Miscibility and properties of poly(vinyl butyral) and thermoplastic polyurethane blends

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This paper describes the use of specific thermoplastic polyurethane elastomers (TPU) in blends with poly(vinyl butyral) (PVB). This work was directed towards the development of an interlayer having improved impact resistance and less sensitivity to variations in impact resistance over the useful temperature range. A family of commercially available cycloaliphatic polyether TPUs was found which produced optically clear, mechanically and thermodynamically miscible blends with PVB. The concept of a miscibility parameter was used to rationalize the compatibility of these blends. Support for compatibility is given by T_g, d.s.c. and d.m.a. data. The Gordon–Taylor relationship has been extended from use as a predictive tool for estimating the T_g of blends to estimating the physical properties of blends. Good agreement between tensile, tear and the measured values was obtained. Impact data on laminates using PVB/TPU (60/40) lightly plasticized (7%) with a glycol ether show almost complete lack of temperature sensitivity.

(Keywords: miscibility; polymer blends; poly(vinyl butyral); polyurethanes; blend properties; miscibility parameter)

INTRODUCTION

Plasticized poly(vinyl butyral) (PVB) has been used for about 50 years as the plastic interlayer in safety glazings, because of its outstanding properties of optical clarity, toughness, tear strength and durability. Although this material has been improved over the years and exceeds all safety requirements, the impact resistance decreases at both low temperatures (it becomes brittle) and high temperatures (it softens). Consequently, we investigated the possibility of improving the impact resistance and reducing its dependence on adhesion while maintaining the optical clarity required for this application. A possible approach to this is in the blending of PVB with thermoplastic polyurethanes (TPUs) because of their toughness and low temperature properties. The chemistry[1], applications[2] and characterization[3] of PUs have been reported. Miscibility of TPUs with PVB then becomes a prime consideration since, in addition to property improvement, the optical clarity must be maintained.

It has been reported[4] that PVB/TPU polyblends are not miscible and it was therefore necessary to understand the factors that affect miscibility in order to accomplish the above objectives. We will therefore address specific considerations of polymer miscibility for PVB/TPU blends. We have previously reported an approach for estimating polymer miscibility using the miscibility parameter[5] and here we will provide physical evidence for this miscibility and the properties of these materials compared to the two virgin polymers. We have also investigated the use of conventional relationships for estimating the T_g of miscible polymer blends. In the present work we have applied the Gordon–Taylor equation in a new way which allows the estimation of the physical properties of miscible blends and comparisons with experimentally determined values which are reported here.

BACKGROUND

The approach used here has been outlined previously[5] and is based on two premises: (1) that copolymers interact through individual functional groups or blocks, and the solubility parameter contributions from these individual groups or species that constitute the blocks should be used instead of the average or total solubility parameter values; (2) that in the case of PVB and TPUs used in this work the strength (magnitude) of the hydrogen bonding resulting from the vinyl alcohol portion of PVB results in association of hydroxyls and little or no interaction with other functional blocks.

We have demonstrated this approach for a number of polymer blend systems[5] as well as for the PVB/TPU blend and have shown that greater ranges of miscibility, evidenced by lower haze values, were experienced when the TPU was based on methylene bis dicyclohexyl diisocyanate (MBDCI) as opposed to methylene bis diphenyl diisocyanate (MBDPI). These results are listed in *Table 1* for reference only. The haze level is a primary consideration because of the optical clarity required of these blends, therefore all blend work used the TPU based on MBDCI, which has haze levels of 2.0% or less.

EXPERIMENTAL

The PVB used had a molecular weight of approximately 170000 and a hydroxyl content of 18.5%. The TPUs

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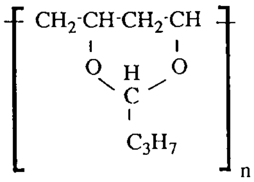
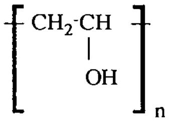
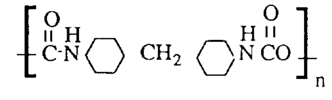
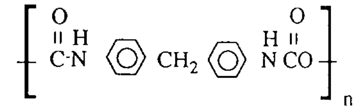
Table 1 Theoretical considerations: solubility parameter contributions from polymer functional blocks

Polymer repeating unit	Abbreviation	Structure	δ_d	δ_p	δ_h	δ_{TTL}
Vinyl butyral	VB		7.72	2.90	3.26	8.87
Vinyl alcohol	VA	 $-[CH_2-CH(OH)]_n-$	7.62	6.80	11.54	15.41
Methylene bis cyclohexyl diurethane	MBDCI		8.87	2.16	4.00	9.97
Methylene bis diphenyl diurethane	MBDPI		9.64	2.60	4.33	11.66
Polytetramethylene ether glycol	PTMEG	$-(O-CH_2-CH_2-CH_2-CH_2)-$	7.76	2.63	3.11	8.76

were obtained from Thermedix, Inc., and their grade designation was Tecoflex EG-85A. This PU was prepared from MBDCI and polytetramethylene ether glycol (PTMEG). Blending of the PU and PVB was accomplished by feeding appropriate mixtures into a twin screw pelletizing extruder. The melt-blended pellets were subsequently extruded into sheet or melt pressed into a cake from which sheets (thickness 0.762 mm) were scived. All subsequent characterization and/or evaluations were performed on the sheet or appropriate samples removed from the sheet.

Dynamic mechanical analysis (d.m.a.) (Rheometrics solids analyser, model RSAII, and Rheometrics dynamic mechanical analyser, model 605) and differential scanning calorimetry (d.s.c.) (Perkin Elmer DSC-7) were used to follow transitions occurring as a function of temperature. Standard physical testing procedures, as described in ASTM D-624, D-882 and D-1004, were used to determine physical properties.

A ball drop test was also carried out; this used a 5 lb ball and measured the height at which 50% of the drops were retained on a laminate using standard laminating conditions.

RESULTS AND DISCUSSION

Polymer miscibility

Mechanical thermal characterization. Both d.m.a. and d.s.c. were used to investigate polymer miscibility. The appearance of a single blend composition-dependent T_g has been generally used as the criterion for blend miscibility[6–9]. In addition to this, however, we also utilized model compound urethanes blended with PVB.

The Rheometrics dynamic mechanical analyser was used to examine the response of Tecoflex EG-85A. The temperature sweep in *Figure 1* shows a low temperature transition (T_g) at about −60°C which is attributable to the soft segments, and a high T_g at about 44°C attributable to the hard segments. PU elastomers normally exhibit both soft and hard T_gs and this has also been reported for other systems[10].

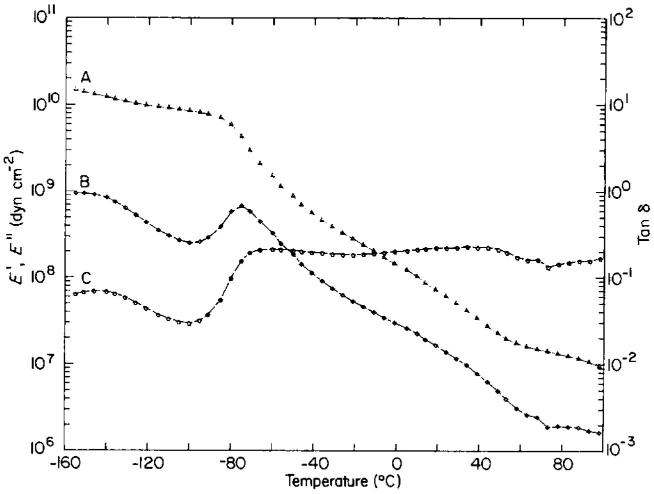


Figure 1 E' (A), E'' (B) and tan δ (C) for Tecoflex EG-85A

At low temperatures, the tan δ curve maximum is not distinct but shows a very broad peak. This is typical of a polymer exhibiting a co-continuous phase. The tan δ peak for the hard segments, which occurs above ambient temperature, is also indistinct. As a consequence, we confirmed the T_g of the hard segments from d.s.c. measurements using a TPU with a higher content of hard segments so that this transition could be observed more closely.

A series of blends of PVB and Tecoflex EG-85A were then prepared and run on the Rheometrics solids analyser. The tan δ scans of these blends (*Figure 2*) show the low temperature T_g of the soft segments and the high temperature T_g of the hard segments. The T_g of the soft segments remained relatively constant, although this is not clearly discernable from *Figure 2*, while T_g of PVB blends decreased monotonically from that of PVB

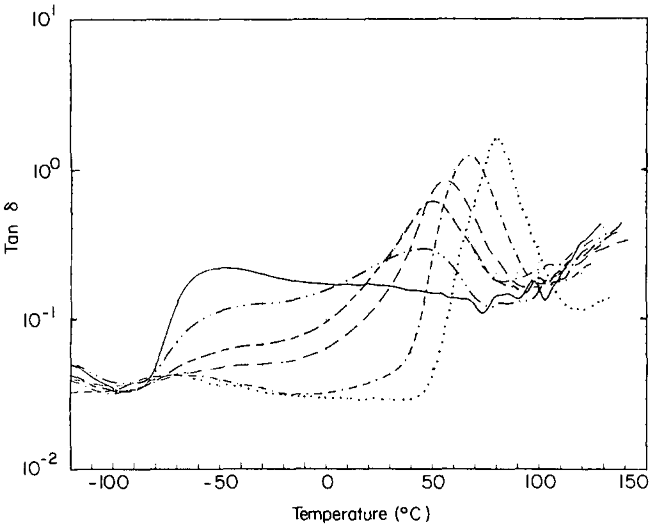


Figure 2 Tan δ *versus* temperature for a series of PVB/TPU blends. Tecoflex EG-85A (——); PVB/EG-85A blends: 20/80 (—··); 40/60 (— -); 60/40 (— —); 80/20 (- - ·); PVB (···)

(80°C). The relatively constant soft segment T_g has been observed previously for a similar system[11]. The gradual decrease in the T_g of the blends from that of the PVB is evidence that miscibility of TPUs with PVB is highly dependent upon interaction of the PVB with the hard segments. This tends to confirm experimentally what was estimated to be the case on the basis of the approach reported previously[5] in which it was found that the blend containing MBDCI showed broader regions of miscibility at a given residual VA (hydroxyl) level in PVB. Miscibility at higher hydroxyl levels requires a higher concentration of hard segments. In the case of MBDPI, the regions of miscibility occurred at much lower concentrations of hard segments.

Both the Fox relation[12] and the Gordon–Taylor (G–T) equation[13] were used to treat the data. The G–T relationship

$$T_g = \frac{W_1 T_{g_1} + K W_2 T_{g_2}}{W_1 + K W_2} \qquad (1)$$

where W = weight fraction of component in the blend and K = a constant, effectively approximated the data as shown in *Figure 3*. This illustrates the potential usefulness of the G–T relationship and its basis on additivity.

Urethane hard segment model compounds and d.s.c. were then used to establish T_gs and their shifts. The model compounds from MBDCI (Desmodur W), methanol and 1,4-butanediol are shown in *Figure 4*; the model compounds with PVB (1:1) are shown in the lower scans. Only one T_g is present in the blends. The measured T_gs of the model compounds and the resultant PVB blends are listed in *Table 2* and compared with the calculated T_gs obtained from the G–T equation.

These results again indicate miscibility and applicability of the G–T relationship to these blends.

TEM characterization. The PVB/TPU blends were then examined using transmission electron microscopy (TEM) in order to determine if the morphology was consistent with the previous mechanical and thermal evaluation data. The curve in *Figure 3* can be approximated by two straight lines which intersect at a blend composition of about 1:1; this may be indicative of a phase inversion of the continuous phase from PVB to that of TPU.

Considerable effort was spent in the development of techniques for obtaining samples which would not compromise interpretation of the morphology. Concern was primarily for the effect of liquids on the samples which might swell, dissolve and in other ways influence the morphology because of the use of only thin sections of samples. Consequently, the samples were cryo-ultramicrotomed at −100°C with no boat liquid. All sections were stained with phosphotungstic acid.

The TEM micrographs in *Figures 5* and *6* illustrate the results. *Figure 5*, shows a 60/40 (%) PVB/TPU blend with small, uniformly dispersed dark circular regions (TPU) in a matrix of PVB. *Figure 6*, a 40/60 (%) PVB/TPU blend, also shows a uniform appearance with no significant structural features. In this case however, the dark areas (TPU) appear to be the continuous phase in contrast to *Figure 5* where the PVB is the continuous phase. Thus the micrographs show uniformity of the blends on a microscopic scale.

These results are consistent with the type of contrast and TEM results obtained in a study of polyether block amide (PEBA) polyamide blends[14], in which the PEBA

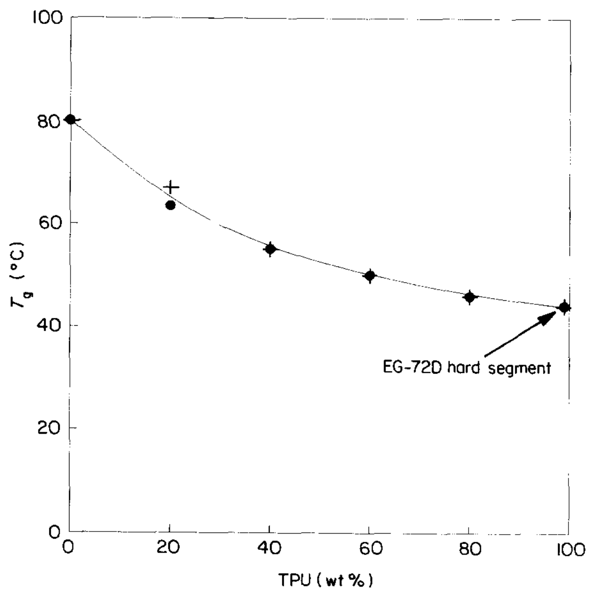
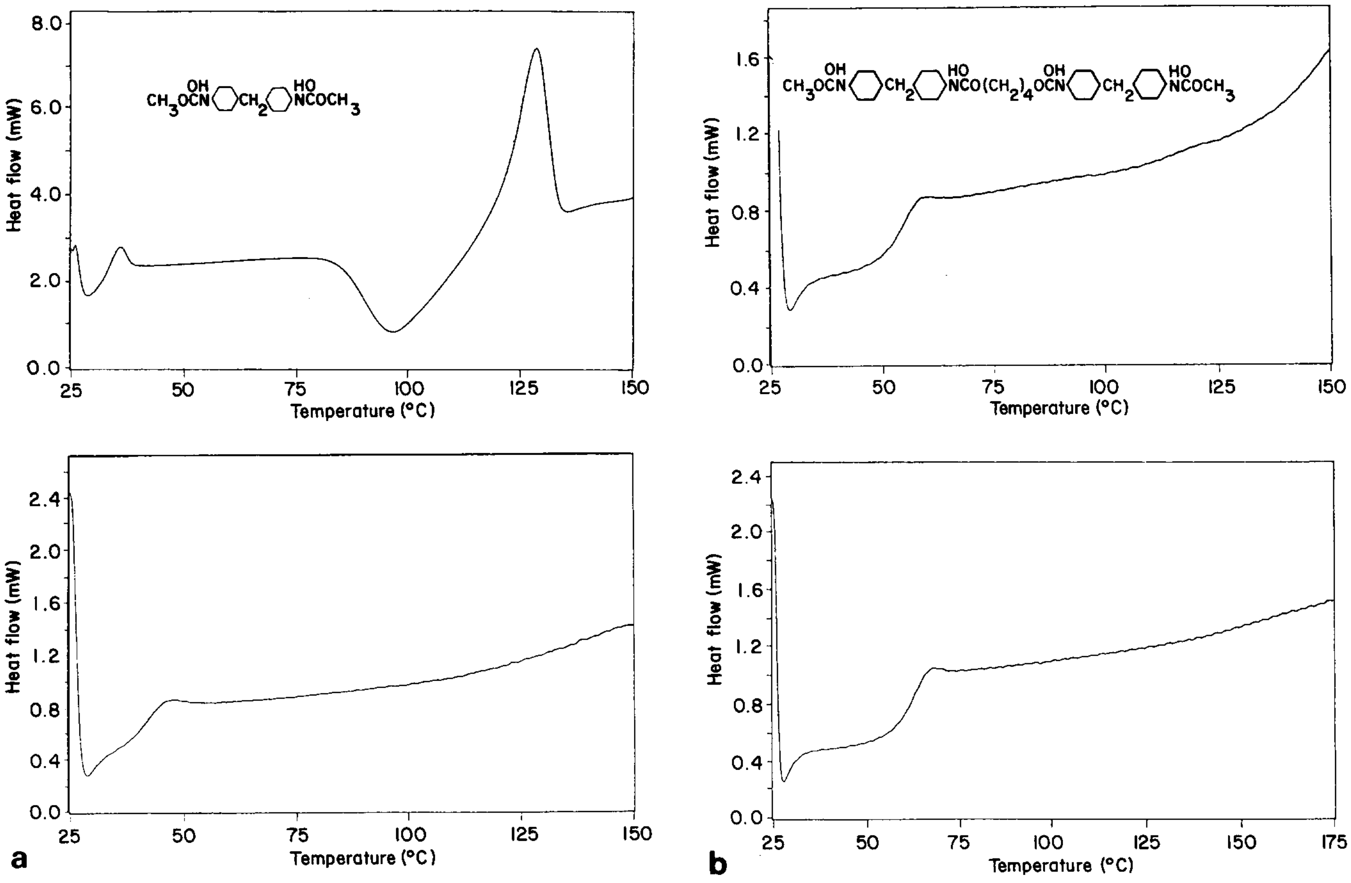


Figure 3 PVB/TPU blend: ●, Gordon–Taylor fit; +, d.m.a. data. $K = 0.29$

Table 2 Hard segment model compounds and d.s.c. data

Model compound	M_w	Cryst. temp. (°C)	Melting temp. (°C)	T_g (°C)	T_g Calc.[a] (°C)
a	326	96	128	33	
b	678			53	
c	442	69	115	13	
a+PVB				41	43
b+PVB				60	58
c+PVB				49	35
PVB	170000			80	

[a] From Gordon–Taylor equation



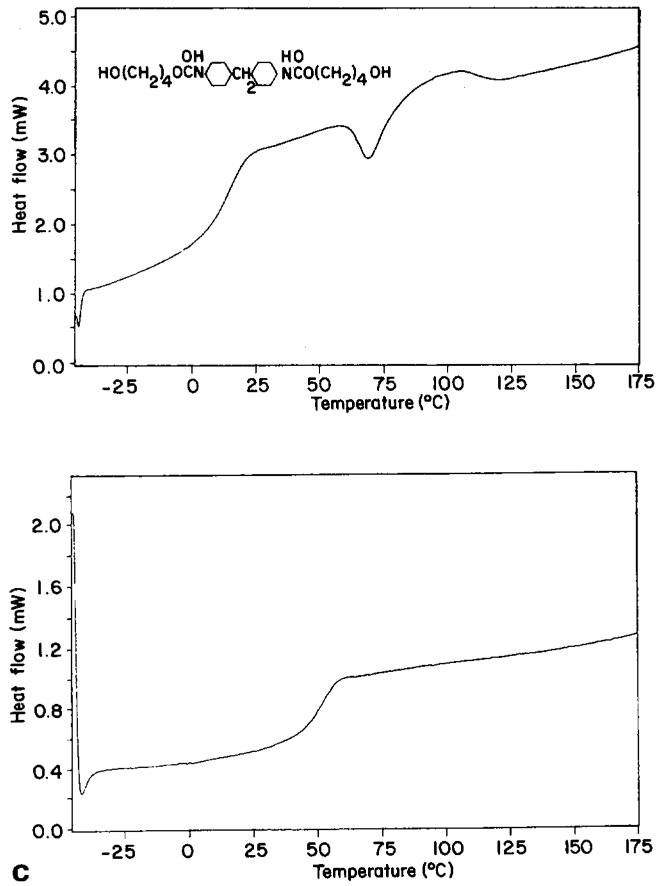


Figure 4 Results of model compound investigations. Compounds prepared from MBDCI and (a) methanol; (b) 1,4-butanediol and methanol; (c) 1,4-butanediol. The three lower scans represent the model compounds with PVB (1:1)

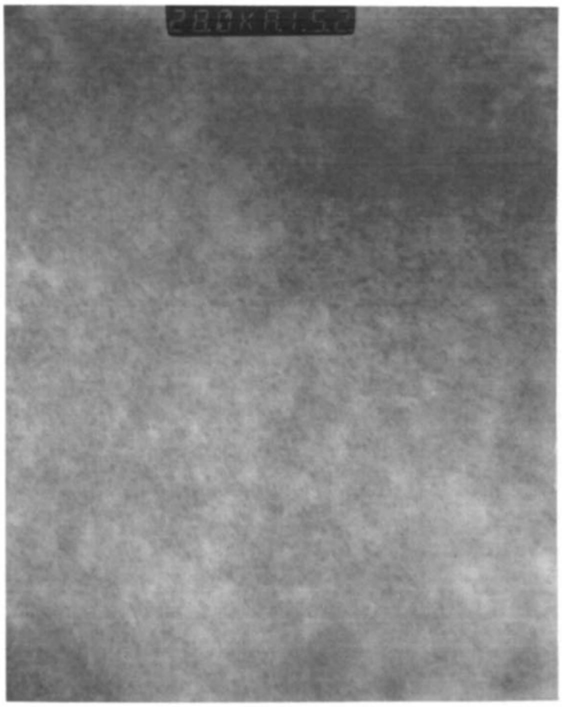


Figure 5 TEM micrograph of 60/40 PVB/TPU blend. 1 cm = 0.357 μm

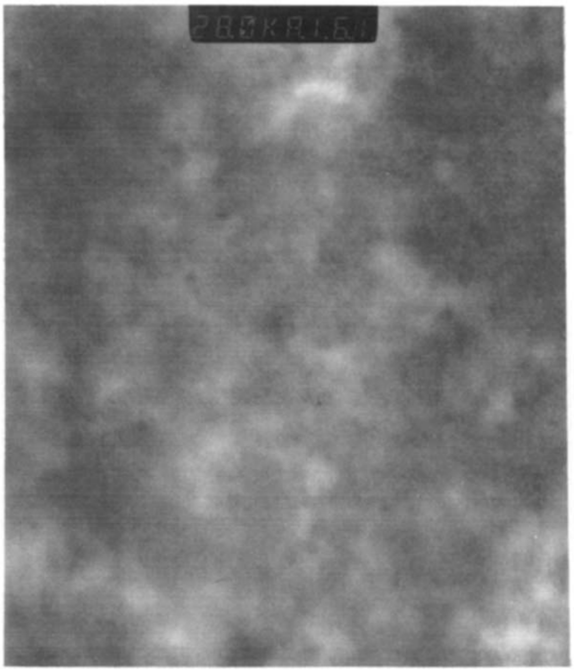


Figure 6 TEM micrograph of 40/60 PVB/TPU blend. 1 cm = 0.357 μm

contrast was also dark when stained with OsO_4. Since the amide group is similar to the urethane group and the polyether was PTMEG, we would expect a similar contrast here.

Physical properties

Since the polymer blends were found to form clear, miscible systems, we were interested in the resultant physical properties. The yield stress, failure stress, per cent elongation at failure, and mean tear resistance are plotted in *Figure 7*. The properties were found to be averaged but in a non-linear fashion. On investigation of the non-linear response of the properties, it was found that the G–T equation could be used to estimate the resultant properties of various blends. The measured data points are compared in *Figure 7* with those estimated from the following extended G–T relationship:

$$P_{\text{blend}} = \frac{W_{\text{TPU}}P_{\text{TPU}} + W_{\text{PVB}}P_{\text{PVB}}K}{W_{\text{TPU}} + W_{\text{PVB}}K} \qquad (2)$$

where P = a particular property of interest. The constant K is based on modulus, E', data from d.m.a. of PVB,

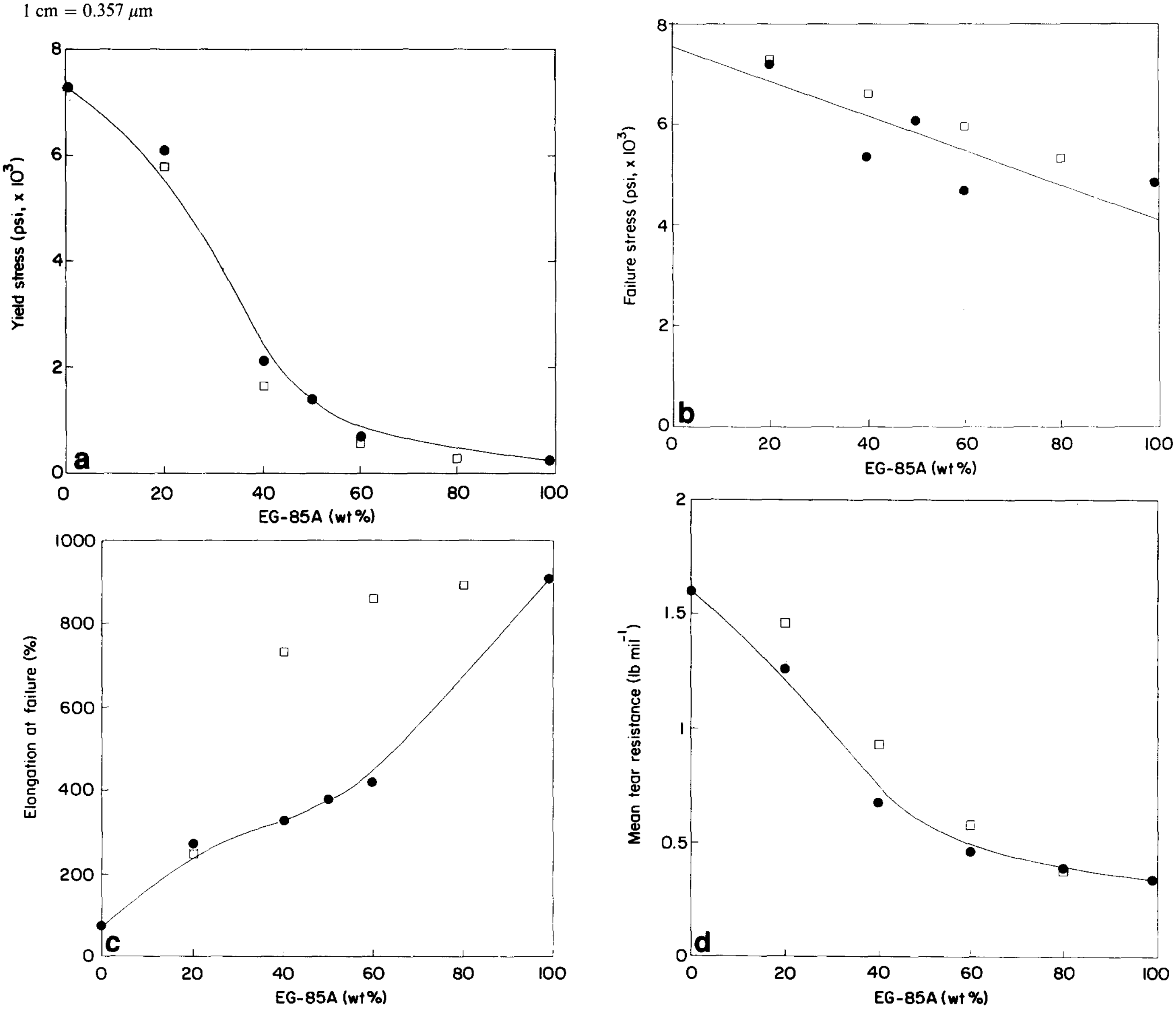


Figure 7 PVB/EG-85A tensile properties: (a) yield stress; (b) failure stress; (c) elongation at failure; (d) mean tear resistance (calculated using K at 40°C). ●, Experimental results; □, calculated using G–T relationship

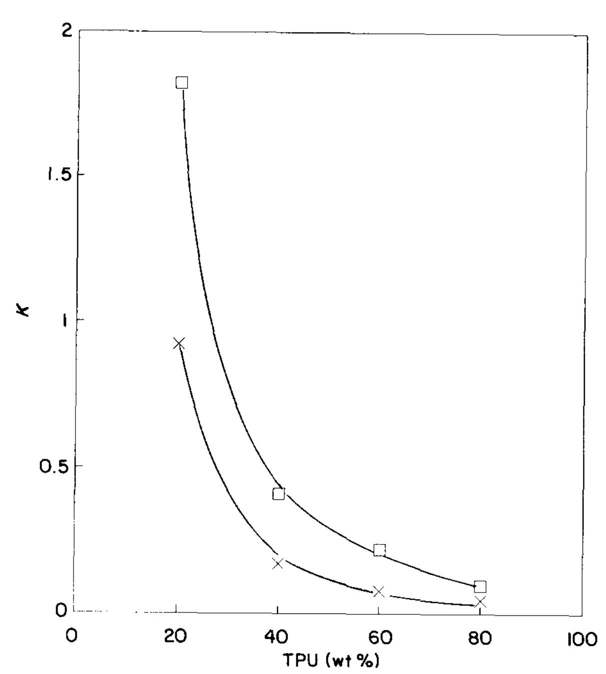


Figure 8 K *versus* TPU (wt%) in blend: □, 30°C; ×, 40°C

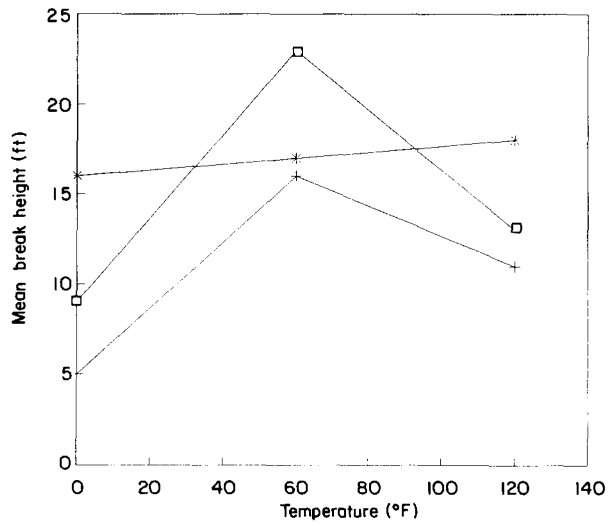


Figure 9 Laminate impact mean break height *versus* temperature: □, 24 N cm^{-1}; +, 36 N cm^{-1}; ✱, blend

Table 3 PVB/TPU adhesion tests

Laminate	Peel (N cm^{-1})
Plasticized PVB (low adhesion)	24
Plasticized PVB (equivalent adhesion)	36
PVB/TPU[a] 7.5 phr PTMEG ($M_w = 650$)	38

[a] Tecoflex EG-85A

TPU and blends (B). The G–T equation was solved for K:

$$K = W_{\mathrm{TPU}}(E'_{\mathrm{B}} - E'_{\mathrm{TPU}})/W_{\mathrm{PVB}}(E'_{\mathrm{PVB}} - E'_{\mathrm{B}}) \qquad (3)$$

K was calculated at 10°C intervals for each blend. Plots of K *versus* TPU (wt%) in the blend at constant temperature (isotherms) were then constructed (*Figure 8*). The physical property data (*Figure 7*) use the identical K value taken from the 40°C isotherm at the composition of interest. The choice of isotherm is based on the K values which produced the best fit to the data.

We have also applied the extended G–T relationship to the estimation of other physical properties, such as coefficient of linear thermal expansion, with good success indicating that K may have a broader significance. The function K may be more than a fitting parameter and may have the molecular significance suggested by Schneider[15]:

$$K = \rho_1 \Delta\alpha_1/\rho_2 \Delta\alpha_2$$

where ρ and $\Delta\alpha$ are the densities and differences between the expansion coefficients of the melt and glass, respectively. The extended G–T relationship thus becomes very useful in estimating properties and should be useful for other miscible blend systems whose miscibility is not a result of chemical incorporation/functionalization of one polymer with another during actual blending. We are not aware of this approach being used previously.

The property curves in *Figure 7* continue to show a break in the composition range where matrix inversion would be expected to occur. This is consistent with the change in slope observed for the glass transition temperatures and the TEM micrographs.

Adhesion and impact

The 60/40 PVB/TPU blend was plasticized with 7% PTMEG ($M_w \approx 650$) and the PVB was plasticized with 24% di-n-hexyl adipate, and glass laminates were prepared from sheet 0.762 mm in thickness. The 90° peel adhesion values of these laminates are listed in *Table 3* and the resultant mean break height (MBH) values, as a function of temperature, are shown in *Figure 9*.

For the plasticized PVB sample with low adhesion, the MBH value of the PVB/TPU blend is somewhat less than the plasticized PVB at room temperature, while at low and high temperatures it is superior. For the plasticized PVB sample of equivalent adhesion, the PVB/TPU blend exhibits superior MBH values across the entire temperature range as described previously[16].

These results indicate that an optimum combination of properties, as a result of judicious choice of miscible blend compositions, can be obtained.

SUMMARY

It is clear that blends of PVB and TPU exhibit miscibility over wide ranges of composition based upon T_g measurement and TEM studies. These results are also consistent with those predicted from theory[5], blend clarity and the additive property data. We have extended the Gordon–Taylor equation and have found that it can be applied in a very general way to physical property estimation.

Control of blend properties can be used effectively to enhance the impact resistance of glass laminates prepared from these blends.

ACKNOWLEDGEMENT

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