Melt Rheology of Ethylene Propylene Diene Rubber Modified with Phosphorylated Cashew Nut Shell Liquid Prepolymer

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Received 12 August 2002; accepted 24 May 2003

ABSTRACT

The melt rheology of ethylene propylene diene rubber (EPDM) before and after modification with 5 and 10 phr each of phosphorylated cashew nut shell liquid prepolymer (PCNSL) and spindle oil was studied using a capillary rheometer over a wide range of temperatures and shear rates. The plasticizing effect of PCNSL in EPDM was evident from the progressive decrease in melt viscosity, consistency index, shear modulus and activation energy of melt flow with increase in dosage of PCNSL. The higher value of pseudoplasticity index and lower value of die swell ratio of PCNSL modified EPDM at lower temperatures and shear rates reflect probable improvement in processability during operations such as mixing and extrusion. The lower values of principal normal stress difference of PCNSL modified EPDM as against that of the unmodified EPDM indicate good compatibility between EPDM and PCNSL.

Iranian Polymer Journal, **12** (4), 2003, 305-313

Key Words:
melt rheology;
ethylene propylene diene rubber;
phosphorylated cashew nut shell liquid prepolymer;
processability;
compatibility.

INTRODUCTION

Processability of many of the polymer compositions is strongly dependent on their melt rheology at elevated temperatures and shear rates on a processing machine. Also, plasticizers play a major role in improving their processability. It has recently been found that phosphorylated cashew nut shell liquid prepolymer (PCNSL) [1,2] can serve as an excellent multifunctional additive in natural rubber (NR) in various roles such as a plasticizer [3], a tackifier [4], a co-agent for vulcan-

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ization [5,6] and an improver of physicomechanical properties of the vulcanizates such as tensile and tear strengths, thermal stability and resistance to fatigue failure and thermo-oxidative decomposition [7 -13] at dosages ranging from 5 to 20 phr.

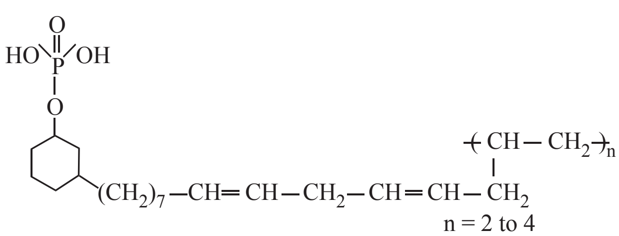
In an earlier work, the cure characteristics, physicomechanical properties and thermo-oxidative decomposition characteristics of carbon black filled ethylene propylene diene terpolymer (EPDM) vulcanizates containing PCNSL as a property modifier have been studied in comparison with that of a commercial plasticizer i.e., spindle oil [14]. Improvements in cure rate and ultimate state of cure have been observed on substitution of spindle oil with PCNSL. Also, the PCNSL modified vulcanizates showed better tear strength, higher thermal stability and resistance to thermo-oxidative decomposition as compared to those containing spindle oil. However, for many of the industrial applications, apart from an improvement in physicomechanical properties, it is essential that the compositions should process smoothly in the conventional processing machinery under the desired conditions of temperatures and shear rates. Since this is dependent on the melt rheology of the compounds, an analysis of the latter will provide a reliable indication of the processability of the compounds [15]. Hence, in the present work the melt rheology of EPDM modified with 5 to 10 phr of PCNSL has been studied in comparison with that containing the same dosage of a commercial plasticizer, viz. spindle oil.

EXPERIMENTAL

Materials

EPDM rubber (Nordel 1040) was obtained from M/s. Jal Jyothi International Pvt. Ltd., Mumbai.

Phosphorylated Cashew Nut Shell Liquid (PCNSL) prepolymer (I) was synthesized at RRL, Thiruvananthapuram, according to the patented process [2].



(I) Prepolymer of PCNSL

Spindle oil used for the present study was an aromatic plasticizer (commercial grade).

Methods

Mixing

Mixes of EPDM containing different dosages of PCNSL and spindle oil (as per the compositions given in Table 1) were prepared by mixing in a Brabender Plasticorder fitted with a measuring mixer (W30) at room temperature and at a rotor speed of 30 rpm for 10 min.

Melt Rheology Measurements

The melt flow characteristics and melt elasticity parameters of the mixes over wide range of shear rates (50 s^{-1} to 2000 s^{-1}) and temperatures (120 °C to 180 °C) were measured using a capillary rheometer (Rheoflixer, Haake-SWO) using a circular die (diameter 1mm, L/D 20) after presetting the temperature and apparent shear rate (γ_a) conditions. The entry to the capillary was conical at an angle of 45°. Apparent wall shear stress (τ_w) apparent melt viscosity (η_a), consistency index (K) and pseudoplasticity index (n) were calculated automatically. K and n were calculated using the Ostwald de Weale power law model, $\eta_a = K \gamma^{n-1}$. The running die swell ratio (B) was measured using a laser die swell detector.

Calculations

Activation energy of melt flow at constant shear rate (E_a) of the mixes for the temperature range 120°C to 180°C was calculated using the Arrhenius - Frenkel - Eyring equation [3], $\eta_a = A e^{(Ea/RT)}$ where, η_a is apparent viscosity at constant shear rate, A is a constant, R is gas constant and T is temperature in absolute scale.

The parameters characterizing the elasticity of polymer melts [16] such as principal normal stress difference (τ_{11}-τ_{22}) recoverable shear strain (S_R) and apparent shear modulus (G) were calculated using the following relations :

$$(\tau_{11}-\tau_{22}) = 2\, \tau_w\, [2\, (B)^6 - 2]^{1/2}$$

$$S_R = (\tau_{11}-\tau_{22} / 2\, \tau_w)$$

$$= \tau_w / S_R$$

Table 1. Composition of the mixes.

Composition (phr)	Mix code				
	EP0	EP5	EP10	ES5	ES10
EPDM	100	100	100	100	100
PCNSL	-	5	10	-	-
Spindle oil	-	-	-	5	10

RESULTS AND DISCUSSION

Melt Flow Characteristics

Pseudoplasticity Index and Consistency Index

The pseudoplasticity index (flow behaviour index) n and the consistency index K as obtained from the power law fluid model indicate the non-Newtonian characteristics and unit shear viscosity of the polymer melt respectively [17]. Tables 2 and 3 give the values of pseudoplasticity index and consistency index of the mixes at the different temperatures. Table 2 shows that the pseudoplasticity indices of EPDM containing 5 and 10 phr of PCNSL are higher than that containing the same dosages of spindle oil and the unmodified EPDM. It is reported that as the behaviour departs more from Newtonian (with lower values of n), the melt flow becomes more plug like with high shear rates being concentrated near the surface of the compounding machine leading to a low shear within the main body of the melt [18]. Thus, the higher flow behaviour index of the PCNSL modified EPDM is expected to lead to a better distribution of shear rate in the bulk of the polymer melt and hence a better mixing.

The results in Table 3 show that at 120°C there is a considerable decrease in the consistency index of PCNSL modified EPDM as compared to that of the samples containing the same dosage of spindle oil and the unmodified sample. The relatively lower values of the consistency index of PCNSL modified EPDM reflects its lower melt viscosity which may in turn facilitate a faster extrusion.

Melt Viscosity

Effect of Shear Rate

The variations in apparent viscosity of the mixes with apparent shear rate at 120°C, 150°C and 180°C are shown in Figure 1. Due to the shear thinning or pseudoplastic behaviour, the viscosity of rubber reduces with increase in shear rate. Figure 1 shows that at any particular shear rate at 120°C, the apparent melt viscosity

Table 2. Pseudoplasticity index n of the mixes at different temperatures.

Mix code	n		
	Temperature (°C)		
	120	150	180
EP0	0.34	0.45	0.32
EP5	0.36	0.42	0.46
EP10	0.48	0.44	0.45
ES5	0.33	0.36	0.40
ES10	0.41	0.35	0.27

of PCNSL modified EPDM is lower than that of the spindle oil modified EPDM and the unmodified EPDM. This shows the comparatively higher softening effect of PCNSL in EPDM at the lower temperature.

Effect of Temperature

The rate of reduction in apparent viscosity of the mixes with increase in temperature and at different constant shear rate is given in Table 4. These results show a comparatively higher rate of reduction in viscosity with temperature for PCNSL modified EPDM as against that for the unmodified mixes. This is particularly prominent at the lower shear rates which indicates the suitability of PCNSL for processing operations such as mixing and extrusion. However, EPDM modified with 5 phr of spindle oil shows higher rate of reduction in melt viscosity with temperature at the different shear rates which indicates the higher temperature sensitivity of this system. The decrease in melt viscosity of EPDM in presence of PCNSL is expected to be due to an increase in plasticizing efficiency of PCNSL . This is analogous to similar results reported earlier for PCNSL modified NR systems [3].

Effect of Dosage of Plasticizer

Table 1 shows that an increase in dosage of PCNSL from 0 to 5 phr and from 5 to 10 phr in EPDM results in progressively greater decrease in melt viscosity at the different shear rates and temperatures as compared to the unmodified EPDM. The effect of increase in dosage of plasticizer on reduction in viscosity as mentioned above is true at 120°C for both PCNSL and spindle oil. At 150°C and at 180°C, some discrepancy has been observed for the mix containing 10 phr of spindle oil.

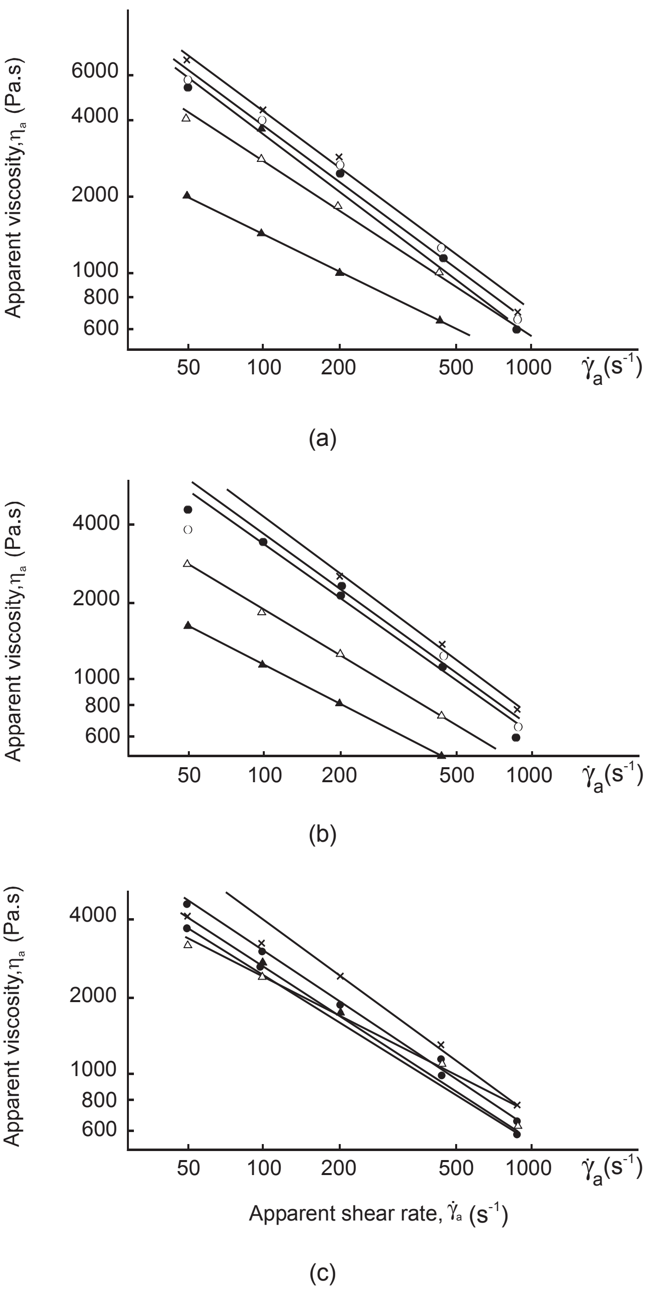


Figure 1. Variation in apparent viscosity of the mixes with apparent shear rate: (a) 120°C, (b) 150°C, (c) 180°C. × EPO; △ EP5; ▲ EP10; ○ ES5 and ● ES10.

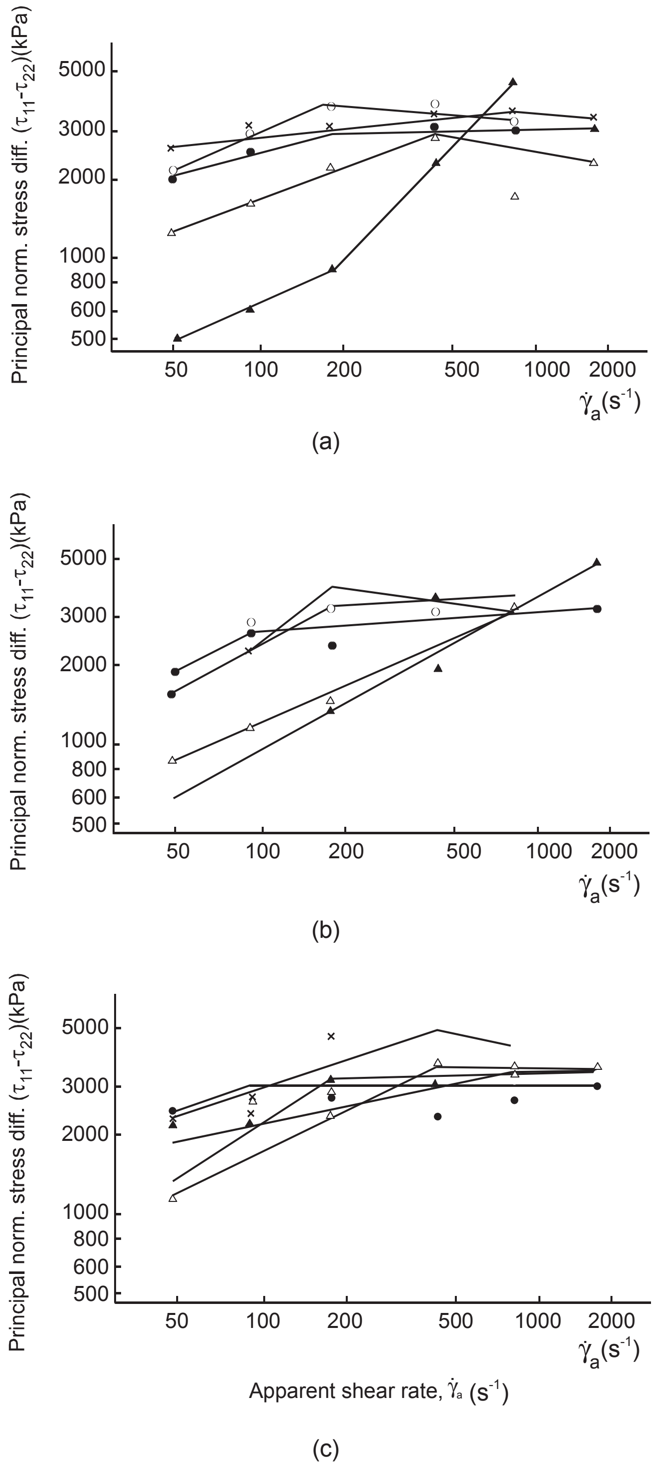


Figure 2. Variation in principal normal stress difference of the mixes with apparent shear rate at (A) 120°C, (B) 150°C and (C) 180°C. × EPO; △ EP5; ▲ EP10; ○ ES5 and ● ES10.

Activation Energy of Melt Flow

The activation energy of melt flow of the mixes at a constant shear rate (50 s^{-1}) over the temperature range from 120°C to 150°C calculated from the slope of Arrhenius plots of log η_a vs. 1/T are given in Table 5. It shows a progressive reduction in activation energy of melt flow of EPDM with increase in dosage of PCNSL from 0 to 10 phr. This is an indication of the plasticization efficiency of PCNSL in EPDM. Generally, plasticizers are known to reduce the activation energy of melt flow of polymers [19]. It is expected that the plasticizing effect of the C_{15} aliphatic side-chain seg-

Table 3. Consistency index, K of the mixes (kPa s^n) at different temperatures.

Mix code	K		
	Temperature (°C)		
	120	150	180
EP0	71.5	34.7	77.4
EP5	42.8	24.3	20.3
EP10	12.7	11.9	9.7
ES5	61.6	15.9	6.8
ES10	44.7	57.8	95.8

ment of PCNSL on EPDM increases the segmental mobility of the rubber, resulting in the lowering of activation energy leading to an improved melt flow. However, in the spindle oil modified EPDM a reduction in activation energy is obtained only in presence of 10 phr of the additive. This may be due to the higher aromatic nature of spindle oil as compared to PCNSL.

Melt Elasticity

Some of the rheological parameters characterizing the elasticity of polymers include die swell ratio, principal normal stress difference, recoverable shear strain and shear modulus [16]. These parameters have a strong influence on the extrusion characteristics of polymers and processability in general. It is reported that during extrusion the high elastic strain at the entry of the die relaxes in the duct and reaches a steady equilibrium value at an L/D ratio of 20 [20].

Die Swell Ratio

Swelling of extradate is presumed to be dependent on

Table 4. Rate of reduction in apparent viscosity of the mixes with temperature at different constant shear rates (Pa.s/°C)*.

Mix code \ Apparent shear rate (s^{-1})	Apparent viscosity (Pa.s^{-1})			
	100	200	500	1000
EP0	6.8	-	0.23	-
EP5	19.53	15.30	4.20	3.10
EP10	7.97	5.83	5.50	3.80
ES5	57.57	46.50	28.90	13.20
ES10	-	-	0.97	-

(*) Temperature range: 120°C to 150°C.

Table 5. Activation energy of melt flow at constant shear rate (Ea) of the mixes*.

Mix code	Activation energy, E_a (kJ/mol)
EP0	22.855
EP5	13.826
EP10	8.092
ES5	50.949
ES10	2.439

(*) Temperature : 120°C - 150°C,apparent shear rate : 50 (s^{-1}).

the phenomenon of elastic recovery which is a function of rate of shear, type of polymer, temperature, etc. [21]. Results on the die swell ratio of the mixes at different shear rates and temperatures are given in Table 6. These results show that at the lowest temperature (120°C) there is a steady decrease in the die swell ratio with increases in apparent shear rate and dosage of the modifier. However, at the higher temperatures (150°C and 80°C) the die swell ratios of EPDM modified with PCNSL and spindle oil are almost similar. The changes in die swell ratio with apparent shear rate and temperature can be explained on the basis of the molecular interpretation of the die swell behaviour [22]. It is expected that at lower temperatures, the shear stress within the capillary predominates over that of the thermal stresses causing disorientation of the chain segments leading to a reduction in die swell ratio with the increase in shear rate. But, at the higher temperatures a greater degree of thermally induced Brownian motion of the plasticized polymer segments leads to an increase in die swell ratio of these systems.

Principal Normal Stress Difference

The die swell of a polymer melt which is a consequence of normal stresses generated during shear flow, depends on the normal stress difference [3]. The principal normal stress difference is found to be related to the pressure and shear stress acting on the melt during extrusion [22].

The variations in principal normal stress difference of the mixes with apparent shear rate at the different temperatures are shown in Figure 2. A high degree of compatibility between EPDM and PCNSL is shown by the comparatively lower values of principal normal stress difference of the PCNSL modified EPDM mixes as against that of the unmodified mix and the spindle oil modified mixes. This is analogous to the results

Table 6. Die swell ratio, B, of the mixes at different shear rates and temperatures.

Temp.(°C)	Apparent shear rate (s^{-1}) / Mix code	Die swell ratio					
		50	100	200	500	1000	2000
120	EP0	1.44	1.42	1.40	1.37	1.33	-
	EP5	1.33	1.35	1.36	1.48	1.49	1.53
	EP10	1.26	1.30	1.30	1.45	1.46	-
	ES5	1.42	1.38	-	1.37	1.33	1.33
	ES10	1.47	1.42	1.42	1.35	1.33	-
150	EP0	1.66	1.54	1.47	1.41	1.32	1.33
	EP5	1.33	1.41	1.41	-	1.48	1.75
	EP10	-	1.28	1.31	1.34	-	-
	ES5	-	-	1.70	1.64	1.59	1.62
	ES10	1.63	1.61	1.47	1.36	1.31	1.33
180	EP0	1.68	1.57	1.49	1.40	1.32	1.32
	EP5	-	1.58	1.47	1.45	1.33	1.28
	EP10	1.48	1.48	1.43	1.41	1.39	-
	ES5	1.84	1.87	1.89	1.85	1.86	-
	ES10	1.58	1.50	1.42	1.37	1.31	1.30

Table 7. Apparent shear stress (kPa) of the mixes at different shear rates and temperatures.

Temp.(°C)	Apparent shear rate (s^{-1}) / Mix code	Apparent shear stress					
		50	100	200	500	1000	2000
120	EP0	276.6	321.6	413.4	592.1	-	-
	EP5	164.5	225.6	326.7	432.7	538.8	625.5
	EP10	82.9	112.6	155.2	261	360.4	457.1
	ES5	204.6	254.4	382.7	585	586.6	627.2
	ES10	215.2	295.7	381.8	552.7	-	-
150	EP0	164.1	301.2	436.9	587.4	647.8	-
	EP5	119.9	167.0	234.8	369.6	446.2	553.8
	EP10	68.9	88.7	120.2	178.7	246.2	349.5
	ES5	63.8	81.7	103.6	151.5	191.3	230.7
	ES10	203.5	304.9	410.9	538.7	583.6	-
180	EP0	258.1	324.1	451.7	566.8	652.3	-
	EP5	121.4	162.5	238	405.2	528.9	606.4
	EP10	59.5	75	99.8	158.3	226	-
	ES5	32.4	44.9	57.1	81.8	111	-
	ES10	260.4	332.5	400.1	499.9	582.1	-

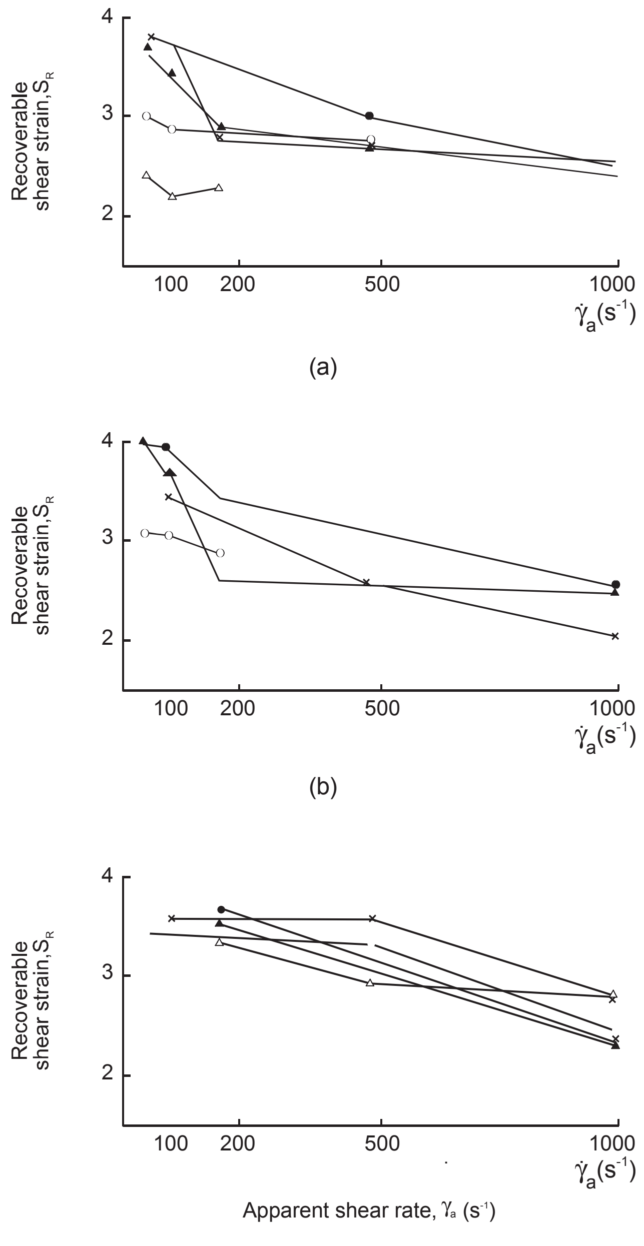


Figure 3. Variation in recoverable shear strain of the mixes with apparent shear rate at (A) 120°C, (B) 150°C and (C) 180°C. × EPO; ○ EP5; △ EP10; ● ES5 and ▲ ES10.

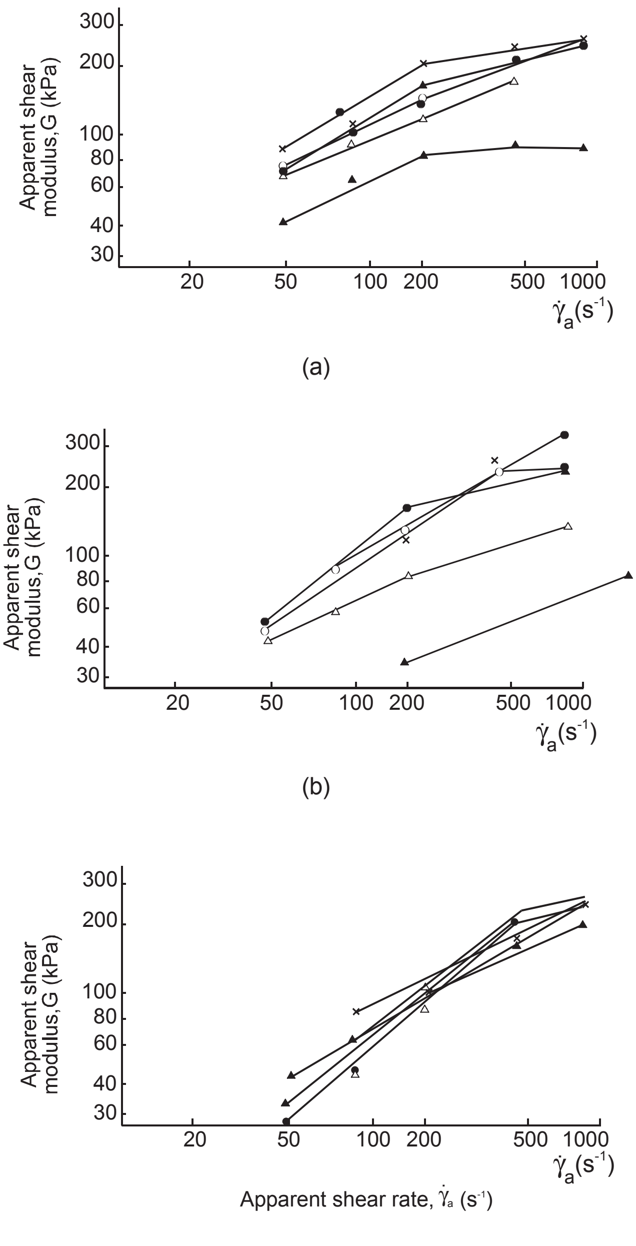


Figure 4. Variation in apparent shear modulus of the mixes with apparent shear rate at (A) 120°C, (B) 150°C and (C) 180°C. × EPO; △ EP5; ▲ EP10; ○ ES5 and ● ES10.

reported earlier for PCNSL modified NR systems [3].

Recoverable Shear Strain

Figure 3 shows the variations in recoverable shear strain of the mixes with apparent shear rate at 120°C, 150°C and 180°C. The lower values of recoverable shear strain of PCNSL modified EPDM compared to that of the other mixes indicate a reduction in melt elasticity of the former.

Shear Modulus

The variations in apparent shear modulus of the mixes with apparent shear rate at the different temperatures are shown in Figure 4. The distinct reduction in apparent shear modulus of EPDM with increase in dosage of PCNSL as shown in Figure 4 (A) and (B) is again a reflection of the reduction in melt elasticity arising out of the plasticization effect of PCNSL in EPDM. This is supported by the comparatively lower values apparent shear stress of PCNSL modified EPDM as given in Table 7.

CONCLUSION

The results of the present study lead to the following conclusions:

1. At dosages ranging from 5 to 10 phr, PCNSL shows plasticizing effect in EPDM as evidenced by increase in pseudoplasticity index and decreases in consistency index, melt viscosity and activation energy of melt flow.

2. The lower values of principal normal stress difference of PCNSL modified EPDM as against unmodified EPDM and spindle oil modified EPDM indicate good compatibility between PCNSL and EPDM.

3. Reduction in melt elasticity of the PCNSL modified EPDM is shown by the comparatively lower die swell ratio, recoverable shear strain and shear modulus.

ACKNOWLEDGEMENTS

The author would like to thank Dr. C.K.S. Pillai, Head, Polymer Science Division and Dr. G. Vijay Nair, former Director, RRL, Thiruvananthapuram, for providing the necessary support and encouragement for the work.

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