Processability Characteristics and Thermal Stability of Blends of LDPE and EVA Copolymer Modified with Phosphorylated Cashew Nut Shell Liquid Prepolymer

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ABSTRACT

Melt processability and thermal stability of blends of low density polyethylene and ethylene vinyl acetate copolymer modified with different dosages of phosphorylated cashew nut shell liquid (PCNSL) prepolymer have been studied using Brabender Plasticorder and thermogravimetric analysis, respectively. In all the blends having varying proportion of blend components, there was a progressive reduction in melt viscosity index with increase in dosage of PCNSL. The reduction in bandwidth of the Brabender torque profiles with increase in dosage of PCNSL from 0 to 10% indicated a decrease in melt elasticity of the blends. The reduction in indices of melt viscosity and melt elasticity of the blends in presence of PCNSL show the plasticizing effect of the additive and the consequent improvement in processability. The improvement in processability of the blends in presence of PCNSL was further evidenced by the decrease in power consumption during mixing. Modification of the blends with PCNSL resulted in significant improvement in thermal stability of the blends as evidenced by the progressive and significant increase in thermal stability index (T₅₀) and shift in the thermograms to the high temperature region during thermogravimetric analysis.

Key Words: processability, LDPE, EVA copolymer, blends, phosphorylated cashew nut shell liquid, thermal stability

INTRODUCTION

Polyolefins constitute a major group of commercial thermoplastics having wide range of applications even today, mainly because of their excellent combination of properties, low cost and reusability. However, for a specific application it may be necessary to tailor-make a composition having the desired rheological behaviour and physicomechanical properties, which the service conditions demand. This is often achieved by optimal blending of the base polymer with another polymer and/or other additives, normally under melt mixing

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conditions [1]. Such a blending technique may lead to a composition having an optimal combination of the positive features of each of the blend components. Thus, for example though the weather resistance of ethylene vinyl acetate (EVA) copolymer is better than that of conventional polyethylenes, the barrier properties and chemical resistance of the former are poorer than that of the latter [2]. Also, the torsional stiffness and softening temperature of low-density polyethylene (LDPE) are higher than that of EVA. Hence, for applications demanding a combination of toughness with high processing efficiency, blends of polyolefins are prepared with EVA copolymer [1].

The processability characteristics and other physicomechanical properties of the blends can be further modified by the use of other additives such as plasticizers or fillers. In addition to their effect on processability characteristics, these additives may alter the physicomechanical properties of the base polymers as well. Thus, recent studies on modification of LDPE and EVA with a novel flame retardant 3-(tetrabromopentadecyl) 2,4,6-(tribromophenol), TBPTP, synthesized from cardanol, the major component of cashew nut shell liquid (CNSL), indicated the plasticizing effect of the additive apart from improved flame retardancy [3-5]. The plasticizing effect of TBPTP on LDPE [4] and EVA [5] has been confirmed by the increase in flow behaviour index and decreases in melt viscosity, melt elasticity and activation energy of melt flow,

The improvement in processability of the TBPTP modified EVA over the unmodified sample was reflected in a reduction in power consumption during mixing of the former [5]. CNSL, a renewable natural resource abundantly available in the tropical countries is a rich source of cardanol (*m*-pentadecenyl phenol) used as a precursor for the synthesis of a wide variety of chemicals/ derivatives for various applications [6].

Recent publications and patents [7] indicate that there is an upsurge in interest on the use of CNSL for various applications. This may be mainly because of its renewable nature, low cost and the depleting source of other petrochemical based raw materials. A non-halogenated derivative of CNSL, phosphorylated cashew nut shell liquid (PCNSL) prepolymer has been synthesized in our laboratory [8]. The multifunctional behaviour of PCNSL in different polymer systems has been reported earlier by Pillai et al. [9]. The multifunctional roles of PCNSL in natural rubber as a cross-linkable plasticizer, a tackifier and an improver of some of the physicomechanical properties of the vulcanizates have also been studied in detail recently [10-13]. Hence, the present study has been carried out to investigate the occurrence if any, of similar behaviour in thermopiastic systems. Thus, a preliminary study has been carried out to determine the effect of PCNSL on processability characteristics and thermal decomposition characteristics of blends of LDPE and EVA, the results of which are reported in this paper.

EXPERIMENTAL

Materials

LDPE of grade Indothene 20 CA 002 was obtained from Indian Petrochemicals Ltd., Vadodara, India. EVA of grade Pilene EVA 2806 was supplied by M/S Polyolefins, Mumbai, India. CNSL (8007-24-7), conforming to Indian standard specification IS: 840 (1964), was purchased from Kerala State Cashew Development Corp., Kollam, India. PCNSL was synthesized according to a patented process [8].

Methods

Preparation of Blends and Processability Evaluation

Base mixes as given in Table 1 were prepared by melt mixing the blend components in a Brabender Plasticorder fitted with a measuring mixer (W-50) preset at 120 °C and at a rotor speed of 30 rpm. Modification of the blends with 5% and 10% of PCNSL was carried out under the same conditions and the mixing was continued

Table 1. Composition of base mixes.

Mix code	A	В	С	D	E
Composition (LDPE/EVA)	(100/0)	(75/25)	(50/50)	(25/75)	(0/100)

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	Mix code	А	В	С	D	E
PCNSL (%)	Parameter					
0	Equilibrium torque (m.g)	994	969	994	1071	1173
	Viscosity index (m.g/rpm)	33.1	32.3	33.1	35.7	39.1
	Power consumption during mixing (W)	30.6	29.8	30.6	33	36.1
	Bandwidth of torque profile at 10 th min (mm)	1.5	1.5	2	3	3
5	Equilibrium torque (m.g)	867	943	969	1045	1122
	Viscosity index (m.g/rpm)	28.9	31.4	32.3	34.8	37.4
	Power consumption during mixing (W)	26.7	29	29.8	32.2	34.6
	Bandwidth of torque profile at 10 th min (mm)	1	1.5	1.75	2	2.5
10	Equilibrium torque (m.g)	841	867	918	1020	1071
	Viscosity index (m.g/rpm)	28	28.9	30.6	34	35.7
	Power consumption during mixing (W)	25.9	26.7	28.3	31.4	33
	Bandwidth of torque profile at 10 th min (mm)	1	1.5	1.5	1.5	2

Table 2. Processability characteristics of the mixes on Brabender Plasticorder at 120 °C and 30 rpm.

for 10 min to obtain a homogeneous mix as indicated by a uniform, stable torque output. Melt viscosity index, and power consumption for mixing were calculated from the equilibrium torque values using the relations reported earlier [4,5]. Bandwidth of the torque profile at 10th min was taken as a measure of melt elasticity of the blends. The bandwidth of the Brabender torque trace has been considered as an index of melt elasticity [3,14]. A reduction in bandwidth under equilibrium conditions is a clear indication of reduced melt elasticity. Thus, a reduction in melt elasticity is considered to indicate a plasticizing action and hence an improvement in processability [14].

Thermogravimetric Analysis of the Blends

The blends as prepared above were compression moulded on a hydraulic press at 140 $^{\circ}$ C for 5 min. Thermogravimetric analysis of the samples in air at a heating rate of 20 $^{\circ}$ C/min was carried out on a thermogravimetric analyzer (DuPont 951) coupled to $^{\circ}$ data analyzer (Thermal Analyst 2000).

RESULTS AND DISCUSSION

Processability Characteristics

Processability characteristics such as indices of melt viscosity and melt elasticity and power consumption

during mixing of the blends containing different dosages of PCNSL as obtained from the Plasticorder are given in Table 2. Figure 1 shows the variation in melt viscosity index of the blends at various dosages of PCNSL.



Brabender plasticorder, 120 °C, 30 rpm.

Figure 1. Melt viscosity index of blends of LDPE and EVA containing different dosages of PCNSL.



Figure 2. Thermograms of LDPE modified with different dosages of PCNSL (-0%, --- 5\%, -. - 10%).

The results given in Table 2 in general show a steady increase in equilibrium torque, melt viscosity index and power consumption for mixing with increase in proportion of EVA in the blends. The steady increase in the bandwidth with increase in proportion of EVA in the blends indicates an increase in melt elasticity. However, it is to be noted that these parameters decrease progressively with the increase in dosage of PCNSL in each of the blends. This indicates the



Figure 3. Thermograms of a blend of LDPE and EVA (75/25) modified with different dosages of PCNSL.

plasticizing effect of PCNSL in the blends. This is further substantiated by the reduction in melt elasticity of the blends in presence of PCNSL as reflected by the reduction in bandwidth of the Brabender torque profile. Thus, the uniform bandwidth and steady low values of torque of the blends containing PCNSL show an improvement in melt processability in presence of PCNSL. Figure 1 shows that though melt viscosity of the blends increases with increasing proportion of EVA, the level of viscosity and the rate of increase are always lower in presence of PCNSL. It is probable that the aliphatic unsaturated side chain fragment of PCNSL may enhance the segmental mobility of LDPE and EVA leading to the plasticization effect. This is analogous to similar results reported in LDPE and EVA systems in presence of another cardanol derivative [4, 5].

Thermal Decomposition Characteristics

Thermograms of LDPE modified with different dosages of PCNSL (0 to 10%) as obtained from thermogravimetric analysis are given in Figure 2. Thermograms of blends of LDPE and EVA in various proportions such as 75/25, 50/50 and 25/75 containing different dosages of PCNSL are shown in Figures 3, 4 and 5, respectively. Figure 6 gives the thermograms of EVA modified with different dosages of PCNSL. Thermal decomposition characteristics of the mixes such as initial decomposition temperature (IDT, T_i), peak temperature (T_{max})



Figure 4. Thermograms of a blend of LDPE and EVA (50/50) modified with different dosages of PCNSL.

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	Mix code	A	В	С	D	E
PCNSL (%)	Parameter					
0	IDT, T ₁ (C)	308	306	306	306	309
	DTG, T _{max 1} (C)	378	371	348	342	349
	DTG, T _{max 2} (C)	398	420	451	451	468
	TSI, T ₅₀ (C)	402	415	442	444	463
5	IDT, T, (C)	300	301	309	305	304
	DTG, T _{mex 1} (C)	362	361	355	357	354
	DTG, T _{mex 2} (C)	408	440	468	472	476
	TSI, T ₅₀ (C)	407	444	463	464	464
10	IDT, T, (C)	314	245	294	292	310
	DTG, T _{max 1} (C)	378	340	353	348	356
	DTG, T _{max 2} (C)	402	461	469	464	477
	TSI, T ₅₀ (C)	408	461	465	462	465

Table 3. Thermal decomposition characteristics of the mixes (thermogravimetric analysis).

IDT- Initial decomposition temperature, TSI- thermal stability index

as obtained from derivative thermograms (DTG) and thermal stability index (TSI, T_{50}) are given in Table 3. Plots of TSI of the blends of LDPE and EVA containing different dosages of PCNSL as a function of dosage of EVA in LDPE are given in Figure 7.

The thermograms given in Figures 2–6 show that in all cases there is a clear shift in the curves to high temperature region with the increase in dosage of



Figure 5. Thermograms of a blend of LDPE and EVA (25/75) modified with different dosages of PCNSL.

PCNSL in the polymer matrix indicating an improvement in thermal stability. Also, the results given in Table 3 in general show a similar shift in the peak temperatures obtained from DTG. The thermal stability index (T_{50}) increases progressively with the increase in dosage of PCNSL in all the mixes. This is particularly prominent in the blends of LDPE and EVA as shown by the results in Table 3 and Figure 7. It may be noted from



Figure 6. Thermograms of EVA modified with different dosages of PCNSL.

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Figure 7. Thermal stability index of blends of LDPE and EVA containing different dosages of PCNSL.

the results given in Table 3 that the thermal stability index (T₅₀) of the blends increases steadily with the increase in the proportion of EVA. This may be due to the increasing interaction between the polar groups of EVA. Also, the result shows that as the dosage of PCNSL in the blend increases the thermal stability also increases as well. This is particularly prominent in the blends containing EVA. This indicates the probability for some sort of interaction between the polar groups of EVA and that of PCNSL leading to an alteration in the thermal decomposition pattern and consequent improvement in thermal stability. Similar results are reported by the authors in natural rubber (NR) systems modified with PCNSL [13]. It is possible that PCNSL may alter the decomposition pattern of the aliphatic hydrocarbon polymers from an essentially free radical type to one that is more of a condensed phase type with probable formation of cyclized aromatic rings

CONCLUSION

The results discussed above lead to the following conclusions. The plasticizing effect of PCNSL in LDPE, EVA and their blends at low dosages (5 to 10%) is clearly shown by the decrease in indices of melt viscosity, melt elasticity and power consumption for mixing. This in turn could lead to improved melt processability of the blends. Besides, the progressive increase in thermal stability index of the blends with increase in dosage of PCNSL from 0 to 10% and the shift in the thermograms to the higher temperature region indicate the capability to design blends having improved thermal stability by modification with PCNSL. Hence, it is expected that such PCNSL modified systems may be used as precursors for the design and development of compositions for specific applications.

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