

# Translucent Blends of Chlorinated Polyethylene with Poly(Vinyl Chloride)

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## SYNOPSIS

Some experimental chlorinated polyethylene (CPE) resins that produced translucent blends with PVC were used to study the effects of CPE chlorine content and chlorine distribution on the morphology, optical clarity, and toughness of blends with PVC. The CPE resins were characterized in terms of the glass transition temperature, residual crystallinity, density, and refractive index. Increasing residual crystallinity and increasing chlorine content both increased the refractive index closer to that of PVC. A linear relationship was observed between the fourth power of the refractive index and the CPE glass transition temperature. With a phase-separated blend morphology in all cases, improved transparency was achieved in this system by reducing the refractive index difference between CPE and PVC. Both haze and transparency showed the predicted linear dependence on the square of the refractive index difference. To a first approximation, modifications of the experimental CPE resins that improved optical transparency of the blends also tended to reduce the toughness enhancement.

## INTRODUCTION

The impact modification of poly(vinyl chloride) (PVC) with chlorinated polyethylene (CPE) has been studied previously with blends that are generally opaque under normal CPE loading.<sup>1,2</sup> Other common impact modifiers such as ethylene vinylacetate polymers, ABS, and some grades of acrylics also give opaque blends on mixing with PVC. Optical transparency is, however, an important consideration in many commercial applications such as bottles, films, and sheets. Methylmethacrylate-butadiene-styrene (MBS) terpolymers and modified ABS impact modifiers have been developed commercially to give clear blends with PVC by refractive index matching and controlled compatibility of the phases.<sup>3</sup>

Transparency in multicomponent polymer blends can be achieved in four ways<sup>4</sup>: (1) thin films with thickness on the order of 250  $\mu\text{m}$ , (2) homogeneous mixing or complete miscibility, (3) microheteroge-

neity with particle size of the dispersed phase smaller than the wavelength of visible light, and (4) matching refractive indices of the phases. For impact modification, only items 3 and 4 are applicable. The light-scattering theories of Mie, Rayleigh, and van de Hulst have been used to predict the effects of various blend parameters on the transparency with the result that the maximum turbidity was shown to coincide with the particle size range for optimum impact strength.<sup>5</sup> Thus, to obtain reasonable transparency over a wide temperature range, the match in refractive indices of the two phases was an important consideration.

Recently, a series of experimental CPE resins that produced translucent blends with PVC at 5 and 10 phr was prepared by Dow Chemical Company. The purpose of this study was to determine the effects of CPE chlorine content and chlorine distribution on the morphology, optical clarity, and toughness of blends with PVC.

## MATERIALS AND METHODS

Experimental chlorinated polyethylene (CPE) resins were obtained from Dow Chemical Company,

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Louisiana Division, Plaquemine, LA. They were all prepared from 0.1 melt index high-density polyethylene. The resin powders were compression molded to the desired thickness in a preheated press at 140°C at 2000 psi and cooled under pressure. Unless otherwise indicated, the compression molded sheets were used for the measurements described here.

Blends of 5- and 10-phr CPE with a low molecular weight poly(vinyl chloride) (Georgia Gulf 2066,  $K = 55$ ) were dry blended, then roll-milled at 175°C for 5 min after fusion. The blends also contained 2.5-phr heat stabilizer (Mark 1900, Argus Chemical), 1.5-phr processing aid (Paraloid K-175, Rohm and Haas), 1.5-phr internal lubricant (Loxiol HOB 7111, Henkel Corporation), and 0.3-phr UV stabilizer (Tinuvin 328, Ciba-Geigy). Specimens of the desired thickness were molded in a preheated press at 175°C at 2000 psi and cooled under pressure.

Thermal transitions of the CPE resins and the blends with PVC were determined with a Perkin-Elmer DSC-7 using a heating rate of 20°C min<sup>-1</sup>. After the first heating, specimens were quenched and a second heating scan was obtained. The melting point and heat of melting were obtained from the endothermic peak temperature and area. The heat of melting of the CPE resins was reported as joules per gram of equivalent polyethylene. Dynamic mechanical measurements over the temperature range of -100° to 120°C were made with the dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories. The single cantilever mode was used, the heating rate was 1°C min<sup>-1</sup> and the frequency range was 0.3–20 Hz. The thickness of the compression molded specimens was 1.0–1.5 mm.

The phase morphology of the blends was observed directly in the low-voltage scanning electron microscope. Blocks were finished at -100°C with the Model 6000-XL cryomicrotome from RMC, Inc., coated with about 5 nm of carbon and viewed in the JEOL JSM-840A scanning electron microscope in the secondary electron (SEI) mode using a voltage of 6 kV.

The refractive index was measured on solution-cast films prepared by dissolving the resins in *o*-dichlorobenzene at 110–120°C. The 2–3% w/v hot solution was poured into a silane-treated petri dish, covered with filter paper, and dried at 110–120°C to prevent gelation. The films were then dried in vacuo at 90°C for 3 days. The glass transition temperature was measured to confirm that the solvent was completely removed. The refractive index was then measured on the 50- to 100- $\mu$ m thick films at 25°C using an Abbe refractometer without a contact liquid according to ASTM D542. The average of six mea-

surements was reported. The density of the compression-molded sheet was measured at 25°C in duplicate according to Method A-1 of ASTM D792-66.

The percent transmittance and percent haze were measured by Dow Chemical Company according to Procedure A of ASTM D1003-61 with the Model D25 Optical Sensor from Hunter Associates, Inc. The compression molded specimens were 1.3 mm thick.

Microtensile specimens (ASTM D1708-79) were machined from 3.8-mm-thick compression-molded sheet, notched according to the Izod geometry, and annealed at 80°C for 4 h. Tensile tests were performed at ambient temperature with an Instron 1331 mechanical testing machine using crosshead speeds up to 0.4 ms<sup>-1</sup>. The force-time curve was recorded on a Nicolet Model 3091 digital oscilloscope. Fracture surfaces were coated with Au/Pd and viewed in a JEOL 35CF scanning electron microscope.

## RESULTS AND DISCUSSION

### Thermal Behavior of CPE Resins

The glass transition temperatures of all the CPE resins, measured by DSC, are listed in Table I. The values given were obtained on the initial heating of the resin powder; values from subsequent heating scans of the melt recrystallized resin were within the experimental error, about  $\pm 2^\circ\text{C}$ . In general, the glass transition increased with the amount of chlorine, but it also varied considerably among resins with the same chlorine content indicating that another factor also affected the glass transition. From the literature,<sup>6</sup> this factor is known to be the amount of residual crystallinity and the blockiness of the chlorine substitution.

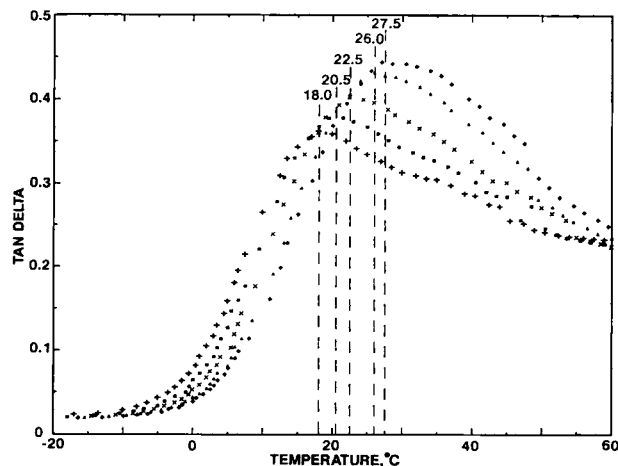
The frequency dependency of the primary relaxation was determined for some of the resins by dynamic mechanical analysis. The results for experimental resin 4709, shown in Figure 1, were typical. The DMTA peak temperature at 1 Hz was consistently higher than the glass transition temperature measured by DSC because of the low effective frequency of the latter. The activation energy obtained from the linear Arrhenius plot generally increased as the peak temperature increased (Table I).

In addition to the glass transition, DSC thermograms of most of the resins had an endothermic peak due to melting of residual crystalline polyethylene. On the initial heating thermogram the peak temperature was about 136°C for all the resins. After

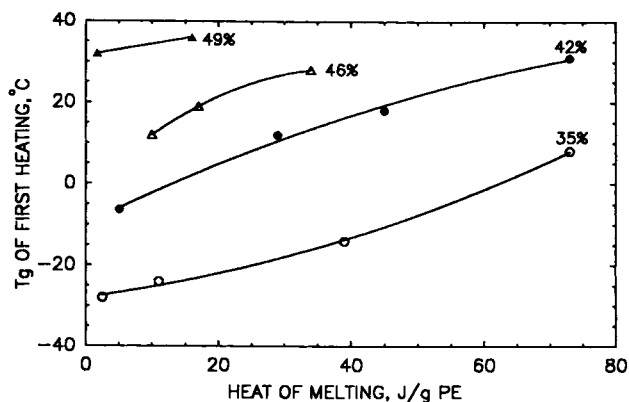
**Table I Thermal Properties of Experimental CPE Resins and Their Blends**

Experimental CPE Resin (Run No.)	% Cl	$T_g$ (DSC) (°C)	$T_g$ (1 Hz) (°C)	$\Delta H_a$ (kJ/mol)	Blend $T_g$ (1 Hz) (°C)	$T_{m,1}$ (°C)	$\Delta H_{m,1}$ (J/g PE)	$T_{m,2}$ (°C)	$\Delta H_{m,2}$ (J/g PE)
4709	35	8	20	371	1	136	73	119	46
4676	35	-14	-1	287	—	133	39	118	28
4884	35	-24	-12	238	—	136	11	121	6.8
4712	35	-28	-14	224	-31	134	2.5	118	1.2
4641	42	31	—	—	—	134	73	115	46
4890	42	18	—	—	—	134	43	118	25
5148	42	12	—	—	—	136	29	119	16
4991	42	-6	5	279	-10	137	5.1	120	3.1
4891	46	28	—	—	—	138	34	119	18
4969	46	19	—	—	—	137	17	119	9.9
4971	46	12	20	329	12	137	10	120	5.6
4932	49	36	42	318	30	136	16	119	6.5
4934	49	32	42	337	22	134	1.7	119	0.8
PVC	57	85	84	500	83	—	—	—	—

recrystallization from the melt, the peak temperature decreased to about 119°C and the heat of melting decreased to about half that measured on the initial heating. The initial melting temperature was typical of high-density polyethylene and reflected residual crystalline polyethylene that had not melted during chlorination. The melting point depression after melt recrystallization was due to cocrystallization of chlorinated chain segments.<sup>6</sup> The large variation in residual crystallinity among resins with the same chlorine content was achieved by varying the chlorination process conditions in such a way that the blockiness of chlorine substitution along the chain was altered; thus, the lower the residual crystallinity, the more random the distribution.<sup>6</sup>


**Figure 1** DMTA curves of experimental resin 4709 at 0.3, 1, 3, 10, and 20 Hz.

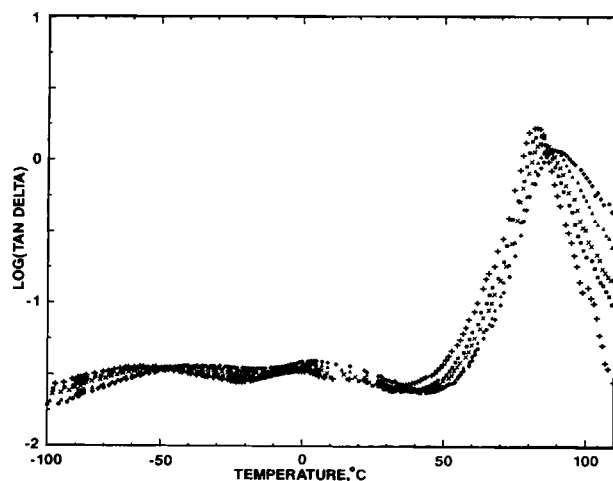
The relationship between residual crystallinity, and incidentally blockiness of the chlorine substitution, and the glass transition temperature was shown by plotting the latter versus the heat of melting on the initial thermogram for each of the four chlorine contents (Fig. 2). The plot shows how both chlorine content and chlorine distribution affected the glass transition temperature. Chlorine substitution on the chain increased polarity and restricted chain mobility causing an increase in the glass transition temperature and a higher activation energy. Similarly, if some of the chain segments were crystallized and not exposed to chlorination, substitution would have occurred preferentially on the amorphous chain segments, which consequently would have had a higher chlorine content, and higher glass transition temperature, than if substitution had occurred randomly along the entire length of the chain.


**Figure 2** Glass transition temperature of experimental CPE resins versus heat of melting.

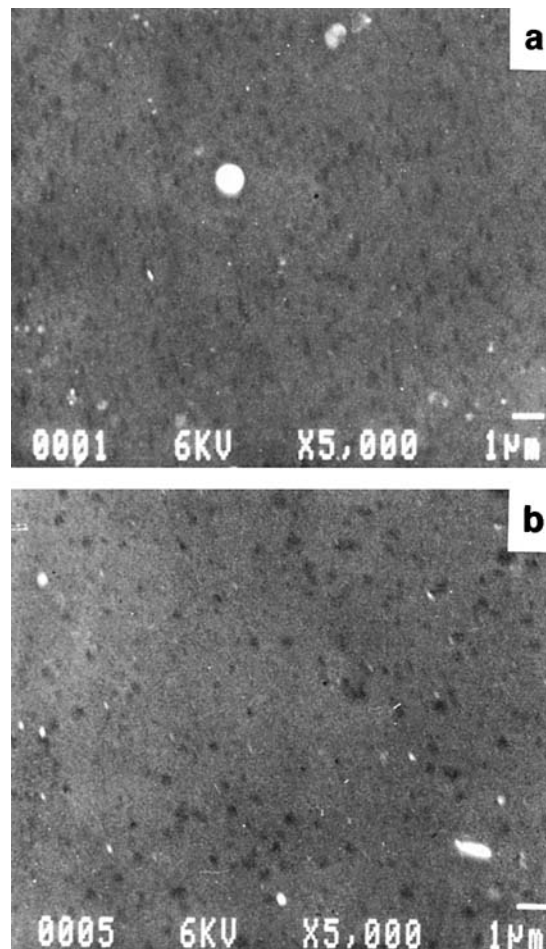
### Blends of CPE with PVC

The glass transition of the CPE phase could not be resolved from the baseline in DSC scans of blends with 10-phr CPE; however, in a typical DMTA curve (Fig. 3) a blend with 10 phr of experimental resin 4709 showed a peak at about 1°C (1 Hz) corresponding to the glass transition of the CPE, in addition to the  $\alpha$  and  $\beta$  processes of PVC at about 84° and -50°C, respectively. Previous studies of PVC-CPE blends have consistently revealed two glass transition temperatures leading to the conclusion that CPE is not miscible with PVC.<sup>1</sup> The primary transition of PVC was not significantly shifted by blending, however, the peak for experimental resin 4709 was 19°C lower than that observed in the DMTA at the same frequency for the unblended resin. Similar shifts in the CPE primary transition were observed when the other CPE resins were blended with PVC (Table I). This shift was attributed to plasticization of the CPE phase by processing aids used in preparation of the blends. The DSC thermograms of the blend with 10-phr experimental resin 4709, the CPE with the highest heat of melting, showed a small melting endotherm at 117°C. The peak temperature was the same as that of the melt-recrystallized CPE, however, the heat of melting in the blend was reduced to about half that of the melt-recrystallized CPE.

Secondary electron images obtained with the low-voltage scanning electron microscope permitted the morphology to be viewed directly on microtomed surfaces without prior treatment such as staining or etching. This technique showed a blend morphology of CPE domains less than 0.5  $\mu\text{m}$  in diameter dispersed in the PVC matrix. Figure 4(a) shows elongated



**Figure 3** DMTA curves of blend with 10-phr experimental resin 4709 at 0.3, 1, 3, 10, and 20 Hz.

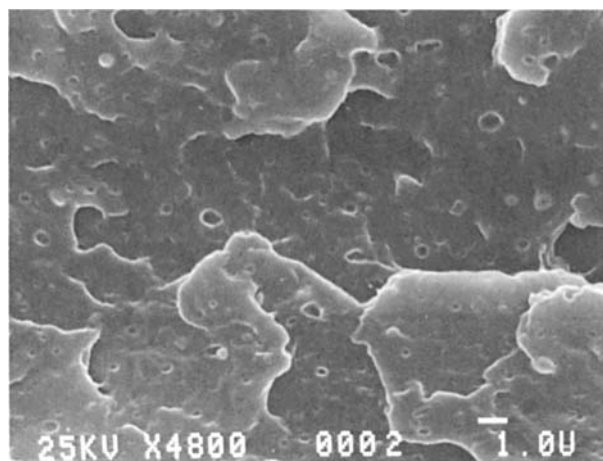


**Figure 4** Secondary electron images of (a) blend with 10-phr experimental resin 4712 and (b) blend with 10-phr experimental resin 4891.

gated dark areas that are the CPE domains in a blend of PVC with 10-phr experimental resin 4712. The elongated CPE domains of this blend resembled the morphology described in previous studies where a staining technique was used.<sup>1</sup> In all the other blends the CPE domains appeared spherical [Fig. 4(b)]. Since the SEM technique relied on the difference in density between PVC and CPE, the contrast became poorer as the chlorine content of the CPE increased. To confirm the morphology of these blends, brittle fracture surfaces were examined. The brittle fracture surface of a blend with 10 phr of one of the CPE's with the highest chlorine content, experimental resin 4932, also showed the 0.5  $\mu\text{m}$  dispersed CPE phase (Fig. 5).

### Optical Properties

The refractive index of the CPE resins was measured on solution-cast films. The properties of these films



**Figure 5** Brittle fracture surface of blend with 10-phr experimental resin 4932.

were similar to those of the melt-recrystallized resins (Table II). Specifically, the glass transition temperature and the melting temperature were the same and the heat of melting was also comparable. Table II shows that the refractive index increased with both chlorine content and crystallinity from the lowest value of 1.5170 to 1.5424, which was close to the PVC value of 1.5435.

The molar refraction  $R_M$  is defined from the Lorentz relation as<sup>7</sup>

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \frac{R_M}{M} \quad (1)$$

where  $\rho$  is the density and for polymers and  $M$  is the molecular weight of the repeat unit. The quantity

on the left side of the equation was calculated with values of  $n$  and  $\rho$  determined experimentally and was found to be a constant for each composition. This meant that among CPE resins with the same chlorine content the increase in density caused by increasing crystallinity was directly related to an increase in refractive index as predicted from Eq. (1).

To analyze the composition variable,  $R_M$  was obtained independently from group contributions,<sup>8</sup> and an average  $M$  was calculated from the composition. Comparison of the quantities on either side of Eq. (1), the one obtained from experimental data and the other from literature values of group contributions showed reasonable agreement (Table III). While the quantity  $R_M/M$  varied by more than 10% from the lowest to the highest chlorine content, actual values of the refractive index were much closer and in fact overlapped from one chlorine content to the next. The reason is that although the molar refraction  $R_M$  increased significantly with chlorination, the molar volume  $V_M = M/\rho$  also increased and for CPE the effects largely canceled. As a result, the increase in refractive index with chlorination was relatively small and comparable in magnitude to the effect of residual crystallinity. It follows that Eq. (1) would not be very sensitive to refractive index changes caused by variation in the chlorine content.

An alternative approach was to seek a relationship between the refractive index and the glass transition temperature. A qualitative relationship was expected since both have been related to the cohesive energy  $E_c$  or the solubility parameter  $\delta$ , defined as  $\delta = (E_c/V_M)^{0.5}$  where  $V_M$  is the molar

**Table II** Film Properties of CPE Resins

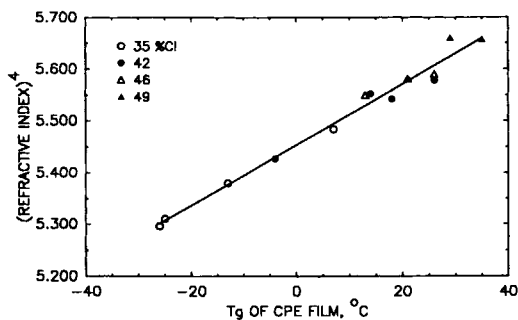
Experimental CPE (Run No.)	% Cl	$n^{25}$	Density (g/cc)	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g PE)
4709	35	1.5303	1.190	7	116	38
4676	35	1.5230	1.160	-13	113	19
4884	35	1.5180	1.150	-25	121	9.5
4712	35	1.5170	1.139	-26	113	1.9
4641	42	1.5368	1.248	26	112	37
4890	42	1.5344	1.246	18	112	22
5148	42	1.5351	1.261	14	117	17
4991	42	1.5263	1.230	-4	121	3.6
4891	46	1.5376	1.280	26	124	18
4969	46	1.5370	1.295	21	118	12
4971	46	1.5349	1.289	13	116	7.3
4932	49	1.5422	1.334	35	116	10
4934	49	1.5424	1.350	29	117	1.3
PVC	57	1.5435	1.392	—	—	—

**Table III** Specific Refraction of CPE Resins

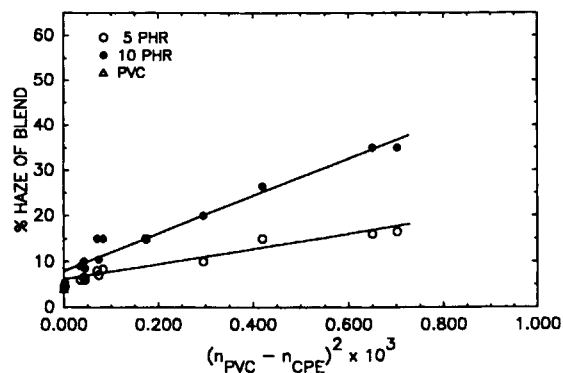
% Cl	$(n^2 - 1)/[(n^2 + 2)\rho]$	$R_M/M$
35	$0.2630 \pm 0.0017$	0.2682
42	$0.2491 \pm 0.0011$	0.2557
46	$0.2423 \pm 0.0013$	0.2481
49	$0.2346 \pm 0.0014$	0.2428

volume. The Maxwell identity between the square of the refractive index and the dielectric constant  $\epsilon$ ,  $\epsilon = n^2$ , and the proportionality observed for polymers between the dielectric constant and the solubility parameter,<sup>9</sup>  $\epsilon = 7\delta$ , were combined with the empirical relationship,<sup>10</sup>  $E_c = 0.5mRT_g + C$ , where  $C$  is an empirical constant,  $T_g$  the glass transition temperature,  $R$  the gas constant, and  $m$  a structural parameter that is the same for both  $\text{CH}_2$  and  $\text{CHCl}$  groups, to predict a linear relationship between  $T_g$  and  $n^4$ . This was tested in Figure 6 with data from the solution-cast films. The excellent correlation was particularly surprising because the effects of crystallinity were not considered in the analysis. Although the result was unexpected, for this system the refractive index empirically correlated better with the glass transition temperature than with any of the other physical properties examined.

The two common measurements of transparency are the percent haze or loss of contrast and clarity or resolution as characterized by the percent transmittance. Most of the blends had haze values less than 30% and would be categorized as translucent according to ASTM D1003-61. It has been indicated that when the refractive index mismatch is small the Rayleigh-Gans-Debye theory should describe adequately the variation in scattering for dispersions of spherical particles in the micron size range.<sup>11</sup> This treatment predicts that both transmittance and haze should be proportional to the square of the refractive



**Figure 6** Glass transition temperature of CPE resins versus the fourth power of the refractive index. Correlation coefficient is 0.990.

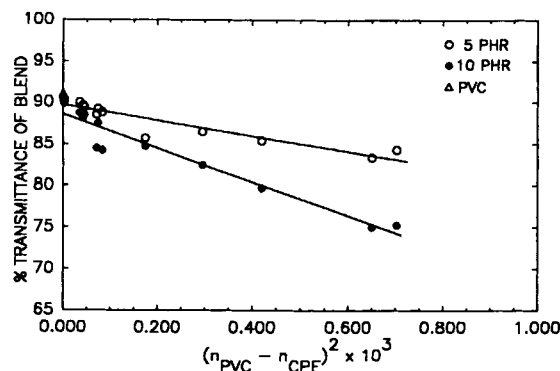


**Figure 7** Haze of blends versus the square of the refractive index difference. Correlation coefficients are 0.890 (5 phr) and 0.979 (10 phr).

index difference between PVC and the CPE  $(n_0 - n)^2$ . Haze and transmittance were plotted in Figures 7 and 8 for two blend compositions, 5- and 10-phr CPE. The transmittance increased linearly approaching that of unmodified PVC as the refractive index of the CPE approached that of PVC, and similarly the haze of the blends decreased in a linear manner as predicted.

### Toughness

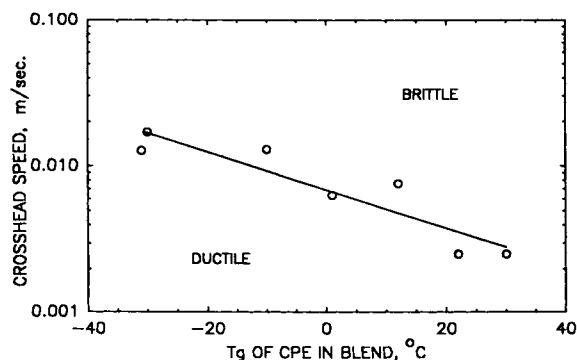
The relative toughness of the blends with 10-phr CPE was determined by examining the fracture surfaces of notched tensile specimens. The approach was similar to that used previously in which the test temperature was varied and the ductile-to-brittle transition identified from the first appearance of a brittle region on the fracture surface.<sup>12</sup> This technique gave the same results as more conventional methods of measuring toughness when the ductile-to-brittle transition temperatures of a series of com-



**Figure 8** Transmittance of blends versus the square of the refractive index difference. Correlation coefficients are  $-0.934$  (5 phr) and  $-0.966$  (10 phr).

positions were compared. Either temperature or strain rate could have been varied; for the PVC-CPE blends it was most convenient to vary the latter.

At low crosshead speeds the tensile fracture surfaces of the PVC-CPE blends were completely stress whitened; however, as the crosshead speed was increased, a featureless region of brittle fracture with no stress whitening appeared. This region increased in size as the crosshead speed increased, although even at the highest speed a small area of stress whitening could be observed at the notch tip. The ductile-to-brittle transition was taken as the lowest crosshead speed at which a brittle fracture region was observed on a majority of the specimens tested. This characteristic speed decreased as either the chlorine content or the crystallinity of the CPE increased. The effect of crystallinity was shown by testing blends prepared from CPEs with the same chlorine content 35% and varying crystallinity (experimental resins 4709, 4676, 4884, and 4712); to show the effect of chlorine content, the CPE resin with the lowest crystallinity from each composition was used (experimental resins 4709, 4641, 4891, and 4932). The crosshead speed at which the ductile-to-brittle transition occurred was plotted in Figure 9 as a function of the CPE glass transition temperature. The approximately logarithmic dependence suggested that in this system the material property that had the major effect in determining the effectiveness of a CPE for toughening PVC was its glass transition temperature. This led to the conclusion that modification of the experimental CPE resin to increase the refractive index closer to that of PVC in order to improve transparency of blends with PVC also reduced toughness of the blends. This occurred because both CPE refractive index and blend toughness could be correlated with the glass transition temperature of the CPE.



**Figure 9** Glass transition temperature of CPE in the blend with 10 phr versus the crosshead speed of the ductile-to-brittle transition. Correlation coefficient is  $-0.938$ .

## CONCLUSIONS

This study described the effects of chlorine content and chlorine distribution in CPE resins on the morphology, optical clarity, and toughness of blends with PVC with the following conclusions:

1. With a phase-separated blend morphology in all cases, improved transparency was achieved in this system by reducing the refractive index difference between CPE and PVC.
2. The chain structure of CPE was varied by increasing the residual crystallinity to make the chlorine substitution more blocky and by increasing chlorine content; both increased the refractive index closer to that of PVC.
3. A linear relationship between the fourth power of the refractive index and the glass transition temperature of the CPE was observed.
4. To a first approximation, modifications of the CPE resin that led to improved transparency of blends with PVC also tended to reduce toughness enhancement.

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