as a polymer which results in formation of pseudostructure and thus viscosity increases marginally with addition of TOR.
2. Die swell marginally decreases with incorporation of TOR because of structure induced interaction between polymer and TOR which may reduce anisotropy in extruder and calender shrinkage.
3. A theoretical model has been developed to determine maximum recoverable deformation (ν_m) from die swell (α) in capillary flow.
4. N_1 decreases with TOR probably because of more particle-polymer gel formation.
5. Activation energy decreases with incorporation of TOR due to plasticizing effect.

6. Considering effect of TOR on true viscosity, die swell and activation energy optimum dose (of TOR) for processing in high filled SBR systems may be 10–20 parts depending on application.

Acknowledgements

Authors acknowledge permission of Institute to publish the work and they are thankful to M/S Hüls, Germany for giving the free sample of TOR for the work.

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