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Melt-rheology of Natural Rubber Modified with Phosphorylated Cashew Nut Shell Liquid Prepolymer- A Comparative Study with Spindle Oil

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ABSTRACT

The mixing behaviour and melt rheology of natural rubber (NR) modified with 10 phr of both phosphorylated cashew nut shell liquid (PCNSL) prepolymer and an aromatic process oil (spindle oil) have been studied on a Brabender Plasticorder at rotor speed ranging from 30 to 90 rpm and temperature ranging from 30 to 140 °C. The plasticizing effect of PCNSL and spindle oil on NR is evident from the significant reduction in melt viscosity, power consumption for mixing and activation energy of melt flow of NR with the increase in rotor speed and temperature. PCNSL showed a higher degree of plasticization as compared to spindle oil, particularly at lower rotor speed and temperature.

Key Words: mixing, melt rheology, phosphorylated cashew nut shell liquid, natural rubber

INTRODUCTION

The importance of polymer melt rheology in determining the pattern and intensity of shear within a polymer system and the processability in general on a larger scale, is very well established [1–5]. The shear rate distribution within a polymer melt is known to be directly dependent on the 'velocity-profile' [5] which in turn is strongly influenced by the rheological behaviour of the melt, apart from the geometry of the compounding machinery and the relative rate of movement of its members [1]. Various rheological parameters such as melt elasticity [2], melt viscosity [3] and flow behaviour index [4, 5] have crucial roles in the deformation and flow of polymer melts during various processing operations such as mixing, extrusion and injection moulding. The Brabender Plasticorder [1] has been shown to be an ideal torque rheometer for studying the compounding of rubbers [6, 7], particularly the ease of mixing of different varieties of reinforcing pigments, plasticizers, processing oils etc. and their effects on rheological behaviour [8]. The results of studies on a Brabender Plasticorder using smaller batches may be used for satisfactory prediction of the consistency and processability of polymers on larger production machines [9, 10].

Conversion of Brabender torque rheometer data to fundamental rheological units has been reported by

Goodrich and Porter [11]. They have described an approximate method of converting torque rheometer data into fundamental rheological units. Thus, Brabender torque M is proportional to apparent shear stress τ, rotor speed S is proportional to shear rate γ and melt viscosity of polymer, η is related to the torque M and the rotor speed S as:

$$\eta = K(M/S)$$

where K is a constant depending on the mixer measuring head [11, 12]. Also, activation energy of melt flow of a polymer E_a was determined from the dependence of melt viscosity η with absolute temperature T as given by the relation:

$$E_a = R[d\ln\eta / d(1/T)]$$

where R is the universal gas constant.

Mun et al. have defined the Brabender breakdown index (obtained from the torques at 2 and 10 min) as a quantitative measure of the processability of NR [13]. Blyler and Daane used the torque data from Plasticorder to create fundamental flow curves [14]. The flow behaviour index n was obtained from the flow curves using the relation:

$$M = C_n K S^n$$

where n is the flow behaviour index, K is the consistency index and C_n is a function depending on n and machine geometry [14]. Mc Cabe has determined the melt flow parameters and activation energy of melt flow of various elastomers using Brabender Plasticorder [15]. Lee and Purdon found that the flow behaviour index obtained from a Brabender Plasticorder was the same as that from a capillary rheometer [16]. Practical process engineering data can be developed by converting Brabender torque M to units of power P using the relation:

$$\text{Power (P)} = \text{Torque (M)} \times \text{input shaft rotation} \quad (1)$$

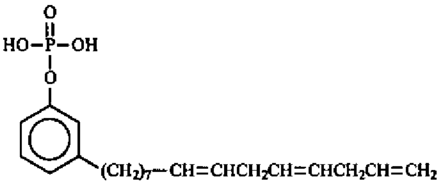
where, input shaft rotation $\omega = 2\pi S/60$, torque M is given in m.kg and rotor speed S in rpm (17). Also, the thermal processing stability of cross-linkable materials may be determined from the length of the stable portion of the Brabender torque profiles, before the onset of cure [18].

The phosphorylated cashew nut shell liquid (PCNSL) prepolymer [19] and phosphorylated cardanol prepolymer [20] (oligomeric resins synthesized from cashew nut shell liquid and cardanol, respectively) and their bromo- derivatives [21] have been found to be ideal 'multifunctional additives' in polyethylene (PE), ethylene vinyl acetate copolymer (EVA) and natural rubber (NR).

Studies on a Brabender Plasticorder showed substantial improvements in processability characteristics of PE modified with a bromo- derivative of cardanol, apart from other improvements in flame retardancy and low smoke density [12]. Also, Brabender torque rheometry of EVA modified with the same flame retardant indicated the plasticizing effect of the flame retardant on EVA, as evidenced by the increase in flow behaviour index and decreases in melt viscosity, melt elasticity and activation energy of melt flow [22].

The multifunctional roles of PCNSL in NR as an improver of physico-mechanical properties of the vulcanizates such as tensile and tear strengths, elongation at break, fatigue resistance, stress relaxation [23–25], resistance to thermo-oxidative degradation [26], as a tackifier [27], as a plasticizer [28], as a coagent for vulcanization [29, 30] and as a precursor for the synthesis of flame retardants [31] have been reported earlier.

Studies on the vulcanization characteristics of gum NR formulations modified with various dosages of PCNSL in a Brabender Plasticorder at different rotor speeds and temperatures showed significant plasticizing effect of PCNSL on NR along with low rates of cure and cure reversion [32]. The effects of compositional variables, temperature and shear rate on the cure characteristics of fire retardant NR formulations based on a bromo- derivative of PCNSL have also been studied using the Brabender Plasticorder, which showed considerable cure retardation at higher dosages of the flame retardant and restoration of cure with the increase in dosage of ZnO [33].



Scheme I

It has been shown earlier that an optimum improvement in the processability of PCNSL modified NR compounds and physico-mechanical properties of their vulcanizates can be obtained in presence of 10 phr of PCNSL in NR [23–30].

Subsequent studies on similar systems containing 10 phr each of PCNSL and an aromatic process oil (spindle oil) have again shown better physico-mechanical properties and processability for the PCNSL modified NR compounds. However, it is essential to evaluate the ease of mixing of NR modified with the same dosage of PCNSL and spindle oil at low shear rates and temperatures. Hence, the melt rheology and mixing behaviour of NR modified with 10 phr each of PCNSL and spindle oil, have been studied using a Brabender Plasticorder, the results of which are reported in this paper.

EXPERIMENTAL

Materials

NR conforming to the grade 'ISNR-5' was obtained from the Rubber Research Institute of India, Kottayam. PCNSL prepolymer was synthesized at the Regional Research Laboratory (CSIR), Trivandrum, by a patented process (19) involving the phosphorylation of CNSL (grade IS:840, 1964) with *o*-phosphoric acid at 175±5 °C.

The structure in Scheme I depicts the triene component of phosphorylated cardanol, the major constituent of PCNSL.

The aromatic process oil (spindle oil) was of the commercially available rubber grade, obtained from Calcutta.

Methods

Unmodified NR and mixes of NR with 10 phr each of PCNSL and spindle oil were prepared on a Brabender Plasticorder (model PLE-651) fitted with a cam type mixer measuring head, at room temperature, under a rotor speed of 30 rpm for 10 min. The composition of the mixes are given in Table I.

The torque profiles of 40g each of the samples were measured at 30, 100 and 140 °C at preset rotor speeds of 30, 60 and 90 rpm. Parameters such as melt viscosity index, power consumption for mixing and activation energy for melt flow of the mixes were calculated from the steady value of the torque M at 12th min using the following relations. Since the Brabender torque M is proportional to apparent shear stress τ and the rotor speed S is proportional to apparent shear rate γ, the ratio of the torque M in m.g to the rotor speed S in rpm was calculated as an approximate index of melt viscosity η. The power consumption for mixing was calculated using the relation presented in eqn (1).

The activation energy of melt flow E_i, was estimated from the slope of the plots of log (M/S) vs. l/T (Arrhenius plots) using the following relation:

$$E_a = R\,[d\ln(M/S)/d(1/T)]$$

where R is the universal gas constant and T is the temperature in absolute scale.

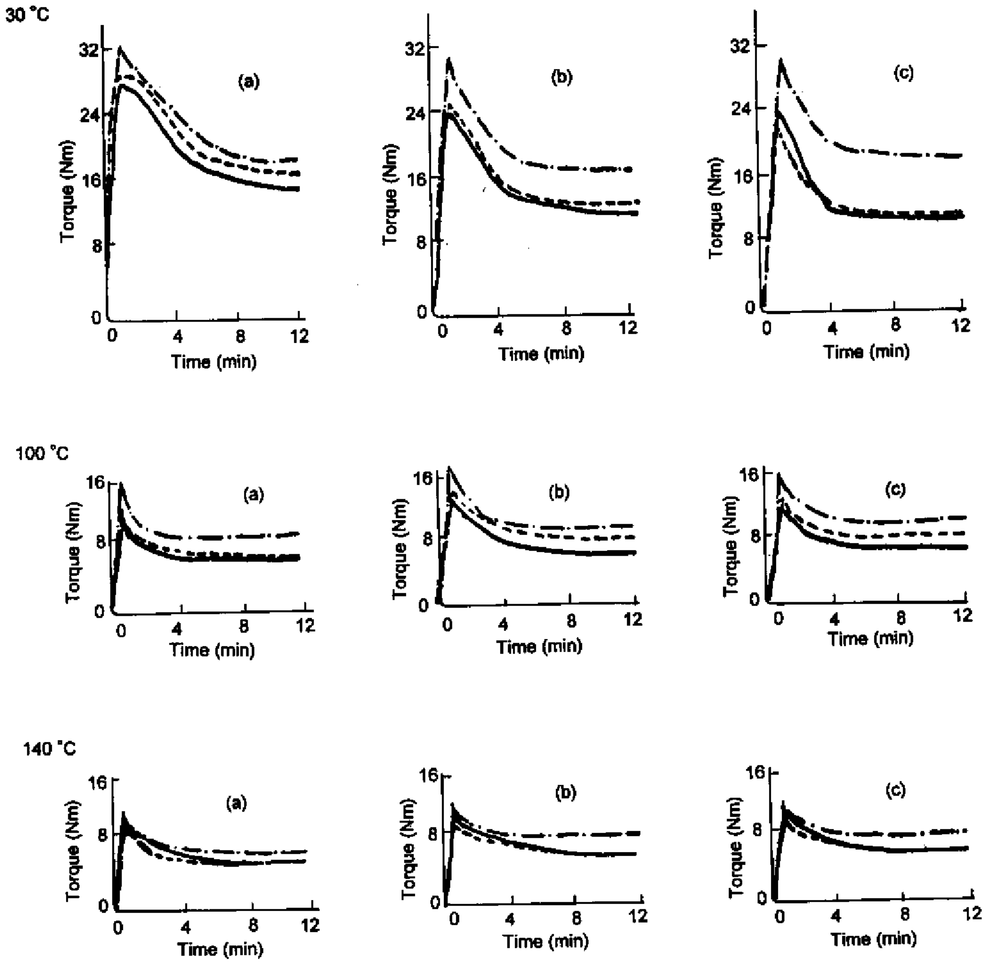
RESULTS AND DISCUSSION

General Observations

Figure 1 gives the variation in maximum torque obtained from the Plasticorder of unmodified NR,

Table 1. Composition of mixes.

Ingredients	Mix code		
	U	P	O
NR	100	100	100
PCNSL	–	10	–
Spindle oil	–	–	10



Rotor speed (rpm) (a) 30, (b) 60, (c) 90. –·– Unmodified NR, —— PCNSL modified NR, - - - Spindle oil modified NR.

Figure 1. Brabender torque profiles of unmodified NR, PCNSL modified NR and spindle oil modified NR at different rotor speeds and temperatures.

PCNSL modified NR and spindle oil modified NR at the rotor speeds of 30, 60 and 90 rpm and temperatures of 30, 100 and 140 °C. In general, there is an overall improvement in the processability of NR in presence of either PCNSL, or spindle oil as reflected by the lower levels of torque at the various rotor speeds and temperatures studied.

Melt Elasticity

The band-width of the torque traces obtained from Plasticorder has been considered as an index of melt elasticity of polymers [2, 35]. Generally, a lower band-width indicates a reduction in melt elasticity [2, 12, 22] and the smoothness of the profile shows an improvement in melt processability. The torque profiles of the PCNSL modified NR obtained from the Plasticoder showed a reduction in band-width (at higher shear rates and temperatures) as compared to spindle oil modified NR and unmodified NR. This reduction in band-width of NR upon modification with PCNSL may be taken as a qualitative indication of the reduction in melt elasticity of the system.

Melt Viscosity

The viscosity of polymer melts and its dependence on temperature and shear rates are factors of crucial significance with respect to processing operations involving melt flow such as compression moulding, extrusion and injection moulding (3, 4). The pressure build-up in the barrel of an extruder is known to be dependent on the melt viscosity of the polymer melt (2). Quite often, a lower melt viscosity facilitates easier melt flow during extrusion.

The melt viscosity index of the mixes are given in Table 2. The table shows a regular decrease in the melt viscosity index of the different mixes with the increase in temperature from 30 to 140 °C and the increase in rotor speed from 30 to 90 rpm. However, this decrease in melt viscosity is comparatively greater for the PCNSL modified mix, particularly at the lower temperature (30 °C) and rotor speeds (30 and 60 rpm). It is possible that the unsaturated aliphatic side chain segment of PCNSL prepolymer may enhance the mobility of the isoprene chains of NR, leading to the reduction in melt viscosity. The reduction in melt viscosity of PCNSL modified NR indicates its better processability during mixing at room temperature and under low shear rate conditions. This is of particular significance with respect to a fundamental processing operation such as mixing on a roll mill.

Table 2. Melt viscosity index of the mixes.

Temperature °C		30	100	140
Mix code	Rotor speed (rpm)	Melt viscosity index (mg/rpm)		
U	30	61	31	27
	60	21	16	16
	90	13	11	11
P	30	48	24	24
	60	19	12	11
	90	11	8	7
O	30	54	24	24
	60	20	14	11
	90	11	9	7

(U): unmodified natural rubber (NR); (P): PCNSL modified NR and (O) spindle oil modified NR.

Power Consumption for Mixing

Power consumption during processing of a rubber compound is almost often a factor of major significance. It is essential that at the different stages of processing, the compound should process smoothly with minimum power consumption. Generally, this is achieved by the use of an appropriate plasticizer at an optimum dosage.

Figure 2 shows the power consumption for mixing unmodified NR, PCNSL modified NR and spindle oil modified NR at different rotor speeds (30 to 90 rpm) and temperatures (30 to 140 °C). Unlike the unmodified NR, the mixes containing 10 phr each of spindle oil and PCNSL show high degree of sensitivity to variation in temperature. Also, at all the temperatures the PCNSL modified NR shows the lowest power consumption for mixing at the various rotor speeds. This again indicates the better processability of PCNSL modified NR as against that containing the same dosage of spindle oil (Table 3).

Activation Energy of Melt Flow

Quite often, the activation energy of melt flow of polymers either at constant shear stress or constant shear rate gives a direct indication of the ease of melt flow at elevated temperatures which dictates processability under these conditions. Generally, the melt viscosity of polymer melts is considered to be inversely dependent on temperature according to the Arrhenius relationship:

$$\eta = Ae^{-Ea/RT}$$

where E_a is activation energy of melt flow, R is the universal gas constant and T is temperature in absolute scale [4, 5]. Table 4 gives the activation energy of melt flow of the mixes calculated at the rotor speeds of 30, 60 and 90 rpm.

Table 4 shows a steady decrease in activation energy with the increase in rotor speed for all the mixes. However, at the rotor speeds of 30 and 60 rpm the activation energies for melt flow of PCNSL modified NR are lower than that of unmodified NR and spindle oil modified NR. This indicates comparatively easier melt flow for PCNSL modified NR under low shear rate conditions and consequently an improvement in processability. The decrease in the activation energy of melt flow of NR in presence of PCNSL shows the plasticizing efficiency of PCNSL in NR, which is higher than that of spindle oil.

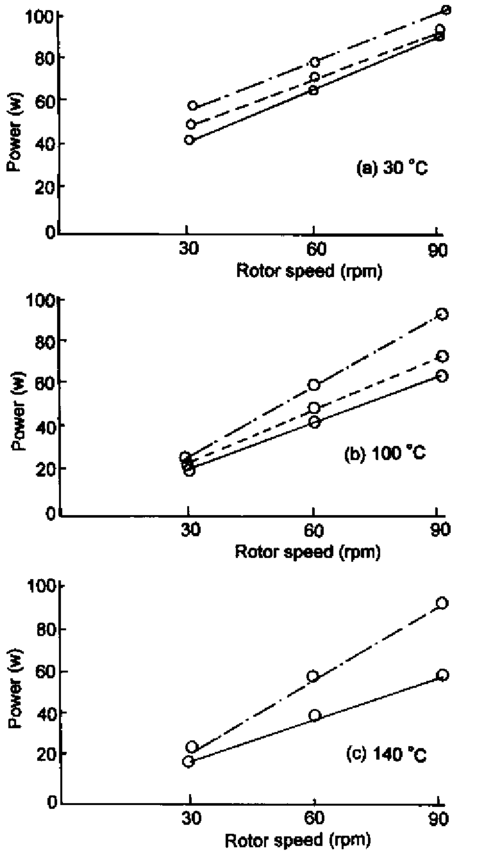


Figure 2. Power consumption for mixing unmodified NR, PCNSL modified NR and spindle oil modified NR.

Table 3. Power consumption for mixing of unmodified, PCNSL modified and spindle oil modified natural rubber at different rotor speeds and temperatures.

Temperature °C		30	100	140
Mix code	Rotor speed (rpm)	Power consumption (W)		
U	30	57	28	25
	60	79	60	61
	90	104	94	94
P	30	44	22	22
	60	69	44	41
	90	94	66	61
O	30	50	25	22
	60	75	50	41
	90	94	75	61

Table 4. Activation energy of melt flow of the mixes.

Mix code	Rotor speed (rpm)	Activation energy of melt flow (kJ/mol)
U	30	3.590
	60	3.212
	90	3.118
P	30	2.834
	60	2.173
	90	1.701
O	30	3.401
	60	2.551
	90	1.701

Generally, the use of plasticizers bring about a reduction in the activation energy of melt flow of polymers [36].

CONCLUSION

Studies on the processability characteristics and melt rheology of NR modified with 10 phr each of PCNSL and spindle oil on a Brabender Plasticorder at rotor speed ranging from 30 to 90 rpm and temperature ranging from 30 to 140 °C show that both PCNSL and spindle oil have a plasticizing effect on NR and that PCNSL is a better plasticizer at low shear rate conditions.

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