Property–Composition Dependence of Isotactic Poly(butene-1)-Chlorinated Polyethylene Blends

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Synopsis

Melt-mixed blends of isotactic poly(butene-1) (PB) with chlorinated polyethylene (containing 48 wt % Cl) (CPE) were studied in the complete composition range. Phase contrast, polarizing, and scanning electron microscopy revealed that the blend is heterogeneous. The results were confirmed by the dynamic mechanical technique and differential scanning calorimetry. The latter technique indicated also that CPE does not influence the crystallinity of PB. Tensile behavior of the blends was good, especially at low CPE contents. The results were analyzed using phenomenological mechanics models. From the correlation obtained one can conclude that the blends are mechanically compatible. Limiting oxygen index data were also determined, to characterize the flammability behavior of the blends in the complete composition range.

INTRODUCTION

Among polyolefins, isotactic poly(butene-1) (PB) gained significant importance in various applications (e.g., piping for home heating), because of some inherent advantages.[1,2] These are excellent resistance to creep and environmental stress cracking, weldability, and flexibility.[2,3] Compared to other plastics (e.g., PVC, PP, and PEs), it has the disadvantage of a higher cost. A practical way to offset this would be to blend it with other plastics suitably chosen so that its property/cost value is not impaired. Thus blending with isotactic polypropylene (iPP) could be of value since studies have shown[4,5] that such blends, being mechanically compatible, retain (within limits) the useful constituents' properties. A further property diversification can be attained by blending PB with chlorinated polymers, and a literature survey indicated that no such studies have been published before.

In this work we report on the physical and mechanical properties of PB/chlorinated polyethylene (CPE) (containing 48 wt % Cl) blends in the complete composition range. Considerations that led to this choice were: CPEs are low cost resins with higher thermal stability than PVC. Their inherent flexibility would not impair this property, as well as the impact strength of PB. Also, their fire resistance was expected to improve the flammability behavior of PB. On the basis of solubility parameters miscibility was not expected. Solubility parameters using various schemes[6] were between

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9.05 and 9.30 for CPE and 8.30 and 8.80 for PB. However, very often in many cases this is of little consequence especially whenever the possibility for mechanical compatibility exists.

Blend properties were studied using the dynamic mechanical technique (DMA) to establish possible miscibility interactions and the small-strain viscoelastic response at an extended temperature range. Tensile testing was applied to ascertain the large-deformation behavior, since it is known[7] that such tests are most suitable to evaluate the degree of compatibility in terms of practical material applications. Differential scanning calorimetry (DSC) was applied to study possible influence of the essentially amorphous CPE component on the crystallization behavior of PB. For the morphological examination, both phase-contrast and polarized optical microscopy as well as scanning electron microscopy (SEM) were employed. On the basis of the above results, mechanics models were tested to obtain information on the connectivity of the phases in the blend. Finally, limiting oxygen index (LOI) tests were made to determine the reduction of PB flammability brought about by the addition of the inflammable CPE. Thus an additional usage parameter for these blends was quantified.
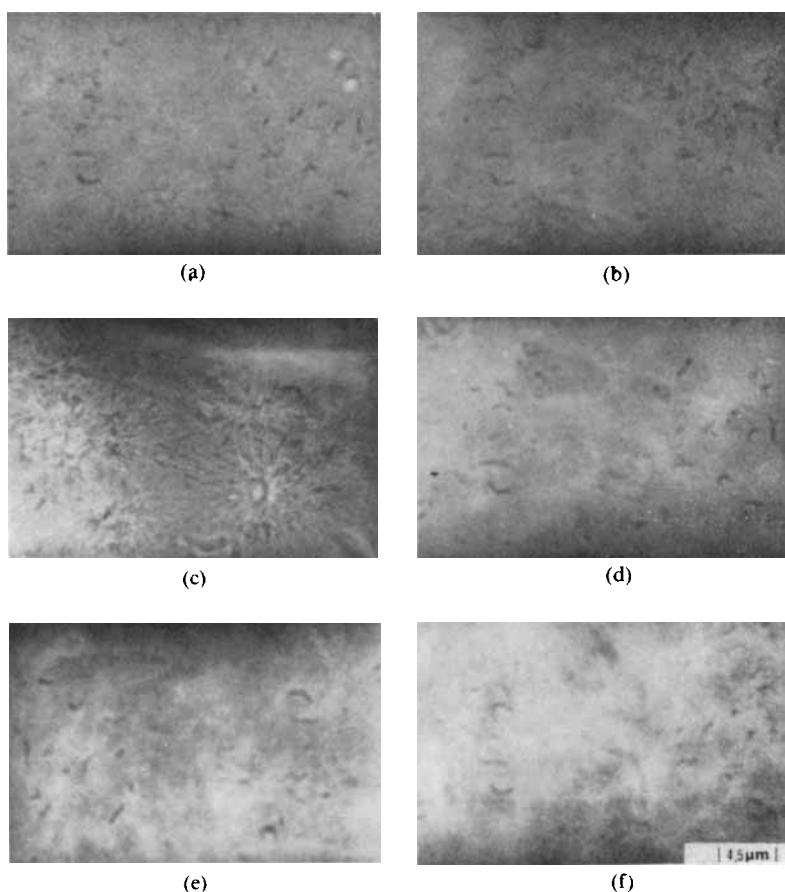

Fig. 1. Phase contrast micrographs of blends: (a) 100PB/0; (b) 90PB/10; (c) 75PB/25; (d) 50PB/50; (e) 25PB/75; (f) 10PB/90.

EXPERIMENTAL

Materials and Specimens Preparation

CPE was obtained from Aldrich-Europe, Belgium. It was prepared by a slurry-phase chlorination of high density polyethylene and used with 2% dibutyltin dilaurate as thermal stabilizer. Specific gravity was given[8] as 1.25 and $\overline{M}_n$ = 6.1 × 10^4 g/mol. PB was also obtained from Aldrich. DSC measurements gave a 55–60% crystallinity. Specific gravity was[9] 0.91 and $\overline{M}_w$ was reported[10] to be 4.09 × 10^5 g/mol.

Blends were prepared either by dissolving in boiling xylene and precipitating in methanol followed by drying *in vacuo* at 125°C, or by melt mixing[11] small quantities at 175–195°C with a laboratory press. The results reported refer to specimens prepared with the latter technique. Thus the possibility of the solvent influencing measured properties was avoided. Films were prepared
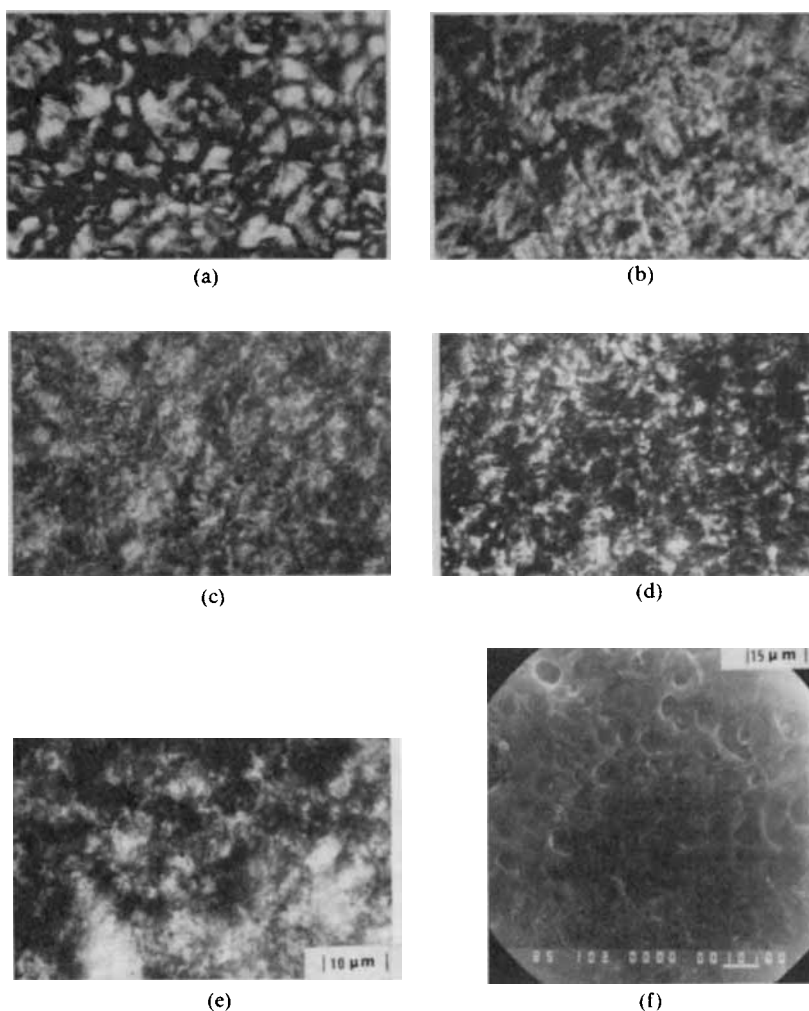

Fig. 2. Optical micrographs with crossed polars: (a) 100PB/0; (b) 90PB/10; (c) 75PB/25; (d) 50PB/50; (e) 25PB/75; (f) SEM micrograph of etched 90PB/10.

by melt pressing at 10 MPa for ca. 2 min and quenching at 0°C. Films prepared were hazy and tough.

The following compositions were studied: 100PB/0, 90PB/10, 75PB/25, 50PB/50, 25PB/75, 10PB/90, and 0PB/100, where the first numeral denotes the percentage by weight of poly(butene-1). All samples, except where indicated, were stored for 1 week prior to measurements. Thus the transformation of PB to its stable modification I can be assumed complete.[12]

APPARATUS AND PROCEDURES

Thin films prepared by melt pressing were examined under a phase-contrast microscope (Orthoplan Leitz) with oil ($n_e^{23} = 1.518$) immersion in bright field. A polarizing microscope (Leitz Wetzlar) was also used.

Samples were prepared by melting the blend on the microscope slide and slightly pressing with the cover glass to obtain a sufficiently thin layer. Scanning electron microscopy (SEM) was performed with a JEOL JSM 35 Model and specimens were examined after etching with chloroform (solvent for CPE) for 4 h.

DSC measurements were carried out using a DuPont 910 Calorimeter system coupled with a 990 programmer recorder. Calibration was made with Indium standard. The sample weight was ca. 19 mg, and the heating rate 10°C/min. The first heating cycle to 150°C was followed by maintaining this temperature for 60 s, quenching at ca. 50°C/min to 0°C followed by a second cycle. Crystallization temperatures T_c were determined after the second cycle.

Dynamic mechanical data, loss tangent $\tan \delta$, and complex modulus $|E^*|$ were obtained between -100 and $120°C$ at 110 Hz, using the direct reading viscoelastometer (Rheovibron Model DDV II-C, Toyo-Baldwin) and the procedure described before.[11] The tensile properties of specimens were determined at room temperature using a J.J. Tensile Testing Machine Type T5001. Two types of test specimens were used. Film strips with dimensions $0.6 \times 24 \times 60$ mm^3 and microtensile test pieces according to ASTM D 1708-66. For the latter an injection-molding machine was used with barrel and mold temperatures of 230 and 70°C, respectively. Crosshead speeds were 30 mm/min and 420 mm/min for the dumbbell and film specimens, respectively.

Flammability tests were carried out in a controlled mixture of oxygen–nitrogen according to ASTM D-2863-70. Specimen dimensions were $0.3 \times 0.6 \times 7.0$ cm^3.

RESULTS

Morphology

Figure 1 shows phase-contrast micrographs at representative compositions. It is expected[13] that, at positive phase contrast, dark and light areas should represent CPE and PB, respectively, since the refractive index of the former is larger. Additional information is provided using the polarizing microscope (see Fig. 2). Increasing the CPE content leads to an increasingly disordered and fragmented PB spherulitic structure. At high CPE compositions there is no evidence of PB spherulites. Micrograph 2f taken with SEM shows the surface of a 90PB/10 etched specimen. The amorphous component is distributed in
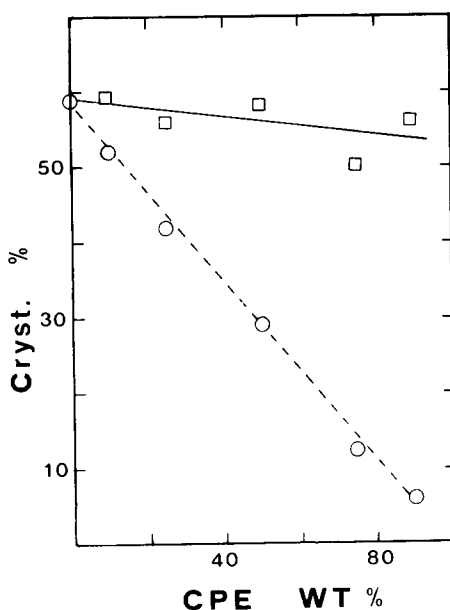
Fig. 3. Composition dependence of crystallinity: (○) crystallinity of blends; (□) crystallinity of PB in the blend.

the form of spherical domains. All the microscopic evidence presented supports the existence of an immiscible blend whose crystalline component loses its compact structure as the amount of the amorphous second component is increased.

Thermal Properties

Data obtained with the DSC are summarized in Figure 3 and Table I. Figure 3 shows that addition of the CPE component decreases the overall blend bulk crystallinity in a linear manner. When crystallinity of the PB is plotted vs. composition, a nearly horizontal line is obtained. On this evidence one concludes that CPE does not serve as a nucleating agent for the crystallization of PB.[14,15] Also the linear decrease of blend crystallinity indicates[16,17] that there is no interaction between the crystalline and the amorphous components of the blend. The small reduction of $T_{m,\text{PB}}$ with composition reported in Table I is to be attributed to smaller and less perfect crystallites at high levels of CPE. Crystallization temperatures $T_{c,\text{PB}}$ show a maximum at low CPE compositions suggestive of more perfect PB crystals. In this event DSC crystallization thermograms should become narrower—a fact not substantiated by the experiment. On the contrary, increasing the CPE content causes some broadening of the crystallization exotherm. The DSC thermograms did not show any premelting phenomena of the PB phase (modification I). Thus no crystallite reorganization takes place during the thermal scan.

Dynamic Mechanical Properties

The dynamic viscoelastic data are reported in Figures 4 and 5 for the storage and loss modulus, respectively, and in Table I. In Figure 4 the stiffness

TABLE I
Transitions and Thermal Properties of Blends

Blend	tan δ_{max} (°C)		E''_{max} (°C)		T_m^c (°C)	T_c^c (°C)	T_m^a (°C)	ΔH_f^a $(J/g*)^d$	Blend crystallinity (%)	PB[a] crystallinity (%)
	α^a	β	α^a	β						
100PB/0	5	—	−4	—	115	93	129	72.8	58.2	58.2
90PB/10	6	—	−4	—	115	104	129	72.9	52.2	58.4
75PB/25	4s[b]	22	−6	20s[b]	115	104	129	70.5	42.0	56.4
50PB/50	—	28	−4s[b]	20	115	94	129	72.9	29.0	58.4
25PB/75	—	33	—	20	115	97	128	62.0	12.5	49.6
10PB/90	—	33	—	16	115	93	126	70.1	5.6	56.1
0PB/100	—	33	—	16	—	—	—	—	—	—

[a] PB modification I.
[b] Shoulder or broad peak.
[c] PB modification II.
[d] $\Delta H_{f,PB} = 125$ J/g (B. Wunderlich, *Macromolecular Physics*, Academic, New York, 1980, Vol. 9, p. 48).
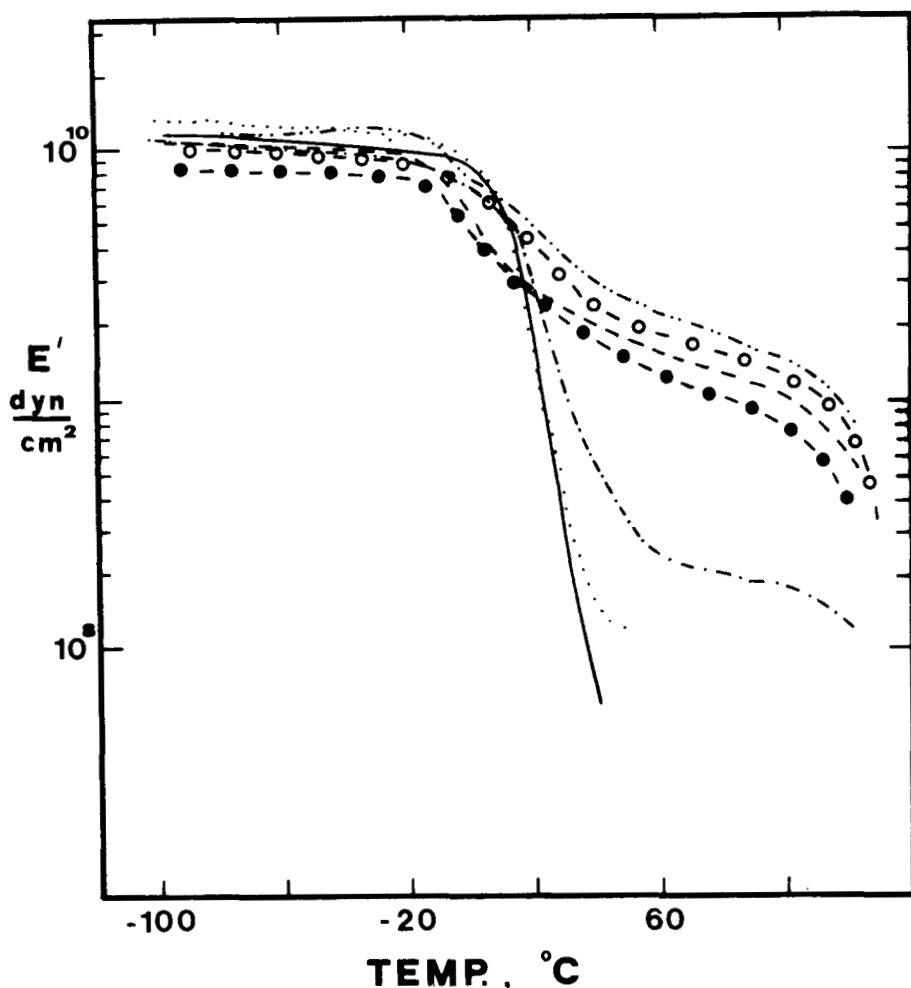
Fig. 4.   Temperature dependence of storage modulus of blends: (-●-) 100PB/0; (- - -) 90PB/10; (- · · -) 75PB/25; (-○-) 50PB/50; (- · -) 25PB/75; (· · · ·) 10PB/90; (——) 0PB/100.

enhancement due to the polarity[18] of CPE is evident. However, increasing the amorphous component leads to an overall reduction of blend crystallinity causing a loss of stiffness at higher CPE compositions. Figure 5 shows that the main relaxations, α for PB[19,20] at $-4°C$ and β for CPE[8] at ca. 20°C, persist in the blends and do not shift significantly with composition. Thus no miscibility interaction between the amorphous components of the two blend constituents takes place.[21] The small shift reported in Table I can be attributed to overlap of peak shoulders.

Tensile Properties

Ultimate strength and elongation as a function of composition is given in Figure 6. A nonlinear dependence with a minimum at high CPE contents is observed. This behavior bears similarities to nonmiscible crystalline–amorphous[22] and crystalline–crystalline blends.[5,23] No synergism in ultimate
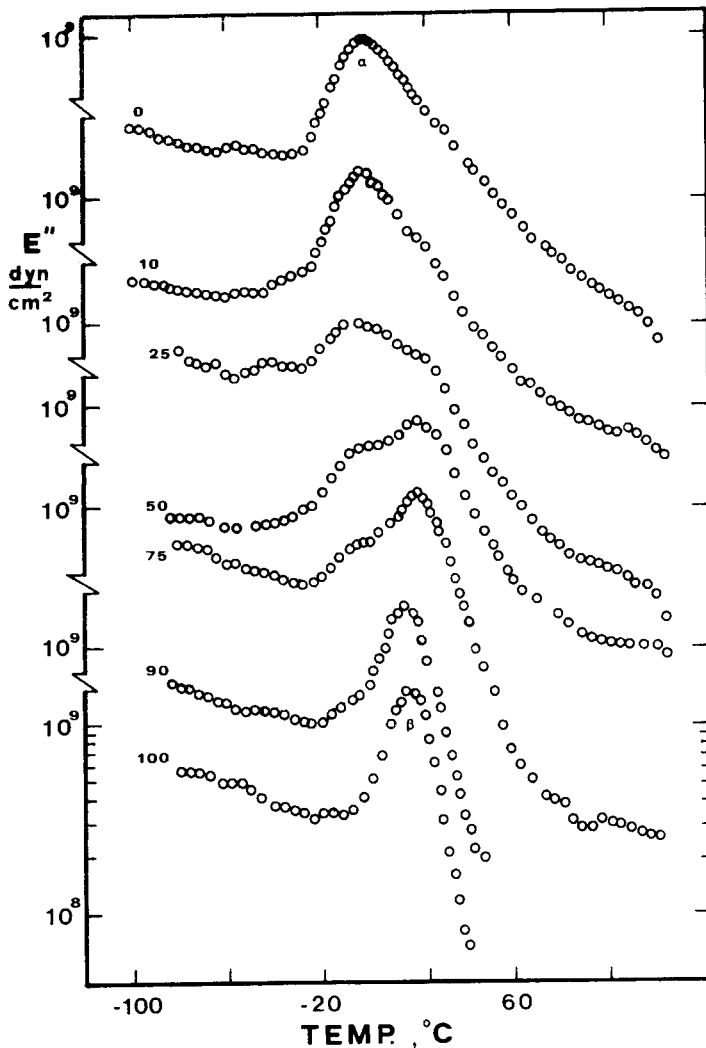
Fig. 5. Temperature dependence of loss modulus of blends. Numbers next to curves denote weight percentage of CPE.

properties is observed. However, it is worth noting that ultimate strain is not essentially impaired (in the case of films), even though the blend is heterogeneous. It is also of practical importance to note that, in these specimens, the ultimate strength of PB is little affected by the incorporation of as much as 25 wt % of CPE. The small elongation and increased strength of the injection molded specimens (see Fig. 6) has been observed before[9] for pure PB and was attributed to the molecular orientation at the specimens skin, leading to reinforcement but brittle behavior.

Flammability

The limiting oxygen index data are given in Figure 7. The blends become self-extinguishing at ca. 35 wt % CPE and above. During burning, no permanent char formation was observed.
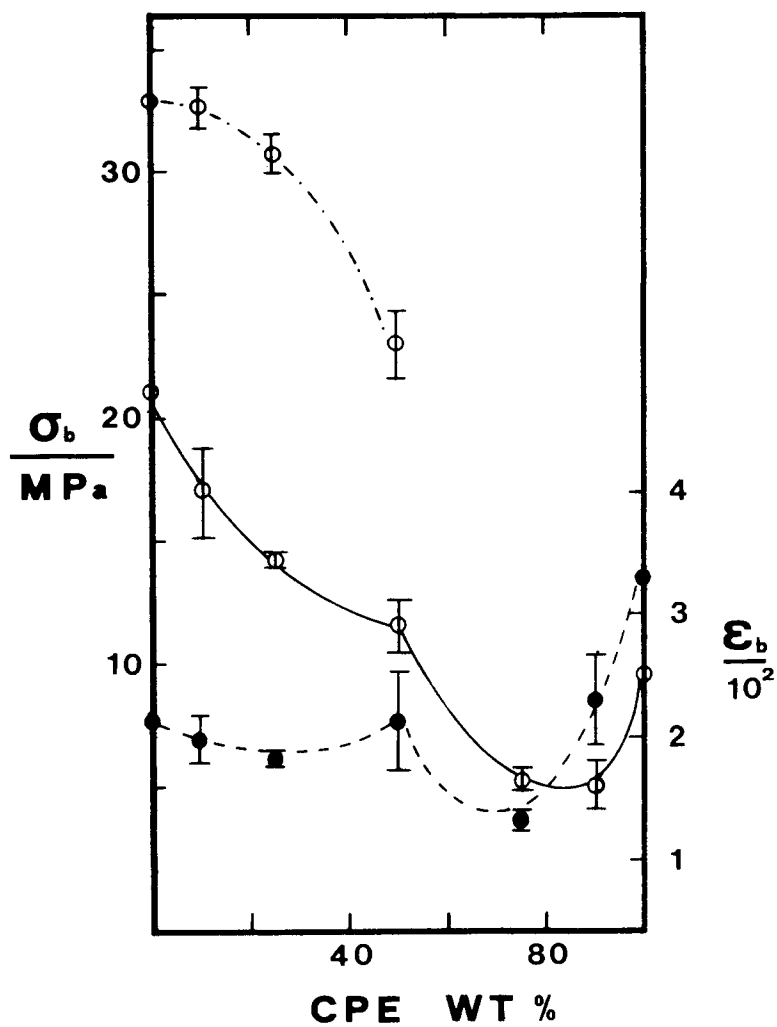
Fig. 6. Composition dependence of ultimate strength and strain of blends: (——) strength; (- - -) strain; (- · -) strength, injection-molded test pieces.
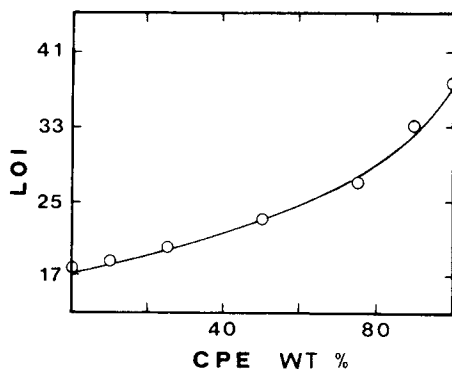
Fig. 7. Composition dependence of limiting oxygen index of blends.
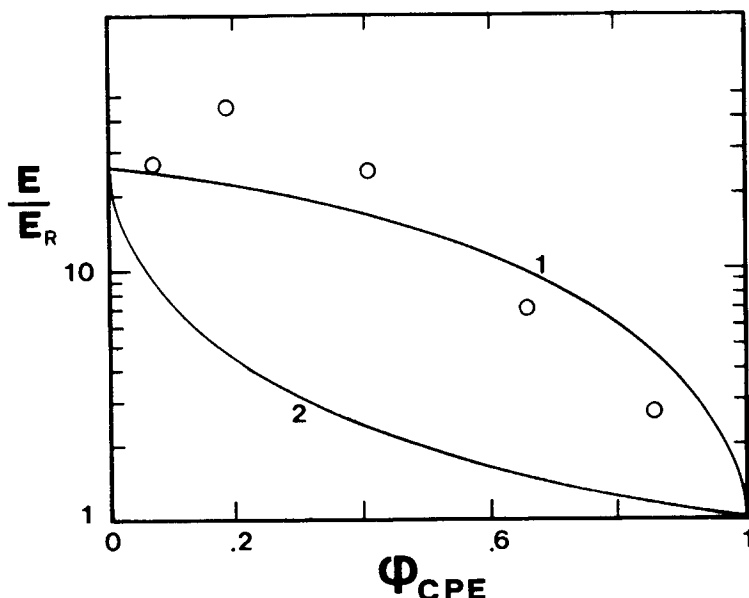
Fig. 8. Comparison of experimental and calculated values E/E(CPE) of blends at 36°C: (○) experimental values; (1) parallel; (2) series connection.

DISCUSSION AND CONCLUSIONS

The satisfactory tensile properties of the blends and their heterophase nature induced us to test whether various phenomenological mechanics models could give insight with regard to phase connectivity.[24] In Figure 8, relative modulus E (blend)$/E$ (CPE) is plotted vs. blend composition. Comparison of the data with the parallel connection model shows satisfactory agreement, a fact not expected for a heterogeneous amorphous–crystalline blend.[25] In fact, stiffness is higher than predicted, a characteristic of synergism. The relative success of the parallel model suggests an improved load transfer between phases each contributing in proportion to its volume. It implies further that the structure of the blend is of a lamellar morphology with the amorphous CPE sandwiched between the PB crystalline layers. Similar findings were reported[26] for the poly(ethylene oxide)–poly(vinyl acetate) blends.

The Kerner's model[24] was also tested at an extended temperature range, at all compositions. The model assumes perfect adhesion between the matrix and spherical inclusions and has been tested with some success before.[24,25] In its complete form the model is defined by

$$E = E_c \left[\frac{\Phi_d E_d}{(7 - 5\nu_c)E_c + (8 - 10\nu_c)E_d} + \frac{\Phi_c}{15(1 - \nu_c)} \right]$$

$$\Bigg/ \left[\frac{\Phi_d E_c}{(7 - 5\nu_c)E_c + (8 - 10\nu_c)E_d} + \frac{\Phi_c}{15(1 - \nu_c)} \right] \qquad (1)$$

where E is the dynamic modulus of the blend and indices c and d signify the
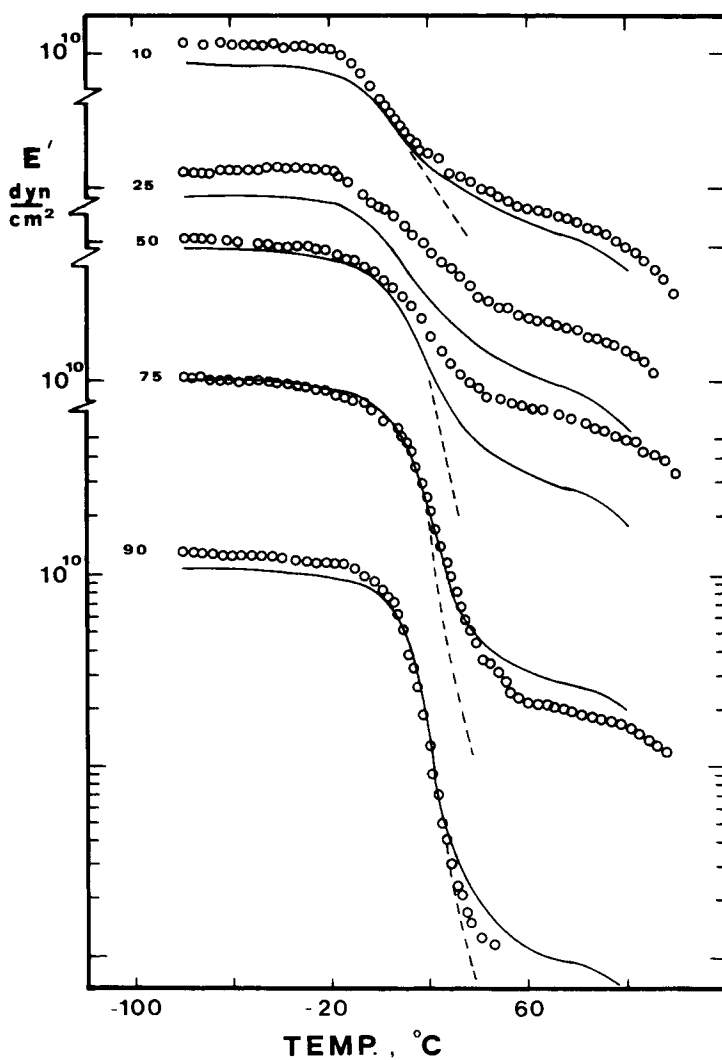
Fig. 9.   Dynamic modulus prediction using Kerner's model: (○) experimental values; (———) calculated with PB matrix; (- - -) calculated with CPE matrix. Numbers next to curves denote weight percentage of CPE.

continuous (matrix) and dispersed phases, respectively. In the calculations the change of Poisson ratio ν at the T_g was taken into account. The Poisson ratio of the blends ν_c was assumed to be real and equal to the arithmetic mean of their components weighted as their volume fraction. Below T_g, ν(CPE) = 0.37 and ν(PB) = 0.40. Above T_g, the Poisson ratio for both components was taken[27] as 0.45.

Figure 9 shows that model prediction is good to fair at all compositions and especially at low temperatures (where adhesion is practically ensured) and when PB is the matrix. The model fails when CPE is the matrix, even at low PB levels. Although there are conceptual difficulties for the model application in these latter compositions, the good correlation with the data suggests that

the crystalline phase, even at low contents, reinforces the solid with the formation of a supramolecular crystalline structure. Thus it effectively serves as the matrix.

On the basis of the experimental evidence presented, it is to be concluded that the PB–CPE blends, though incompatible on the basis of morphological, thermal, and dynamic mechanical studies, show strong component adhesion. This explains the satisfactory ultimate properties, especially at low CPE levels, and the good correlation of data with the mechanics models tested. Thus, as other PB blends studied,[4,5,23] these blends can be characterized as mechanically compatible.

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