Compatibility of Low-Density Polyethylene–Poly(ϵ-caprolactone) Blends

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Synopsis

The compatibility of low-density polyethylene (LDPE)–poly(ϵ-caprolactone) (PCL) was examined using the microscopic, the dynamic mechanical, and the DSC techniques. Morphological examination revealed that at low PCL concentrations, when specimens are severely quenched, a uniform microspherulitic structure is formed. The dynamic mechanical spectra, at isochronous conditions (110 Hz), indicate very limited mixing of the amorphous phase of the two components at the intermediate compositions. More drastic relaxation shifts were observed at the extremes of the composition range. Ultimate strength and elongation at break are characteristic of a mechanically compatible system at high and low PCL contents. In the intermediate composition range their low value indicates phase separation. DSC measurements showed a nonlinear dependence of bulk crystallinity on blend composition; also, that the presence of PE enhances the degree of PCL crystallinity. Thermal history strongly affects bulk crystallinity. At elevated temperatures, near the mp of PE, thermal treatment affects considerably the melting point of the PE crystals.

INTRODUCTION

In this report the compatibility of low-density polyethylene (LDPE) with poly(ϵ-caprolactone) (PCL) is examined. The system is of interest not only on theoretical grounds—not many blends with both crystallizable components have been studied[1,2]—but also because PCL blended with polyolefins and coextruded gives high tenacity, dyeable fibers.[3,4] Of basic interest was also to examine the type of interaction (amorphous–amorphous, amorphous–crystalline, or crystalline–crystalline) that contributes to a possible mechanical integrity of this system. Brode and Koleske[5] reported results on dynamic mechanical properties at a single composition (10% PCL in LDPE). Though they observed some shift to higher temperatures of the α PE relaxation, they could not locate the PCL amorphous β relaxation. This was attributed to miscibility, or to the low amount of PCL used. X-ray investigations could not elucidate the nature of the crystalline–crystalline interactions, or decide on the possibility of cocrystallization because of similarity of the diffraction patterns for the two homopolymers; both have an orthorombic unit cell with almost identical a, b-axes. A related study[6] using SAXS and the DSC techniques indicated that under certain crystallization conditions, epitaxial crystallization (in the form of fibrillar lamellae) of PCL on polyethylene (PE) is possible. This led to an increase of the degree of crystallinity and of the mp of PE. Evidence for hydrodynamically induced crystallization of PCL in guttapercha, both dissolved in benzene, was also presented.[7] More recent work by Krevor and Phillips[8] described the crystallization behavior of a 10% PCL/LDPE blend using the DSC technique. Melting endotherms indicated a crystal–crystal interaction; however, no conclusive evidence of cocrystallization was presented.

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In this work the dynamic mechanical technique was employed since it is known that loss modulus variation can indicate the degree of amorphous phase mixing even in semicrystalline polymers.[9] Melt-mixed samples were studied in the complete composition range using quenched and some annealed specimens. Thermal behavior was studied using the DSC technique, and ultimate tensile data were determined to ascertain the composition range, wherein useful mechanical properties are maintained. Thermal aging effects were also examined. Optical microscopy was employed to ascertain the influence of changing composition on gross morphological features of the crystalline structure of the blends.

EXPERIMENTAL

Materials and Specimens Preparation

LDPE was obtained from BDH Co., UK. Its mp was reported to be 112°C, its density 0.924 g/mL (BS 3412), and its melt flow index 8.0 g/10 min (BS 2782, method 105 c). PCL was donated by Union Carbide and is traded under the designation PCL-700. Its $\overline{M}_w$ was reported to be ca. 40,000. Other characterization data have been given by Koleske[3] and Borri and coworkers.[10] Mixing of the two polymers was performed by dissolving PE in *p*-xylene at ca. 120°C, adding PCL at the proper ratio and coprecipitating in cold methanol. The vacuum dried mass (4 days at 50°C) gave thin films using the Laboratory press. At low PCL contents (10%), the melt and the film produced was transparent. At the intermediate compositions, the films were opaque white, and their surface had a fibrillar texture. At the other extreme of compositions, the films were milky white, flexible with a glassy surface. Quenched films were produced by pressing between aluminum foil at 140°C and ca. 80 kg/cm^2 for 1 min and immersing in liquid nitrogen. Annealing was performed by heating quenched films for 24 h at 100°C and subsequently at 25°C. Preliminary studies with the DSC indicated that, at a cooling rate of 20°C/min, PE and PCL blend components crystallized at the previous temperatures, respectively.

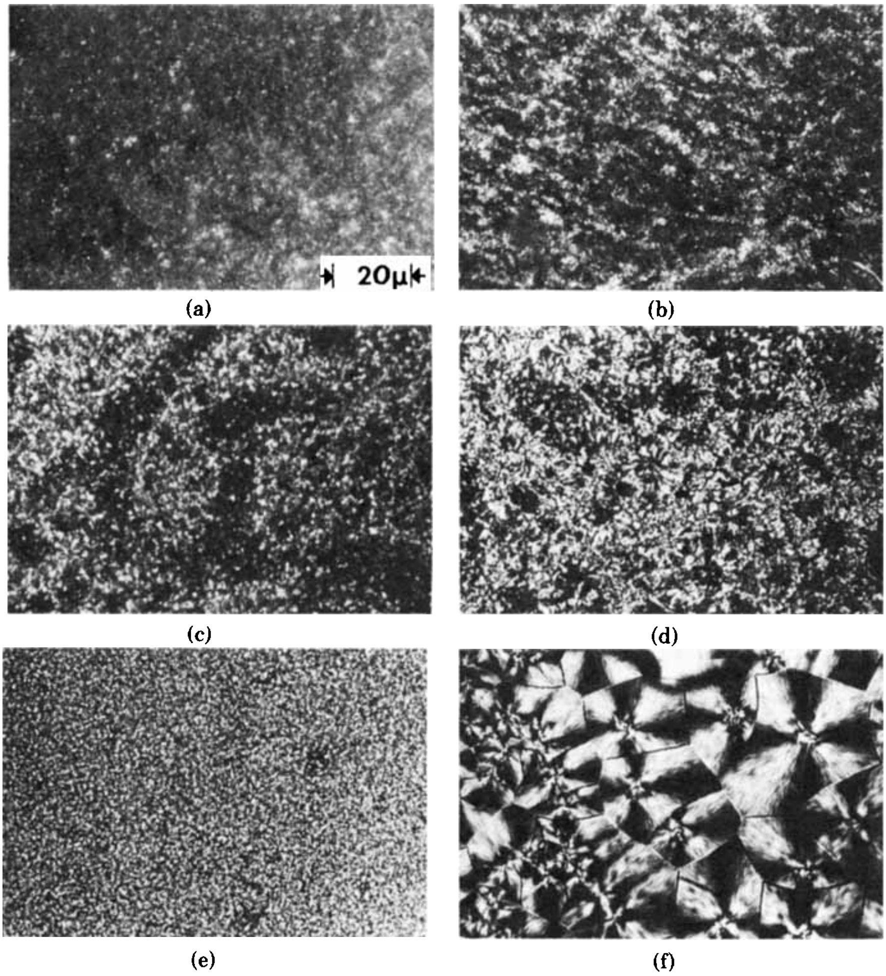
The following compositions were studied; 0P/100, 10P/90, 25P/70, 50P/50, 70P/30, 90P/10, 100P/0, the first numeral denoting the percentage by weight of PCL.

Apparatus and Procedure

Dynamic mechanical data, loss tangent, and complex modulus $|E^*|$, were obtained between −120°C and 110°C at 110 Hz, using the direct reading viscoelastometer (Rheovibron model DDV IIC, Toyo Baldwin Co). The correction due to clamp extension was applied at all temperatures using the recommended procedure.[11] The chamber was kept free of moisture by a slow stream of precooled argon. Specimens dimensions were 3.0 × 0.3 × 0.02 cm.

DSC measurements were carried out using a DuPont 910 Calorimeter System coupled with a 990 Programmer-Recorder. The heating rate was 10°C/min, the cooling rate 20°C/min, and the sample weight about 6 mg. Instrument calibration was carried out using an In standard.

Microscopic examination was performed on quenched films using a Leitz



(a) (b) (c) (d) (e) (f)

Fig. 1. Optical micrographs of quenched blends with crossed polarizers. (a) 10P/90; (b) 25P/75; (c) 50P/50; (d) 70P/30; (e) 90P/10; (f) 100P/0. (a and b) Films quenched in liquid nitrogen; (c, d, e) quenched at 0°C within microscope slides; (f) PCL freely crystallized on microscope slide.

Wetzlar polarizing microscope equipped with an Orthomat camera. Samples 10P/90 and 25P/75 were sufficiently thin and transparent to be directly examined after mounting on the microscope slide. Other compositions were prepared by melting the blend on the microscope slide and slightly pressing the molten film with a cover glass, to obtain a sufficiently thin layer. These were subsequently quenched to 0°C.

RESULTS AND DISCUSSION

Morphology

Microscopic examination with crossed polarizers of the 10P/90 composition showed poorly developed microcrystallites, uniformly dispersed in an amorphous

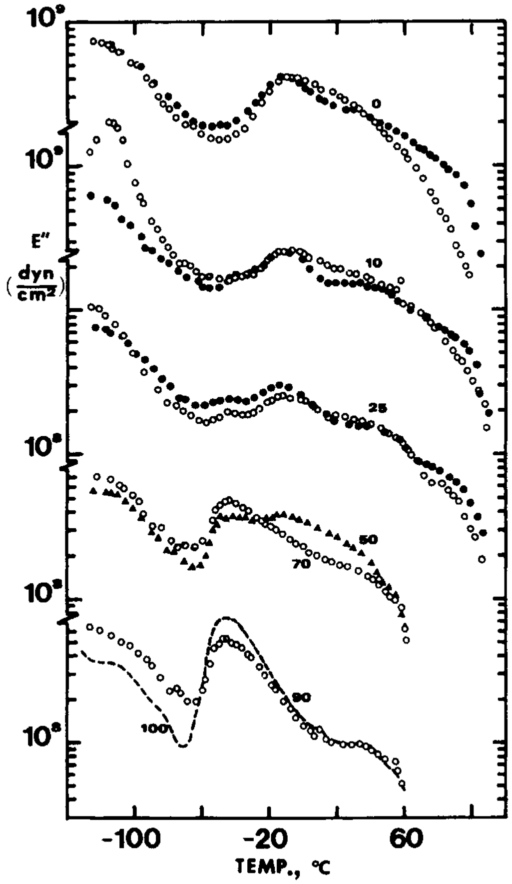


Fig. 2. Temperature dependence of the loss modulus of blends. Numbers next to curves denote wt % PCL: (○, ▲, – –) quenched; (●) annealed.

matrix; see Figure 1(a). Under similar conditions of sample preparation, the 25P/75 sample also displayed the existence of microcrystallites, however, with increased degree of clustering [Fig. 1(b)]. At higher PCL contents an increase of the crystallite size was evident [Fig. 1(d)]. Also, there is evidence of amorphous-crystalline phase segregation, especially, at the 50P/50 composition. More uniform microcrystalline structure was observed at the highest PCL contents [sample 90P/10, Fig. 1(e)].

The main conclusion from the morphology examination is that at the extremes of composition, and in severely or moderately quenched samples, especially, at high PE contents, crystallite size is considerably reduced. This is further corroborated by the DSC melting endotherms at these compositions; see below, DSC results.

Dynamic Mechanical and Tensile Properties

The results on the dynamic mechanical properties are summarized in Figures 2 and 3, in terms of the temperature dependence of the loss and storage modulus, E'' and E', respectively. Less emphasis is given to tan δ spectra since, in the case

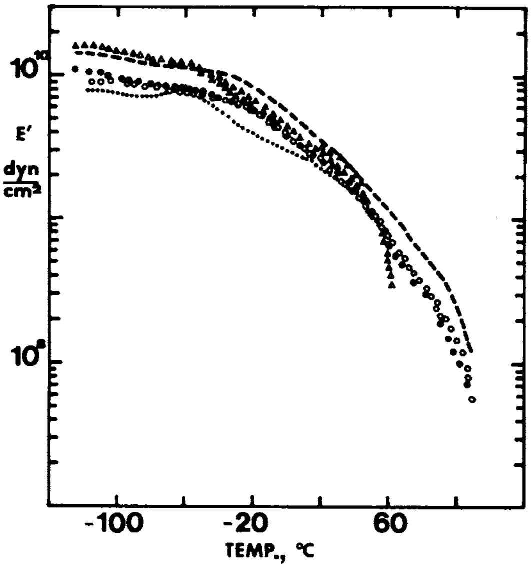


Fig. 3. Temperature dependence of the storage modulus of quenched blends: (– –) 0P/100; (○) 10P/90; (●) 25P/75; (△) 50P/50; (▲) 70P/30; (· · ·) 100P/0.

of semicrystalline polymers, loss tangent is affected[12] by crystallinity either originally present or developed during the measurement as the temperature increases. The effect of annealing at the PE rich compositions is also indicated, in Figure 2. Of the main amorphous PE phase relaxations, the β at −7°C and the γ at ca. −120°C, the former (due to the relaxation of branch points[13]) will be used to assess amorphous phase mixing. The α relaxation due to the crystalline phase[12] is made evident at ca. 40°C, after annealing (see compositions 0P/100 and 10P/90, in Fig. 2). Introduction of 10% PCL does not change the position or strength of the β relaxation. Annealing, however, leads to limited phase separation as evidenced by the emergence of a small peak at ca. −40°C associated with a PCL-rich blend. A considerable variation of the main PCL relaxation because of strong crystalline–amorphous interaction has been reported by Koleske and Lundberg.[14] Thus T_g was reported at −55°C and −60°C (at ca. 2 Hz) for annealed and quenched specimens, respectively, and at −71°C from extrapolation to 100% PCL, using T_g data of amorphous PVC–PCL blends. This coupling of crystalline–amorphous phase causes some peak broadening. At 110 Hz the relaxation maximum of PCL was located at ca. −48°C (see Fig. 2).

Further increase of the PCL component (>10%), causes both β peaks to emerge, the PCL relaxation increasing in magnitude at the expense of the PE peak. The result at the 50P/50 composition is a broad spectrum with considerable peak overlap. At this composition the E'' drops rapidly at ca. 60°C, indicating an inversion of the crystalline matrix in the blend (see below). At higher PCL levels (>70%) the PE β relaxation is not evident and the blend relaxation is shifted to ca. −47°C. The spectra indicate other weak relaxations (see 90P/10 composition) at ca. −75°C and 10°C, which we attribute to thermal stresses as the temperature is raised, and at ca. 35°C due to the onset of additional PCL crystallization. The temperatures of the relaxations maxima observed are re-

TABLE I

Viscoelastic and Melting Transitions of the Blends

Polyblend sample	a. Temperatures of relaxations maxima[a] (°C)			b. Melting data of blend component			
	$E''_{\max}$			PE		PCL	
				T_m (°C)			
	α	β	γ	Peak	End[b]	Peak	End
Quenched							
0P/100	—	−7	<−120s	110	113	—	—
10P/90	—	−6	−115	110	113	56.8	61
25P/75	—	−45w, −12	<−120s	110	114	56.0	59
50P/50	—	−48 to −15	<−120s	109.7	114	55.0	58
70P/30	—	−47	<−120s	109	112	56.0	59
90P/10	—	−47	<−120s	110	113	58.7	61
100P/0	—	−48	−117s	—	—	59	61
Annealed							
0P/100	40s	−10	<−120s	110.5	114	—	—
10P/90	40	−44w, −12	<−120s	110.5	114	58	61
25P/75	40s	−49, −15	<−120s	111	114	58.5	61
50P/50				110	113	58.5	62
70P/30				110	112	58.5	62
90P/10				110	112	59	62
100P/0				—	—	60	63

[a] w = weak relaxation; s = shoulder.

[b] Extrapolated end point.

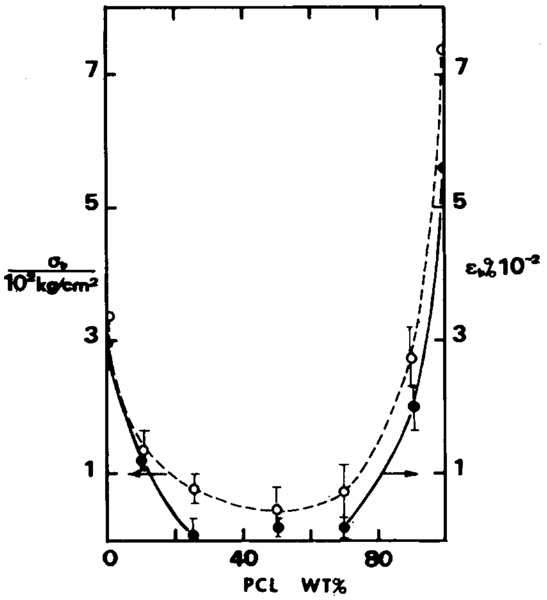


Fig. 4. Composition dependence of true ultimate strength σ_b and percent relative elongation at break ϵ_b of blends at 30°C: (○) quenched; (●) annealed.

ported in Table I. The data indicate considerable plasticization of the PE amorphous phase by the PCL. At high PCL contents the dominating character of this component in the blend is evident in the thermomechanical spectra. In general, these spectra indicate amorphous phase mixing at the extremes of blend composition when specimens are quenched. At intermediate compositions, though the β PE peak showed some shift, the spectra indicate phase separation.

In Figure 3 modulus variation shows the increased stiffness of PE rich compositions in the higher temperature region (above 50°C). Changing composition does not affect significantly the stiffness of the blends since both components are semicrystalline. However, at compositions with PCL $\geq$ 50% the loss of mechanical integrity at ca. 60°C (near the mp of PCL) indicates a matrix inversion from PE to that of PCL.

Additional crystallization of the PCL phase in quenched specimens was also observed when temperature was increased (see the hump at ca. 20°C of the 70P/30 composition, in Fig. 3). This aging effect was examined by heating the specimen near to T_m in the Rheovibron chamber, quenching to 30°C, and following the modulus increase with time. Modulus attained a steady value after ca. 50 h, increasing by 6–11% at the PE-rich blends and by 20–25% beyond the 50P/50 composition. Similar aging effects were reported by Robeson[15] on PCL–PVC blends.

More revealing on the question of compatibility were some preliminary results on the ultimate strength σ_b and the relative elongation at failure ϵ_b of films, obtained at 30°C. It is reported[16] that among tensile properties ultimate strength and elongation are most sensitive indicators of phase separation. The results shown in Figure 4 indicate that the two polymers are incompatible at

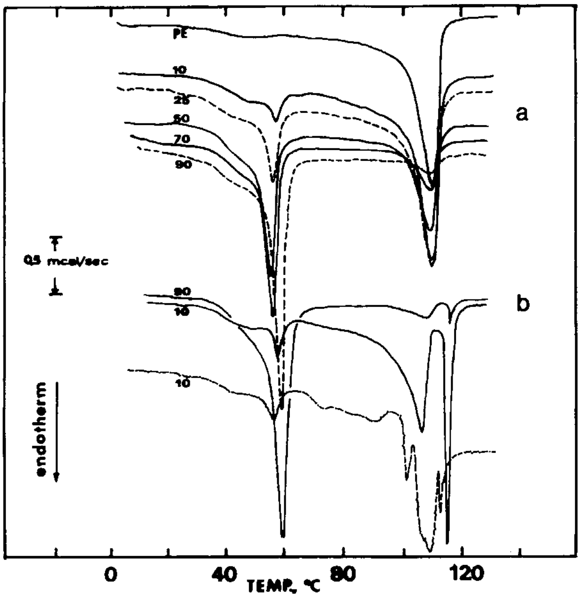


Fig. 5. DSC thermograms of blends: (a) quenched, (b) thermally treated at 110°C; (---) after recycling of (b). Numbers next to curves indicate wt % PCL.

intermediate compositions, while at the extremes of composition they are "mechanically" compatible. The results are consistent with those obtained from the dynamical mechanical spectroscopy. The observed ϵ_b variation with composition shows a pattern similar to that reported for the polybutylene–polypropylene[2] and other polyolefin blends.[16,17]

Thermal Properties

DSC measurements were taken with quenched and annealed samples. Figure 5(a) shows the thermograms obtained for the quenched blends. Both melting endotherms are clearly resolved only at the rich PCL compositions (above 70% PCL). At the other compositions there is considerable overlap increasing with the PE content. Melting points of the individual components are reported in Table I. For the quenched blends the T_m of PCL is slightly depressed. The effect is small and can be attributed to reduction of crystallite size and/or perfection. In Figure 6 total melting area per unit weight of blend has been plotted vs. blend composition. The plot shows that the two components do not crystallize independently of each other since bulk crystallinity does not vary linearly with composition. Crystallinity is enhanced near the extremes of the composition range. Annealing removes this peculiarity. A reasonable explanation would be that, in quenched specimens, the PCL crystals developed (during storage at 25°C, or during the DSC scan) can do so more freely because quenching reduces the amount and size of PE crystals. (This last effect was more clearly evident by the dynamic mechanical technique.) In annealed samples, the development of crystallinity (at 100°C) reduces by interference the amount of PCL

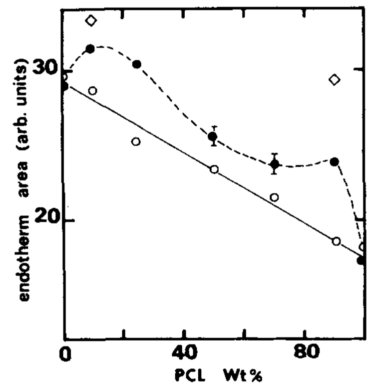


Fig. 6. Composition dependence of the bulk crystallinity of blends: (●) quenched; (○) annealed; (◇) thermally treated at 110°C.

crystallinity that can subsequently be developed when annealed at 25°C. To determine which of the two crystallizable components is responsible for this crystallinity enhancement, an approximate curve resolution of the two peaks was made. The results reported in Figure 7 indicate that, in quenched blends and at the scanning rate employed, PCL crystallizes to a larger extent in the presence of small PE crystals. This is probably due to an epitaxial crystallization of PCL on PE reported by Takahashi et al.[6] The DSC data cannot give any clue as to the possibility of cocrystallization; however, given the exacting requirements for this to happen[18] and the moderate interaction indicated by the mechanical spectra, mixed crystal formation at the above annealing conditions should be excluded.

In an experiment involving thermal treatment of a 10P/90 and 90P/10 com-

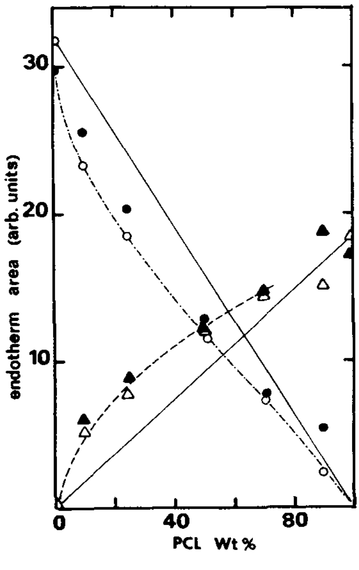


Fig. 7. Composition dependence of the bulk crystallinity of the PE and PCL components in the blend: (●, ○) PE; (▲, △) PCL; (○, △) quenched; (●, ▲) annealed samples.

position at 110°C for 24 h, the PE component gave a double endotherm with T_m (peak) at 107°C and 115°C [see Fig. 5(b)]. Similar findings were reported by Krevor and Phillips[8] when the blend was melted at 125°C and annealed, using however a PCL grade with $\overline{M}_w = 15{,}000$. Takahashi and coworkers[6] reported an increase of the PE mp when PCL was epitaxially crystallized on PE. The appearance of a higher mp fraction compared to the original PE could also be explained if it is assumed that during this process crystal defects are removed, yielding more nearly perfect higher mp crystals. Krevor and Phillips[8] reported a disappearance of the PCL peak after thermal recycling of a 10P/90 sample heated to 125°C. This they attributed to "incorporation" of the PCL in the PE crystal. In our case we observed development of additional peaks [see Fig. 5(b)], suggestive of PE fractionation.[19,20] The conclusions of the above paragraph are tentative, and further experimentation is needed to clarify high-temperature thermal treatment effects on PE crystallization in the presence of PCL.

CONCLUSIONS

1. Microscopic examination revealed a microspherulitic structure at low PCL contents when specimens were quenched.
2. Dynamic mechanical and ultimate tensile properties indicate considerable "mechanical" compatibility at the extremes of blend composition, especially when specimens are severely quenched.
3. In quenched specimens, crystallization of PCL is facilitated by the presence of the PE phase, at the extremes of blend composition. Crystal perfection and possibly MW distribution of the PE component are affected by the temperature of the thermal treatment to which the blends are subjected.

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