Polymer Vol. 39 No. 20, pp. 4765–4772, 1998

0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10326-3

Fracture toughness and properties of plasticized PVC and thermoplastic polyurethane blends

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(Received 13 June 1997; revised 27 August 1997; accepted 11 November 1997)

In this work, fracture toughness and properties of blends of plasticized poly(vinyl chloride) (PVC) and thermoplastic polyurethane (TPU) were investigated. Two kinds of TPU with different hardness, i.e. TPU90 (Shore A hardness 90) and TPU70 (Shore A hardness 70) were compared. PVC/TPU90 and PVC/TPU70 blends with variable weight ratio (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100) were prepared by melt blending. Fracture toughness was investigated using the J-integral by locus method. Blending of TPU with plasticized PVC improved tensile strength, impact strength, abrasion resistance, and thermal stability, with small decline of tensile modulus and hardness. The PVC/TPU blends showed flame retardancy over the composition ranges, regardless of the hardness of TPU, except the PVC/TPU70 of 50/50 composition, in terms of the limiting oxygen index. PVC/TPU70 blends showed higher *Jc* values and thus higher fracture toughness over the entire composition than PVC/TPU90 blends. For the PVC/TPU70 blends, the SEM micrographs showed clear dimple rupture fracture topology, while the PVC/TPU90 blends did not.

(Keywords: plasticized poly(vinyl chloride); thermoplastic polyurethane; fracture toughness)

INTRODUCTION

Thermoplastic polyurethane (TPU) is one of the most versatile products in the group of engineering thermoplastics with elastomeric properties. The TPUs possess higher tensile modulus in comparison to rubber, high abrasion resistance and resistance to oil, grease and many solvents. TPUs are characterized by a two-phase morphology in which a soft phase containing either polyesters or polyethers is reinforced by condensation with a hard domain consisting of an aromatic diisocyanate extended with a short-chain diol. Soft segments which are quite mobile and are normally present in coiled formation, alternate with stiff oligourethane units, so called hard segments[1–6]. By varying the amounts of hard and soft segment, the properties can be varied over a wide range and properties of blends also can be influenced.

Many polymers may be blended with TPUs to enhance physical properties and toughness. The good compatibility of TPU with polar thermoplastics such as polycarbonate, acrylonitrile–butadiene–styrene copolymer (ABS) has opened the door to use TPU as a modifier to create new blends. TPU can be filled with up to 30% inorganic fillers (fibres, powder) to create new components such as glass fibre reinforced TPUs (R-TPUs). Use of special additives give the properties necessary to achieve flame retardancy, antistatic and radiation crosslinking ability. The blending of polyurethane with poly(vinyl chloride) (PVC) allows a broader range of hardness and low temperature flexibility[7–13].

The blends of PVC and other polymers have been extensively studied for their commercial importance[11–13]. The advantages of PVC include cost and flame resistance—the presence of chlorine in large quantities in the polymers renders it flame retardant[13]. This property of PVC can effectively reinforce lack of flame retardancy of TPUs, because TPUs are burnable as many organic materials, but, in many application fields flame retardance is required. An important disadvantage of PVC is limited thermal stability, therefore, improvement of thermal stability is required by blending. The practical purpose of studying PVC blends is to develop a permanently plasticized, high impact-strength material via incorporation of a low *Tg* polymer which is compatible with PVC. The flexible PVC softened with a plasticizer have been finding increasing utilization in the plastic and rubber industries.

The objective of this work was to study the fracture toughness and properties of the plasticized PVC/TPU blends. A few papers have dealt with the compatibility and properties of PVC and polyurethane or PVC and TPU[14–17]. No papers, however, have yet dealt systematically with the properties of plasticized PVC and TPU. Furthermore, the fracture toughness of PVC/TPU blends has not been investigated. It may be expected that blends of plasticized PVC with TPUs have improved toughness due to high toughness of TPUs. It is also expected that the increase of TPU contents in blends causes changes in morphology and thus significantly affects the toughness of final blends. Properties studied include tensile properties, hardness, abrasion resistance, thermal stability, and flame resistance.

EXPERIMENTAL

Materials

Table 1 lists the polymers used in this study. PVC was supplied by LG Chemical Co, and two commercially available polyether based TPUs, Skythan X590A and Skythan S770A, were kindly provided by Sunkyong

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Table 1 Materials and their characteristics

Materials	Source	Grade	Characteristics
TPU90	Sunkyong Industry	SKYTHAN X590A	Thermoplastic polyurethane $Mw = 3.0–3.5 \times 10^5$ sheet type
TPU70	Sunkyong Industry	SKYTHAN S770-A	Thermoplastic polyurethane $Mw = 3.0–3.5 \times 10^5$
PVC	LG Chem.	LS100	Straight PVC particle size: 100–150 μm
DOP	Kangshin Chem.		Dioctyl phthalate (plasticizer)
KBC200	Kolon		Ca/Ba/Zn complex thermal stabilizer
KA699E	Kolon		Epoxy oil (processing aids and wax)
CA-st	Songwon Chem.		Internal and partially external wax
Paraffin wax	Kangshin Chem.		External wax

Table 2 Comparison of TPU90 with TPU70

TPU hardness	Hard segment/soft segment	Hardness (shore A)
TPU90	4.44	90
TPU70	2.10	70

Table 3 Blend compositions

Blend notation	Weight ratio			
	PVC (DOP40)/TPU 90		PVC (DOP40)/TPU70	
PU90-0/10	100	0	–	–
PU90-1/9	90	10	–	–
PU90-2/8	80	20	–	–
PU90-3/7	70	30	–	–
PU90-4/6	60	40	–	–
PU90-5/5	50	50	–	–
PU90-10/0	0	100	–	–
PU70-0/10	–	–	100	0
PU70-1/9	–	–	90	10
PU70-2/8	–	–	80	20
PU70-3/7	–	–	70	30
PU70-4/6	–	–	60	40
PU70-5/5	–	–	50	50
PU70-10/0	–	–	0	100

Industry Co. The basic difference between the two TPUs studied here is their hardness. The differences in hardness arise from different ratios of hard to soft segments, which in turn leads to different soft segment molecular weights. The difference is shown in *Table 2*.

Preparation of blends

PVC lacks thermal stability at processing temperatures. Thus, pre-powder mixing with additives such as a heat stabilizer was necessary before blending. The PVC compounds were formulated with the following ingredients: 3 phr heat stabilizer (KBC200), 2 phr polymeric processing aid (KA699), 3 phr lubricant (calcium stearate) and 0.5 phr lubricant (paraffin wax) as well as 40 phr dioctyl phthalate. PVC/TPU90 and PVC/TPU70 blends with variable weight ratio (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100) were prepared by melt blending in a laboratory-made bench kneader under experimental conditions of 60 rpm, 170° for 8 min. The samples prepared are listed in *Table 3*, and the sample notations are described therein.

Fracture energy determination

Many different specimen configurations are acceptable for the measurement of fracture toughness[18–20]. We used single-edge-notched (SEN) tensile specimens of constant length cut from compression-moulded sheets. The thickness and width of the rectangular specimens were 1.0 and 10.0 mm, respectively. The length between the grips was 100.0 mm. Razor blades were used to create sharp initial cracks, which varied from 0.2 to 0.8 in terms of the ratio of the initial crack length (a) to the specimen width (w), a/w.

Tensile tests were performed at a crosshead speed of 50 mm min^{-1} with an ambient temperature of 25°C and relative humidity of 35%. Load–displacement graphs were recorded and initiation points were marked on each loading line during the test. The fracture toughness was interpreted in terms of the critical J-integral value, Jc, by the locus method[21,22].

The locus method is simply to determine the Jc value by utilizing the locus of crack initiation points on load–displacement plots and consistent Jc values can be determined by this method without restricting the a/w or the specimen length. This method partitions the essential fracture energy along the crack initiation locus line as the first stage of the procedure for determining Jc. If one obtains the load *versus* load-point displacement records for the SEN tensile test with several initial crack sizes, then the crack initiation point observed carefully by a magnifying lens is marked accurately with a solid dot on each loading line. Then the essential energy of fracture is obtained by measuring the enclosed area between the loading line and the locus line of crack initiation points. Once the essential energy is determined, the Jc value can be determined easily. The detailed procedure used to determine the Jc value is described below.

It has been reported that the locus method using tensile specimen was more applicable to highly deformable materials such as a thermoplastic polyolefin compared to the conventional method using three-point bending specimens[23]. Crack initiation points were easily observable since the crack opened widely before it propagated. The areas under the loading curves were calculated numerically from the data points taken from the load–displacement records. Uc, the essential energy needed for crack propagation, per unit thickness *versus* a was plotted, and the linear least-square fitted slope was taken as Jc.

The method determines Jc based on

$$Jc = \frac{-1}{B}\frac{\Delta Uc}{\Delta a}$$

where B is the thickness of the specimen; a, the initial crack length; and Uc the enclosed area between loading line and locus line. The total energy consumed during fracture testing (U_t) includes remote energy loss as well as the energy supplied for the crack propagation. Remote or plastic energy loss (φ) occurs during the loading process if plastic deformation, remote from crack tip, exists.

With the *Jc* value known, φ for each crack size can be determined from

$$\varphi = \frac{Jc}{U_t/B(w-a)}$$

If the point of crack initiation occurred at a constant displacement and the locus of the crack initiation points continued to be a vertical line down to the displacement axis, then all the φ values should have been 1. It was reported that the remote energy absorption can affect the accuracy of the experimentally determined *Jc* values and that eliminating the remote energy term in the early stage of the procedure can help to yield consistent *Jc* values[23]. Details of the locus method are described elsewhere[21–23].

Reproducibility of the fracture energy data was measured by testing different sample lengths. However, for all samples tested the initial sample length was 100 mm unless otherwise specified.

Morphology

The morphology of the blends was observed with the scanning electron microscope. The samples were cryogenically fractured in liquid nitrogen. The fracture topology of the fracture surfaces was directly observed after gold coating.

Tensile properties

Tensile tests were carried out on a tensile tester (Hounsfield 500 L). The specimens were prepared according to ASTM D412-87. The crosshead speed was 50 mm min^{-1} and the gauge length was 25 mm. Five measurements were averaged.

Impact strength

Izod impact strength was measured using an Izod impact tester at −30°C. The sample size was 3 × 2.5 × 6.5 cm^3. Five measurements were averaged.

Abrasion resistance

The abrasion resistance was tested for specimens prepared according to the KS (Korean Standards) M 6534 method. The sample size was 16 mm in diameter and 2–3 mm in thickness. Three measurements were averaged.

Thermal stability

Thermal stability of blends was also measured using thermogravimetric analysis (t.g.a.) (Shimadzu TGA-50) from 25 to 600°C at a heating rate of 20° min^{-1} under a nitrogen atmosphere.

Flammability

For flammability testing, limiting oxygen index (LOI) was determined by ASTM D 2863-77. The oxygen indices of samples are the concentration of oxygen just supporting combustion under steady-state candle-like burning. Five measurements were averaged.

RESULTS AND DISCUSSION

Fracture toughness

Figure 1 shows a typical load–displacement records for the PVC/TPU blends. The bars denote the spread of observed crack initiation points. The locus line slightly deviates from a vertical line.

ΔUc per unit thickness is plotted against each initial crack size for the PVC/TPU90 blends and PVC/TPU70 blends as shown in *Figures 2 and 3*, respectively. The slope of the least-square-fitted line yields *Jc*, and the resulting values are replotted against TPU content in *Figures 4 and 5*.

Figures 2 and 3 show that a linear relationship between *Uc* and *a* has been obtained for the both PVC/TPU90 and PVC/TPU70 blends. The result implies that the *J* values at the crack initiation point, *Jc* is a constant for a given thickness, which is the only assumption made in the locus method and proves the validity for our blends system.

In *Figures 4 and 5*, it is shown that the *Jc* values increased with TPU content for both TPU70 and TPU90 and that the PVC/TPU70 blends exhibit higher *Jc* values than the PVC/TPU90 blends, irrespective of the concentration. The results mean that fracture toughness of plasticized PVC was increased with the addition of TPU and that the toughening effect was more prominently observed in the PVC/TPU70

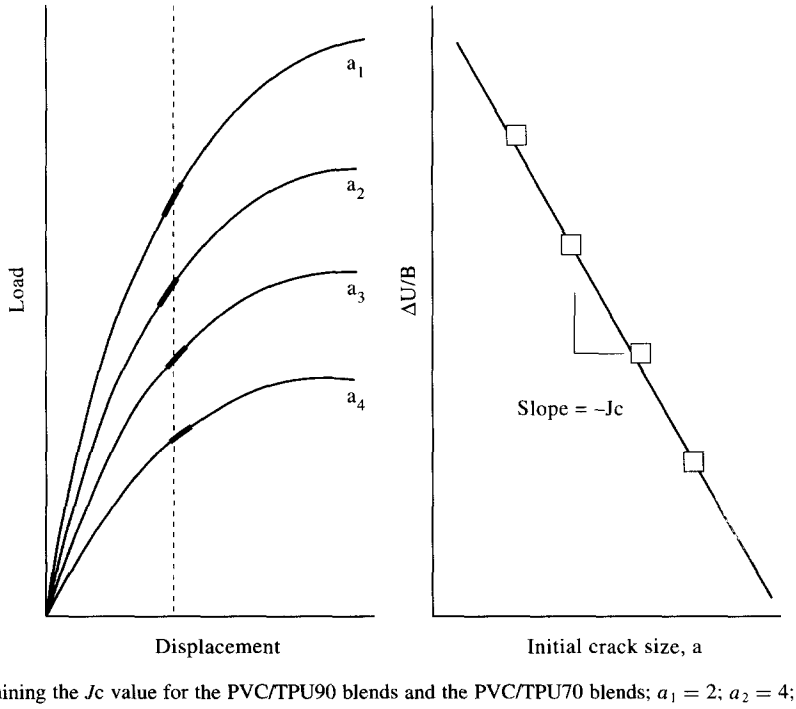

Figure 1 Procedure for determining the *Jc* value for the PVC/TPU90 blends and the PVC/TPU70 blends; $a_1 = 2$; $a_2 = 4$; $a_3 = 6$; $a_4 = 8$ mm

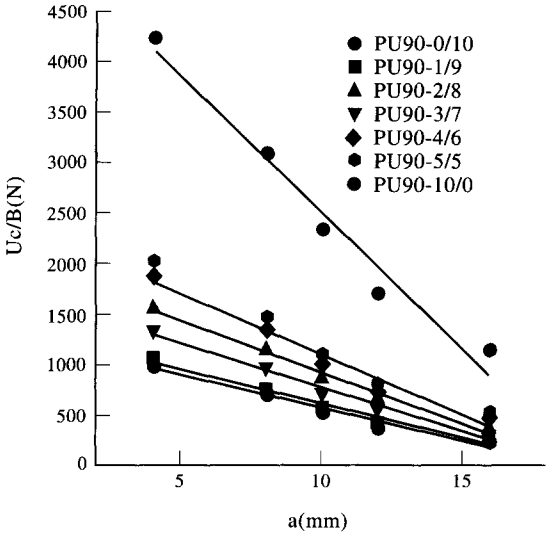

Figure 2 Variation of essential energy needed for crack initiation per unit thickness (*Uc/B*) with initial crack size (*a*). The lines are the least-squared ones: PVC/TPU90 blends

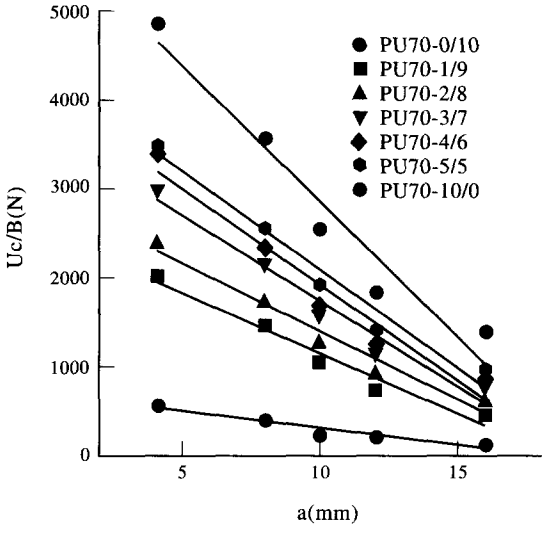

Figure 3 Variation of essential energy needed for crack initiation per unit thickness (*Uc/B*) with initial crack size (*a*). The lines are the least-squared ones: PVC/TPU70 blends

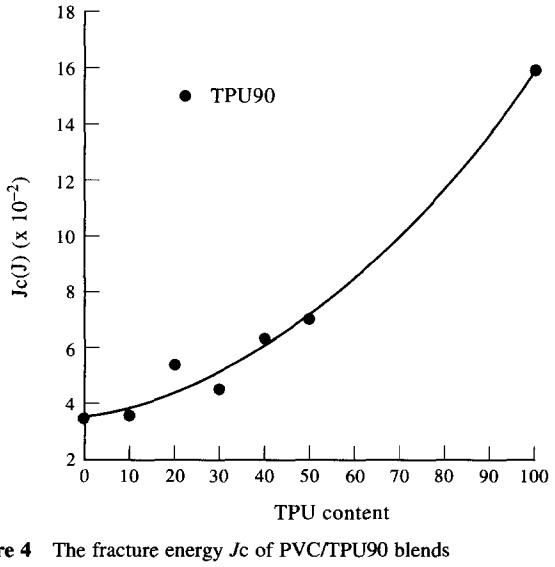

Figure 4 The fracture energy *Jc* of PVC/TPU90 blends

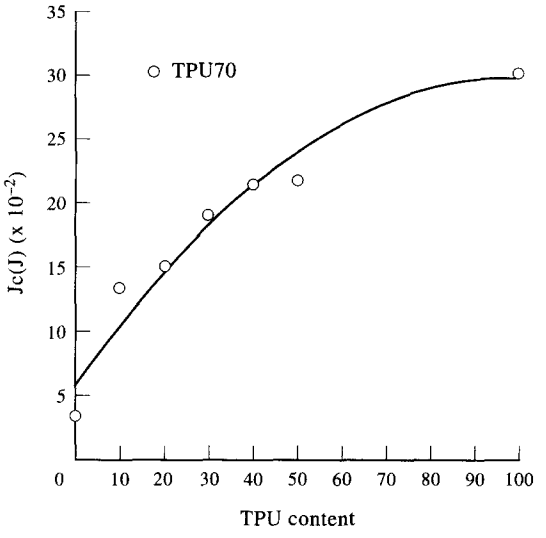

Figure 5 The fracture energy *Jc* of PVC/TPU70 blends

blends than in the PVC/TPU90 blends. The higher toughness of TPU70 containing blends in comparison with TPU90 might be attributed to the lower hardness (i.e. higher ratio of soft to hard segment in TPU) of TPU70 than that of TPU90.

The total energy consumed during fracture testing includes some amount of remote energy loss as well as the energy supplied for the crack propagation. The remote energy absorption away from the crack tip is not negligible if the specimen is not long. In this work, the specimen length, is 100 mm. The remote energy absorption in determining the *Jc* value was also evaluated. In this work, the φ value was equal to or slightly less than 1.0. The result implies that the effect of remote energy absorption is negligible and the effect does not need to be taken into account to estimate *Jc* values from our locus method.

The fracture surface topology was observed by scanning electron microscopy. *Figures 6 and 7* show SEM micrographs of the fractured surfaces taken around the crack-tip. In this case the initial crack length was 8 mm. PVC/TPU90 blends did not show the dimple rupture topology. The quasi-cleavage fracture topology of TPU90 (shown in *Figure 6*) may result from its high hardness (i.e. high ratio of hard to soft segment). For the PVC/TPU70 blends, however, as shown in *Figure 7*, the micrographs showed typical dimple rupture fracture topology, due to the presence of the inherently tough TPU, and thus PVC/TPU70 blends show very similar behaviour to TPU. The dimple rupture topology is usually observed in tough materials[21,22,24]. The rupture topology was more clearly observed as the TPU70 content was increased.

Physical properties

The tensile properties of the PVC/TPU70 and the PVC/TPU90 blends are summarized in *Table 4*. The tensile strength increased with TPU content for both blend systems, while the modulus (100% secant) decreased with increased TPU content. The reduction should be expected as the result of the elastomeric nature of TPU.

The elongation at break increased with TPU content, since TPU possesses inherently elastomeric properties with large elongation (*Figure 8*). For the elongation at break, the relative improvement for the softer TPU70 series was much greater than for the TPU90 series due to the greater soft

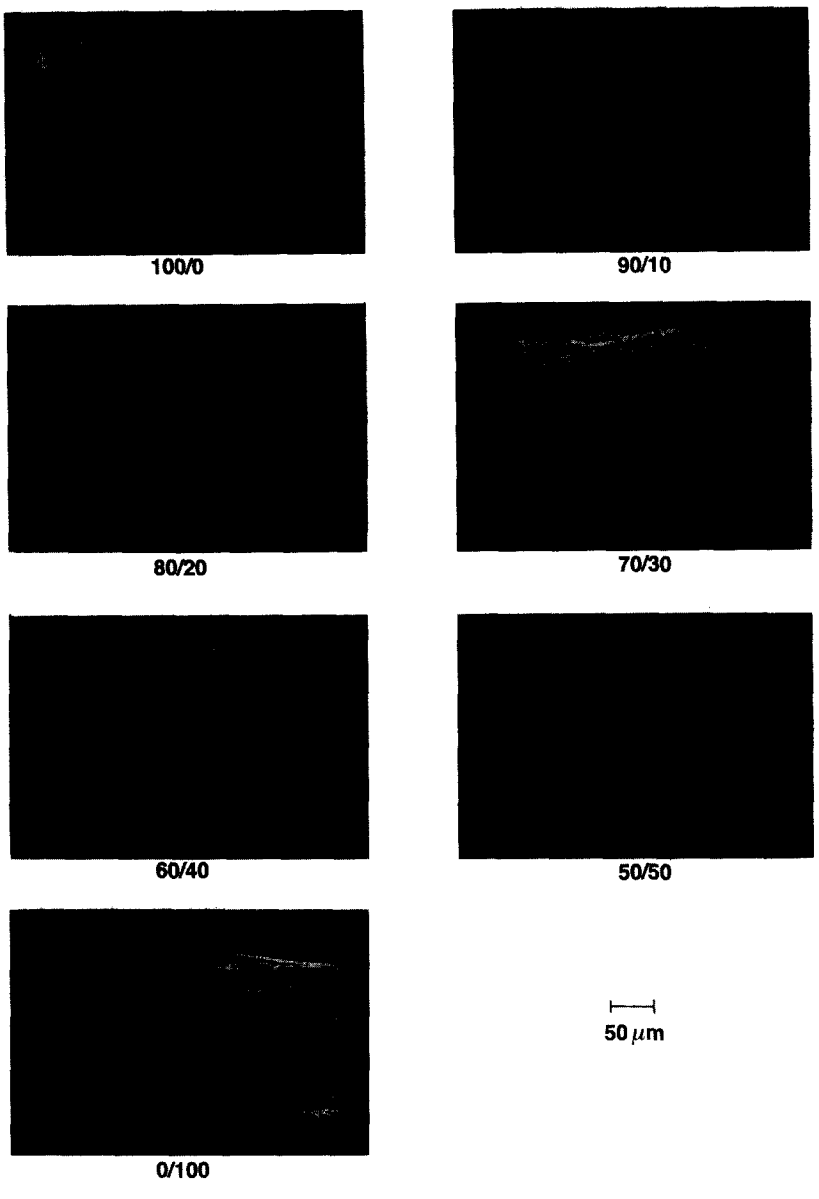

Figure 6 SEM microfractographs of the PVC/TPU90 blends

Table 4 Tensile properties of PVC/TPU blends

PVC/TPU90	Tensile strength (/MPa)	Elongation at break (/%)	Tensile modulus (/MPa)
100/0	22.55	295	14.71
90/10	23.04	290	13.73
80/20	25.49	330	13.43
70/30	28.43	350	12.94
60/40	35.29	390	11.96
50/50	34.80	400	11.37
0/100	59.80	460	9.02
PVC/TPU70	Tensile strength (/MPa)	Elongation at break (/%)	Tensile modulus (/MPa)
100/0	22.55	295	14.71
90/10	24.51	330	12.45
80/20	25.00	395	10.10
70/30	24.80	410	9.019
60/40	24.51	525	6.667
50/50	24.02	610	5.098
0/100	30.39	720	3.137

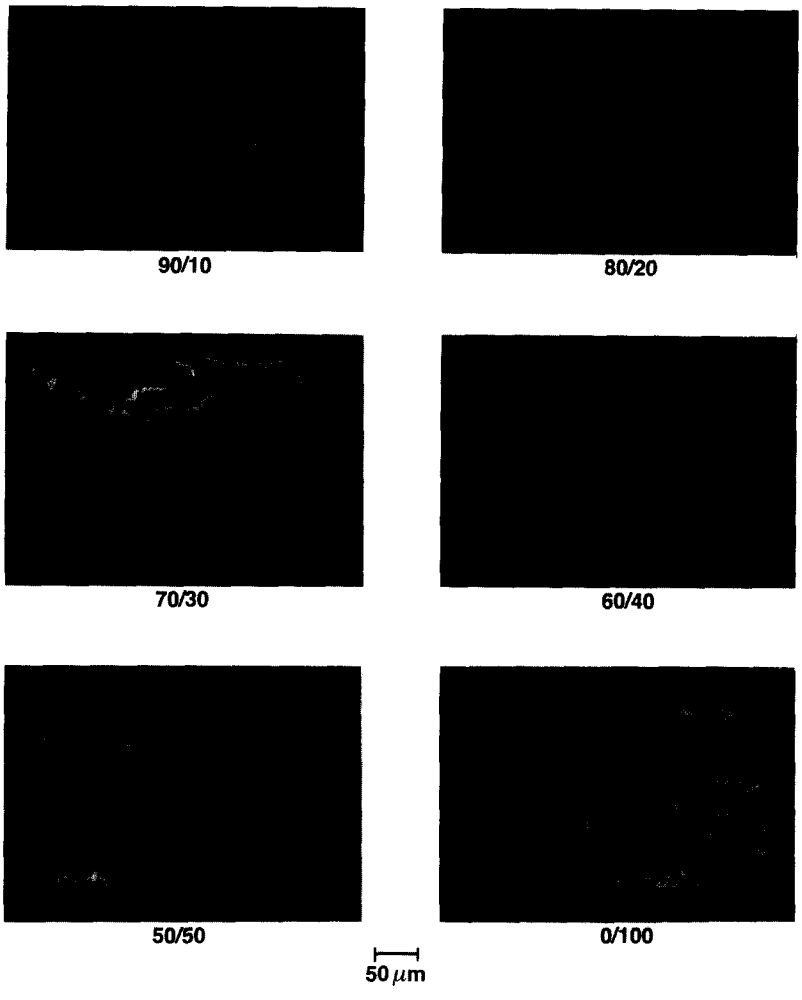

Figure 7 SEM microfractographs of the PVC/TPU70 blends

segment. The increase is mainly due to inherent tough character of TPU. It should also be noted that the impact strength is increased significantly with TPU content as the result of a strong elastic nature of TPU, regardless of TPU kind, as shown in *Figure 9*. The difference in the impact strength in the two blends is, however, not large.

PVC can be toughened by introducing elastomer. Introducing rubber or adding plasticizer contributes flexibility and influences toughness enhancement. But it decreases several other physical properties like tensile strength. It should be noted, however, that in case of TPU, physical properties of plasticized PVC except hardness were greatly enhanced by adding TPU.

The Shore A hardness, measured by ASTM D2240, was decreased with TPU content in the PVC/TPU90 blends, while in the PVC/TPU70 blends the hardness was significantly decreased, since the hardness of TPU70 was lower than that of TPU90 as well as of plasticized PVC as seen in *Figure 10*. The decrease of hardness reduces stiffness and thus contributes flexibility to blends. Thus the increase of elongation at break and impact strength and the decrease of hardness affect toughness enhancement.

For both series of blends, as shown in *Figure 11*, the improvement in the abrasion resistance was significant due to the addition of TPU. The relative improvement for the softer TPU70 series was greater than for the TPU90 series. However the abrasion resistance of TPU70 itself was worse than that of TPU90.

Figures 12 and 13 show typical t.g.a. thermograms of

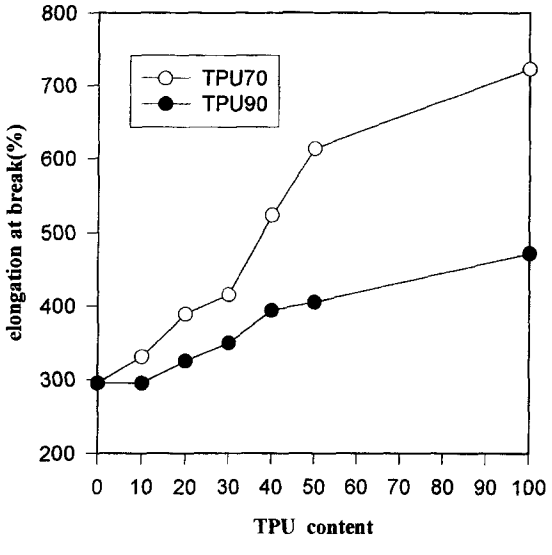

Figure 8 Elongation at break of the PVC/TPU90 blends and the PVC/TPU70 blends

PVC/TPU blends. The thermal stabilities of the blends increased with rising content of TPU, regardless of kinds of TPU. The decomposition temperature increased but the weight residue at 500°C decreased with increasing TPU content. The result means that the incorporation of TPU enhanced the thermal stability of PVC, while flammability

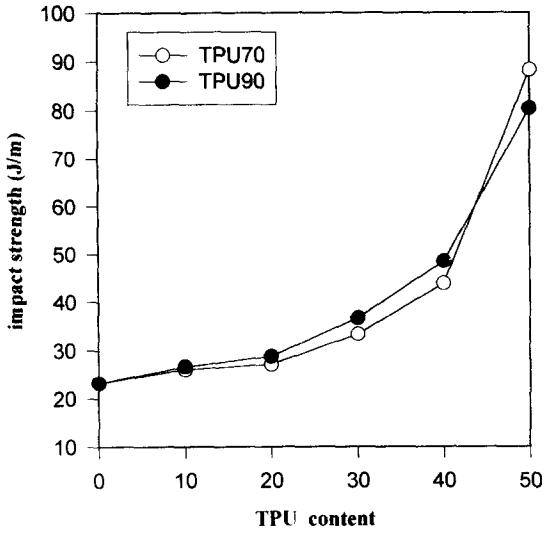

Figure 9 Impact strength of the PVC/TPU90 blends and the PVC/TPU70 blends

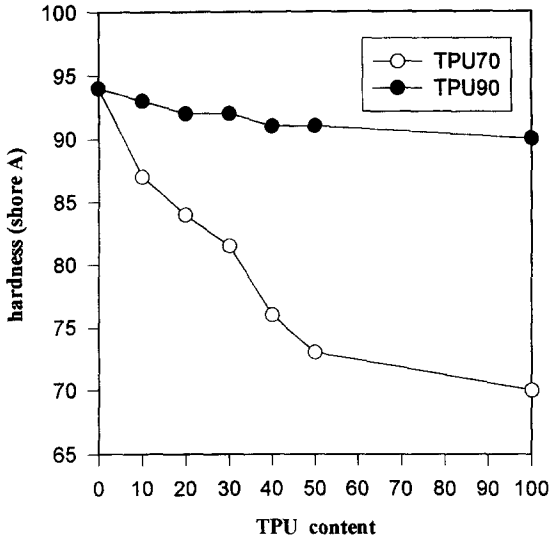

Figure 10 Hardness of the PVC/TPU90 blends and the PVC/TPU70 blends

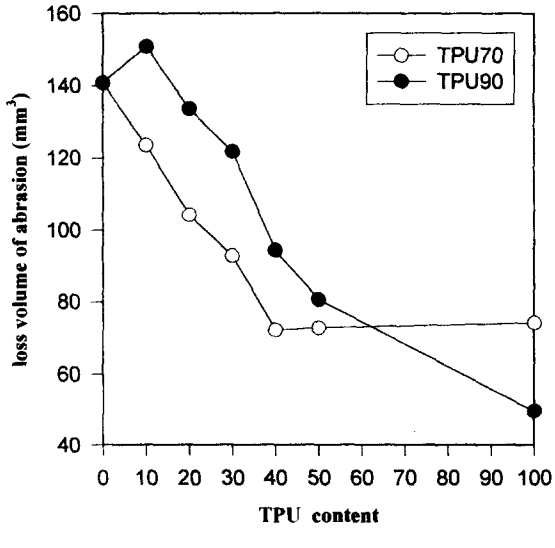

Figure 11 Abrasion resistance of the PVC/TPU90 blends and the PVC/TPU70 blends

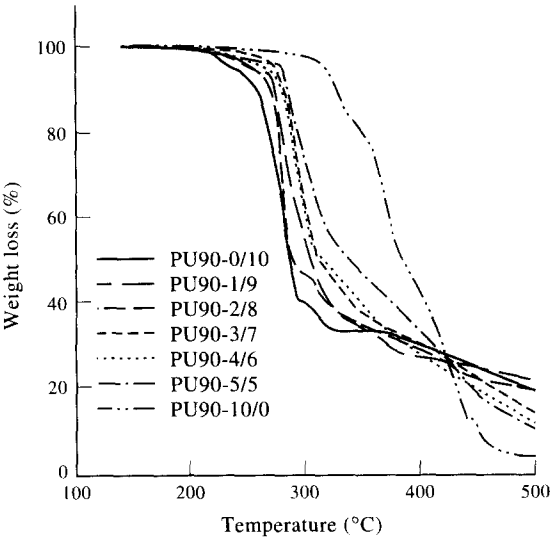

Figure 12 t.g.a. thermograms of PVC/TPU90 blends

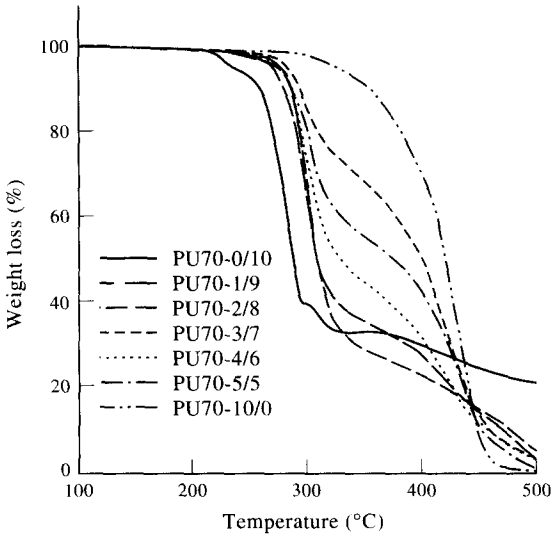

Figure 13 t.g.a. thermograms of PVC/TPU70 blends

Table 5 Flame retardance of PVC/TPU blends

Composition of blend (PVC/TPU)	LOI	
	PVC/TPU90	PVC/TPU70
100/0	25.0	25.0
90/10	24.0	23.5
80/20	23.0	23.0
70/30	22.0	22.0
60/40	21.5	21.0
50/50	21.0	20.5
0/100	Flammable	Flammable

was reduced with increasing TPU content. It is indicated that the greater residue after decomposition suggests better flame retardance[25]. The flame resistance of the blends can be discussed in terms of the limiting oxygen index (LOI).

Table 5 shows the LOI of blends. The LOI of samples is the concentration of oxygen just supporting combustion under steady-state candle-like burning. A material is considered flammable at any temperature where the LOI

is below 21[25]. The flammability of TPU was improved by the blended PVC. It may be said that the flame retardance was achieved for all the blends investigated here since their LOI values are above 21 at all the compositions, except both the TPUs and the PVC/TPU70 blend of 50/50 composition by weight.

CONCLUSIONS

In this work, the fracture toughness and physical properties such as thermal stability, tensile properties, hardness, abrasion resistance, and flame retardance of blends of plasticized poly(vinyl chloride) and thermoplastic polyurethane were investigated. Fracture toughness investigation has been made using the J-integral by locus method. Two kinds of TPU i.e. TPU90 and TPU70 were compared. PVC was plasticized with dioctyl phthalate. PVC/TPU90 and PVC/TPU70 blends with variable weight ratio (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100) were prepared by melt blending.

The tensile strength increased with TPU content for both blend systems. However, it slightly decreased at the 50/50 composition due to the larger phase separation, while the modulus (100% secant) was decreased with the increase of TPU content. The elongation at break and the impact strength increased with TPU content due to the inherently elastomeric properties of TPU. The relative improvement of elongation at break for the softer TPU70 series was greater than for TPU90 series due to greater soft segment.

The hardness decreased with increasing TPU content in the PVC/TPU90 blends, while in the PVC/TPU70 blends the hardness was significantly decreased, For both series of blends, the improvement in abrasion resistance was significant due to the addition of TPU. The relative improvement for the softer TPU70 series, was greater than for TPU90 series. The thermal stabilities of the blends increased with increasing TPU content but the flammability was reduced by increasing the TPU content. It may be said, however, that the flame retardance was achieved for all the blends investigated here since their LOI values were > 21 for all compositions except both the TPUs and PVC/TPU blend having 50/50 (*%w/w*) composition.

It was concluded that the physical properties of plasticized PVC except hardness were greatly enhanced by adding TPU. It was also shown that the addition of TPU70 or TPU90 enhanced the toughness of plasticized PVC and that the toughening effect, in terms of *Jc* values, of TPU was more prominently observed in the PVC/TPU70 blends than in the PVC/TPU90 blends. The morphological studies by SEM showed clearly the dimple rupture topology of the PVC/TPU70 blends, which is typical for ductile materials.

ACKNOWLEDGEMENTS

The authors wish to thank The Sanhak Hyupdong (University–Industry Cooperation) Foundation and the Hanchang Chem. Co. Ltd for their financial support for this work.

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