Studies on Blends of Melt-Processable Liquid Crystalline Polymers and Thermoplastics. I. Blend of Polyesteramide with Polyethylene

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ABSTRACT: The processability characteristics, physicomechanical properties, and thermal decomposition characteristics of blends of low-density polyethylene (LDPE) and polyesteramide (PEA), a thermotropic liquid crystalline polymer, were studied using various analytical techniques. Studies on a Brabender Plasticorder at temperatures ranging from 170 to 230°C showed good melt processability for the blends. The melt rheology of the blends containing 0–15% of PEA at 170°C was studied using a capillary rheometer (Goettfert) fitted with a circular die ($L/D = 30/1$) at apparent shear rates ranging from 12 to 2300 s^{-1}. The samples containing PEA showed a comparatively lower die swell at high shear rates. X-ray diffraction measurements showed a reduction in crystallinity of LDPE in the presence of 2–4% of PEA. Scanning electron microscopic evaluation of the morphology of the fractured surface of the blend showed some degree of orientation, but not to the level typical of LCPs. However, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated significant improvement in the resistance to thermooxidative decomposition of LDPE modified with PEA. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1811–1817, 2000

Key words: blends; liquid crystalline polymer; polyesteramide; low-density polyethylene; processability; physicomechanical properties; melt rheology

INTRODUCTION

Blends of thermoplastics with liquid crystalline polymers (LCP) have emerged recently as a class of materials having an excellent combination of superior processability and physicomechanical properties.[1–41] The improvement in processability is very often indicated by a reduction in melt viscosity.[16] Thus, it has been shown that a decrease of melt viscosity and a decrease of the glass transition are characteristic of the plasticizing effect of LCP in a thermoplastic matrix.[1] Also, it has been reported that a variety of thermotropic liquid crystalline polymers (TLCPs) show a reinforcing effect either with or without compatibilizers when blended with general-purpose thermoplastics and engineering thermoplastics.[3–41] This has been attributed, in many cases, to fibrillar orientation of the liquid crystal domains in the thermplastic matrix.[10,11,16,23–25] Also, it has been shown that interactions between the polar groups of a compatibilizer and the blend components can serve as physical crosslinks at the interface, leading to reduced interfacial energy, improved interfacial adhesion, and, consequently, improved mechanical properties.[18] Recently, we synthesised a novel liquid crystalline PEA (I) exhibiting a nematic phase at the transition temperature of 160°C.[42,43]
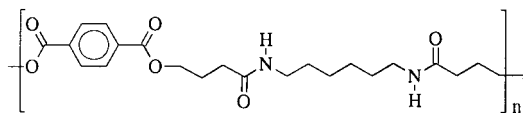
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This temperature is suitable for preparing blends with polyolefins. The polymer also exhibited fiber-forming behavior on cold drawing. In this article, we report the results of studies carried out on the processability characteristics, physicomechanical properties, and thermal decomposition characteristics of blends of low-density polyethylene (LDPE) and liquid crystalline PEA.

EXPERIMENTAL

Materials

LDPE of grade Indothene was obtained from M/s Indian Petrochemicals Ltd. (Gujarat, India). PEA was synthesized at the Regional Research Laboratory (CSIR) (Thiruvananthapuram, India) by melt polycondensation of an amido diol with dimethyl terephthalate.[42]

Methods

LDPE was mixed with various proportions (0–15%) of PEA in a Brabender Plasticorder at 170°C and at a rotor speed of 30 rpm for 10 min each. The melt rheology of the blends at 170°C was studied using a capillary rheometer (Goettfert Rheotester 1500) fitted with a round hole die (L/D = 30/1) at apparent shear rates ranging from 11.5 to 2880 s^{-1}. Test samples for measuring the tensile properties and thermal decomposition characteristics were prepared by compression molding the mixes at 170°C for 5 min each. Tensile properties were measured on a universal tensile tester (Instron 1195) at a crosshead speed of 500 mm/min using dumbell test specimens punched out from the compression-molded samples. Wide-angle X-ray diffraction studies of the blends was carried out with the help of an XRD spectrometer (Philips A-1710) using a CuKα source at 35 kV, 15 mA, in the angular range from $2\theta = 10°$ to $2\theta = 50°$. The topography of the fracture surfaces of the samples from tensile failure was studied under a scanning electron microscope (Jeol JSM 65C). The fracture zones of the samples were taken out carefully without touch-ing the surface, fixed on stubs, sputter-coated with gold in a vacuum within 24 h after testing, and observed under an SEM at a 0° tilt angle. Thermal decomposition characteristics of the samples in air (at a heating rate of 20°C/min) and in oxygen (at a heating rate of 10°C/min) were measured using a thermogravimetric analyzer (DuPont 951) coupled to a data processor (Thermal Analyst 2000). The thermooxidative decomposition behavior of the samples was studied using a differential scanning calorimeter (DSC 2010, TA Instruments) coupled to a data processor (Thermal Analyst 2100).

RESULTS AND DISCUSSION

Processability Characteristics on a Brabender Plasticorder

Brabender torque profiles of LDPE and a blend of LDPE and PEA (4%) at various temperatures such as 170, 200, and 230°C and at a rotor speed of 30 rpm are given in Figure 1. It shows comparatively lower values of torque in the presence of PEA at the higher temperatures of 200 and 230°C. It is possible that at the higher temperatures the PEA phase may melt and the molecular orientation of its crystalline phase along the shear direction may facilitate melt flow together with a reduction in melt viscosity.

Melt Rheology

The apparent melt viscosity of blends of LDPE and PEA at 170°C was measured over a wide range of shear rate using the capillary rheometer. Figure 2 shows that the apparent viscosity of blends containing 5 and 10% of PEA is very close to that of the unmodified LDPE at the different shear rates.

Table I gives the die swell ratio of the blends at different shear rates and at 170°C. In general, the blends containing PEA show a comparatively lower die swell ratio over the shear rate range from 23 to 2300 s^{-1}. This may probably be due to the orientation of the liquid crystalline domains of PEA in the LDPE matrix along the direction of strain which hinders the Brownian motion of the molecules of LDPE outside the capillary leading to die swell.

The results given in Table II shows comparatively higher values of the principal normal stress difference for the blends of LDPE and PEA as
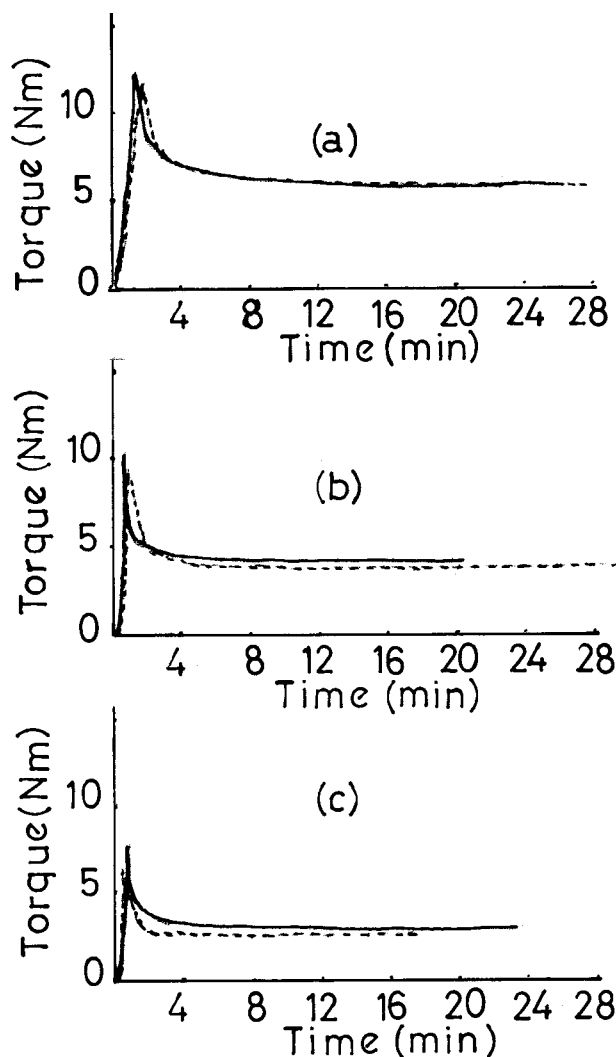
Figure 1 Brabender torque profiles of LDPE and a blend of LDPE with PEA: (a) 170°C; (b) 200°C; (c) 230°C. Rotor speed, 30 rpm.

against that of the unmodified LDPE. This indicates poor compatibility between the blend components in the former. This is in agreement with the observation of Han and Yang that polymeric blends which are not compatible show a higher value of the principal normal stress difference.[44,45]

Tensile Properties

The tensile properties of the blends are given in Table III. The progressive increase in the modulus and decrease in the elongation at break with increase in the proportion of PEA indicate an increase in tensile stiffness of LDPE in the pres-

ence of PEA. However, the results show only a marginal increase in the tensile strength of the blends with increase in the dosage of PEA up to 10%. These results are very much in agreement with similar results reported for systems based on blends of polyethylene and a semiflexible liquid crystalline polymer.[21] It has been shown that the blend components are immiscible in these systems and that the reinforcing effect of the LCP is practically nil for the HDPE grades. A study on the morphology of blends of a thermotropic liquid crystalline polymer (TLCP) and HDPE using SEM by Whitehouse et al. showed spherical droplets of TLCP with diameters of less than 1 micron, irrespective of either TLCP concentration or shear rate.[21]

The SEM micrographs of unmodified LDPE and a blend of LDPE with 4% PEA are given in Figure 3. The figure shows only a limited extent of orientation of LDPE in presence of PEA, accounting for the marginal reinforcing effect of PEA. In many cases, considerable fibrillation has been reported when LCPs are blended with thermoplastics.[23–25] The low level of fibrillation in the present case can be understood from the structure of the PEA. The significance of this polymer is the presence of an aliphatic diamide link that by ex-
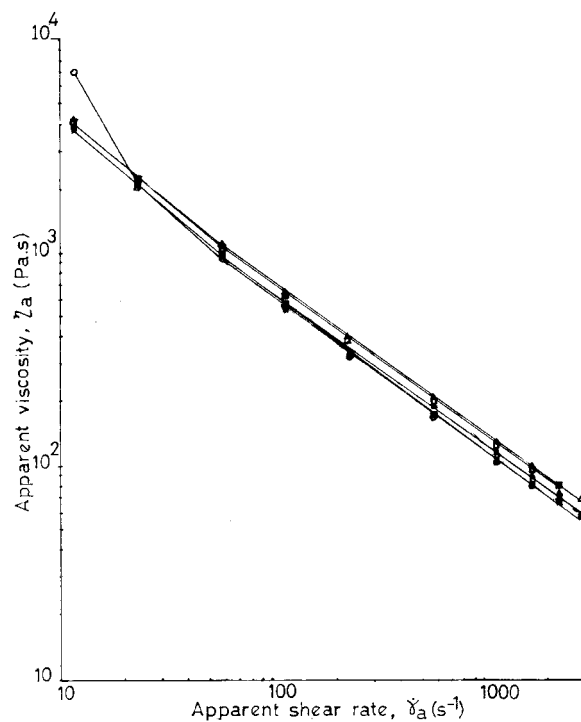

Figure 2 Variation in apparent viscosity with apparent shear rate at 170°C of LDPE containing PEA.

Table I   Die Swell Ratio of the Blends of LDPE and PEA at 170°C and at Different Shear Rates

Apparent Shear Rate (s^{-1})	Dosage of PEA (%)					
	0	2.5	4	5	10	15
11.52	—	2.824	2.981	2.778	2.788	2.767
23.04	—	2.586	2.845	2.515	2.494	2.512
57.60	—	2.485	2.245	2.588	2.590	2.567
115.20	—	2.400	3.897	2.518	2.495	2.458
230.40	2.409	2.363	2.380	2.415	2.424	2.331
576.00	2.259	2.207	2.236	2.230	2.284	2.129
1152.00	2.200	2.169	2.219	2.179	2.195	2.160
1728.00	2.189	2.170	2.250	2.193	2.145	2.202
2304.00	2.215	2.202	2.332	2.286	2.109	2.251
2880.00	—	2.294	2.344	2.229	2.105	—

tended hydrogen bonding is thought to stabilize the liquid crystalline phase.[42] So, at the processing temperature, the comingling of the hydrophobic polyolefin with PEA disturbs the hydrogen bonding and the liquid crystallinity is considerably reduced. In blends of LCP with conventional thermoplastics, the development of infinite, thin, and highly oriented LCP fibrils is considered essential for a substantial mechanical reinforcement.[22] For the deformation of LCP droplets into fibrils in a thermoplastic matrix, the elongational flow of the polymer melt is found to be much more effective than is the shear flow.[22] During the mixing of PEA with LDPE in the Plasticorder at a low rotor speed (30 rpm), the shear flow of the polymer melt occurs at a low rate. It is known that the shear flow of liquid crystals can lead to tumbling of directors unless the shear rate is very high and,

consequently, an overall decrease in the molecular orientation.[22]

The X-ray diffraction patterns of LDPE and its blends with PEA are given in Figure 4. This shows a progressive reduction in the intensity of the crystalline peak with increase in the concentration of PEA from 0 to 4%. It may be possible that PEA, which is polar in nature, may hinder the inherent crystallization tendency of LDPE, which is essentially nonpolar.

Thermooxidative Decomposition Characteristics

Thermogravimetric Analysis (TGA) in Air

The results of the TGA of the samples carried out in air are given in Table IV, and the thermograms, in Figure 5. A progressive shift in the

Table II   Principal Normal Stress Difference (kPa) of the Blends of LDPE and PEA at 170°C and at Different Shear Rates

Apparent Shear Rate (s^{-1})	Dosage of PEA (%)					
	0	2.5	4	5	10	15
11.52	—	284.1	302.5	252.6	257.6	252.3
23.04	—	269.1	282.9	241.3	240.2	243.3
57.60	—	301.3	260.8	291.5	292.3	290.6
115.20	130.6	334.2	327.1	318.8	318.4	315.4
230.40	347.9	394.5	419.3	354.1	360.9	347.4
576.00	405.2	466.4	497.0	405.8	418.7	410.8
1152.00	479.9	567.5	610.9	489.2	483.0	528.0
1728.00	541.3	655.2	709.5	565.0	536.0	624.7
2304.00	615.0	744.0	825.8	658.9	581.1	715.5
2880.00	—	859.6	894.0	694.2	633.9	—

Table III   Tensile Properties of Blends of LDPE and PEA

PEA (%)	Modulus (MPa) 10%	Tensile Strength (MPa)	Elongation at Break (%)
0	9.8	11.7	37
2.5	11.1	11.8	33
10	11.4	12.1	29

decomposition profile of the blends (at the major decomposition around 400°C) toward higher temperature with increase in the dosage of PEA from 0 to 15% is observed. Also, the results given in Table IV show a significant and progressive increase in the thermal stability index T_{50} from 394 to 425°C, with increase in the concentration of PEA in the blend from 0 to 15%. This shows improvement in the thermal stability of LDPE in the presence of liquid crystalline PEA, which may be mostly due to the aromatic content of the latter.
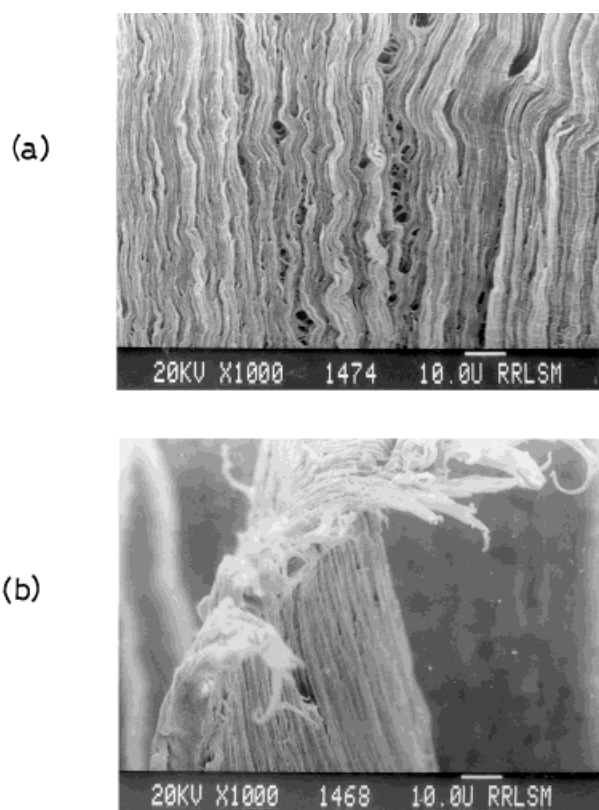
Figure 3   SEM micrographs of tensile fracture surfaces of (a) LDPE and (b) LDPE + 4% PEA.
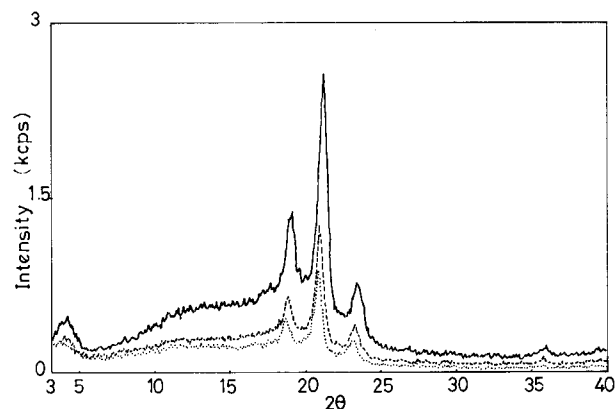
Figure 4   X-ray diffraction patterns of LDPE and blends of LDPE with PEA.

Thermal Analysis in Oxygen [Differential Scanning Calorimetry (DSC)]

Figure 6 shows the thermograms of an unmodified LDPE sample and one containing 4% PEA as obtained from DSC of the samples in an oxygen atmosphere at a heating rate of 10°C/min. The values of the enthalpy of oxidation as obtained from the integrated area under the exotherm peak in the temperature range from 211 to 290°C increased from 35.7 kJ/mol for LDPE to 62.86 kJ/mol for a blend containing 4% PEA.

Generally, a reduction in the enthalpy of oxidation of a polymer in the presence of an additive indicates its antioxidant effectiveness.[46] The above results show more than a fivefold increase in the resistance to thermooxidative decomposition of the sample containing 4% of PEA. This is supported by the result obtained from thermogravimetric analysis of these samples in an oxygen atmosphere at the same heating rate (10°C/min). The thermogravitograms (Fig. 7) show a lower rate of decomposition for the sample con-

Table IV   Thermal Decomposition Characteristics of Blends of LDPE and PEA

Parameter	Dosage of PEA (%)			
	0	4	10	15
Thermal stability index, T_{50} (°C)	400	416	418	425
Activation energy, E_a (kcal/mol)	155.4	279.7	215.7	207.5

TGA in air, 20°C/min.

Figure 5   Thermograms of blends of LDPE and PEA.

Figure 7   Thermogravitograms of LDPE and a blend of LDPE with PEA in oxygen.
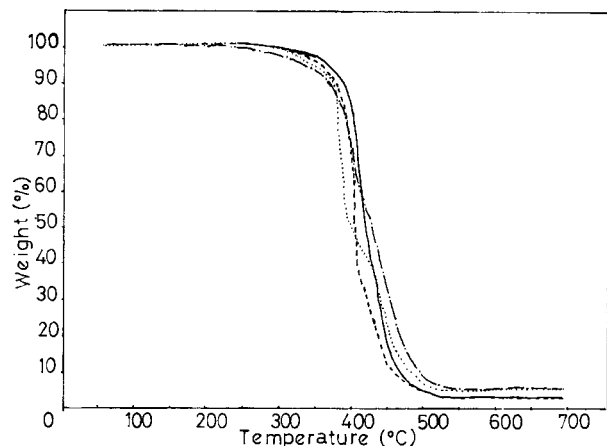
taining PEA as against that of the unmodified sample. The improved resistance to thermooxidative decomposition of the blend is thus indicated.

CONCLUSIONS

Studies on the melt processability, rheology, and physicomechanical properties of blends of LDPE and a thermotropic liquid crystalline PEA showed improvements in some of the processability characteristics and physicomechanical properties. Thus, the reduction in mixing torque observed in a Brabender Plasticorder at higher temperatures
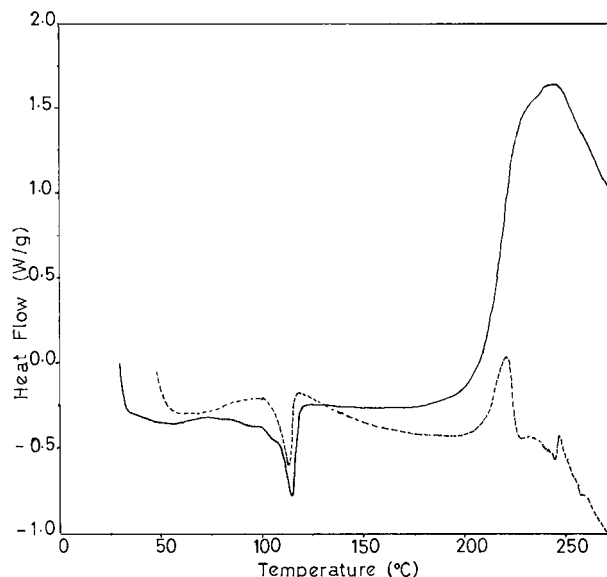
and a lower die swell ratio of the blends at higher shear rates in a capillary rheometer indicate improvement in the processability. TGA and DSC showed significant improvement in the thermal stability and resistance to thermooxidative decomposition of the blends. Although there was some increase in the tensile modulus of the blends, the increase in tensile strength was not considerable. This was again indicated by the morphology of the blend observed under an SEM.

Figure 6   DSC thermograms of LDPE and a blend of LDPE with PEA in oxygen.

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