

Comparative study on the properties of PVC/TPU blends prepared by single screw and twin screw extruder

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ABSTRACT

In this work, we have compared the mechanical and thermal properties PVC/TPU blends with variable weight ratio prepared using single screw and twin screw extruder. Two grades of TPUs differing in hardness (Shore A hardness 66 and 85) are used in making the blends. The tensile strength of PVC/TPU-1 and PVC/TPU-2 blends obtained from twin screw extruder is higher by 39% - 98% and 89% - 143% than that obtained from single screw extruder, which indicates intimate mixing of two phases in twin screw extruder. Beyond 30 % of TPU content, the blends of TPU-2 (high hardness grade) exhibit relatively high modulus compared to blends of TPU-1. The blends prepared by twin screw extruder were relatively harder. The rebound resilience of blends prepared by twin screw extruder was found to be always more. The rebound resilience of PVC/TPU-1 blends is relatively more compared to PVC/TPU-2 blends due to more number of soft segments in TPU-1. The blends were also characterized by abrasion resistance, MFI, DSC and TEM.

Key words: PVC, TPU, hard segment, soft segment, compatibility, extruder, mixing, blending.

INTRODUCTION

The formulation of polyurethane-based alloys has developed over the past 15 years as a means of improving some properties and/or reducing manufacturing costs. Thermo Plastic Urethanes (TPU) are linear block copolymers composed of hard and soft blocks. The hard segments of the chain mainly consist of urethane linkages and diisocyanate groups which make the segment rigid and polar. The soft segments mainly consist of long chain diols. The presence hydroxyl groups make the segment soft and flexible and non-polar. Hence TPU possesses two phase morphology and the ratio of the hard to soft segments determines many of its properties like hardness, crystallinity and Tg. This unique molecular structure leads to a combination of many physical properties including high elongation, and tensile strength, excellent abrasion and tear resistance, high resilience and good compression set, good

resistance to oil, grease and many solvents. Thus TPU is one of the most versatile products in the group of engineering thermoplastics with elastomeric properties. In comparison to rubbers, TPU is a highly tough material with very good impact resistance. It has good low temperature flexibility and high melt flow characteristics, but poor flame resistance. The advantages of PVC include cost and flame resistance. The presence of chlorine atom causes an increase in the inter chain attraction and hence an increase in hardness and stiffness, and imparts high flame retardency. But PVC has limited thermal stability due to dehydrohalogenation reaction that takes place at elevated temperatures of about 170°C and makes processing difficult. Therefore pre-powder mixing with additives such as heat stabilizers is necessary before blending. Moreover, PVC has low toughness and abrasion resistance and hence blending with a low Tg material can be of commercial advantage.

Since 1998, a great deal research is focused on developing these blends as they find place in automotive and large number of engineering applications. In spite of commercialization of PVC/TPU blends [e.g. Shutane (Reichold Chem), Vyhene (Alpha Chem.), Uravin, Nitrovin (Vichem Corp.)], still there is large and untapped potential in the generation of compatibilized polymer blends of polyurethanes and PVC. Most of the published literature is focused on property-composition dependence of PU/PVC polyblends. Nikos¹ reported in 1981 that these polymer alloys are essentially heterogeneous and their useful mechanical properties are due to good adhesion between the two phases.

Studies of Shilov *et. al.*,² on blends of synthesized PU (based on oligo-caprolactone glycol, chain extended by diphenylmethane diisocyanate) and 75% PVC reveals high extension (> 700%) with a comparatively high value of the initial modulus of elasticity. PVC is reported to be compatible with soft segments in its blends with polyester polyurethanes³. However, when hydroxy-terminated poly (propylene glycol) was used as the soft segment, PVC/TPU blends showed two separate T_g 's of PVC and TPU⁴. The mechanical properties melt blends of plasticized PVC with two kinds of TPUs (Shore A hardness 90 and 70) were compared by Chang-Sik Ha *et. al.*,⁵. The authors reported improved tensile strength, impact strength, abrasion resistance, and thermal stability, with small decline of tensile modulus and hardness in comparison with pure TPU. The compatibility of melt mixed PVC/TPU blends was investigated using DMA and SEM by Yiyen Kim *et. al.*,⁶. It was concluded by these authors that the compatibility of plasticized PVC and TPU are dependent on the ratio of hard to soft segments in TPU.

Hernandez *et. al.*,⁷ observed that the PVC plasticized with common Dioctyl phthalate (DOP) shows a considerable higher elongation at break and a lower Young modulus than PVC mixed with TPU. A remarkable reduction in the viscosity of the polymer blends observed by these authors indicates that these compounds worthy of attention from a technological point of view. Pita et al [8] studied the influence of processing condition on the mechanical properties of plasticized PVC and PVC/TPU blend.

It is suggested that the structure of TPU/PVC mixtures could be maintained efficiently up to 50 phr TPU content. Processing of the corresponding melts is obviously a very interesting and promising problem in the study of polymeric materials.

The reported literature reveals that no detailed studies on processibility, mechanical and thermal properties of PVC/TPU have been carried out. In this work, we have compared the mechanical and thermal properties PVC/TPU blends with variable weight ratio prepared using single screw and twin screw extruder. Two grades of TPUs differing in hardness are used in preparing the blends.

MATERIAL AND METHODS

Suspension PVC (code 67ER092, K value-67) was supplied by Indian petrochemicals co-operation Ltd. To improve the thermal stability of PVC, Ca/Ba/Zn complex stabilizer (KBC200, Ala Chemicals) was employed along with other compounding ingredients such as DOP (KLJ Chemicals), epoxy oil and calcium stearate. Two commercially available ester type TPUs namely Desmopan DP1966AW (TPU-1) and Desmopan 385L (TPU-2) were kindly provided by Bayer. The basic differences between the two TPUs studied here is their hardness (Share A Hardness values; TPU-1 = 65 and TPU-2=85). The differences in hardness arise from different ratios of hard to soft segments, which in turn lead to different soft segment molecular weight.

The compounding ingredients (Table 1) along with PVC were mixed in a sigma kneader for about 20 minutes. All the batches were calculated

Table 1: Ingredients used for PVC Compound

Ingredients	Quantity (PHR)	Role
PVC	100	Base polymer
Ca/Ba/Zn complex	3	Heat stabilizer
DOP	40	Plasticizer
Epoxy resin	2	Processing oil
Calcium stearate	3	Lubricant

for a PVC loading of 2.5 kg. PU materials are hygroscopic and undergo hydrolytic degradation during processing. Hence TPUs were pre-dried in hot air oven for 2-4 hrs at 110°C and stored in desiccators till further use. PVC compound and TPUs were mixed thoroughly in a tumbler and then transferred to the extruder hopper. The melt mixing of PVC compound and TPUs was carried out in (i) single screw extruder (Klockner Windsor extruder,

Model HM 300, L/D ratio 26:1 and a (ii) twin screw extruder (Haake Rheomix OS PTW L/D ratio 40; Co-rotating). The temperature setting for different zones were as follows. Feed zone- 40°C, Z1-140°C, Z2-150°C, Z3-160°C, Z4-170°C, Die-175°C. A screw speed of 30 rpm was maintained in both cases. Various compositions of the blends prepared are shown in Table 2. The extrudate was cooled and pelletized to get granules.

Table 2: Blend formulations considered in this study

Sample code	Set-1		Sample code	Set-2	
	TPU-1	PVC Compound		TPU-2	PVC Compound
T1-0	0	100	T2-0	0	100
T1-10	10	90	T2-10	10	90
T1-20	20	80	T2-20	20	80
T1-30	30	70	T2-30	30	70
T1-40	40	60	T2-40	40	60
T1-50	50	50	T2-50	50	50
T1-100	100	0	T2-100	100	0

The rectangular shaped test specimens (4mm X 13mm X 115 mm) were prepared by injection molding at 180°C. The tensile test were carried out at 25°C using universal testing machine (Model: H 50KM, load cell-50000N, Hounsfield, UK) with a cross head speed of 25mm/min. The MFI of Plasticized PVC, TPU-1, TPU-2 and their blends were determined at 190°C/2.16 kg load in a standard melt indexer. Abrasion resistance was evaluated using plastic abradant with Aluminum oxide as abradant. The weight loss due to abrasion under standard conditions is considered as a measure of abrasion resistance. The sample preparation for TEM was done at -140°C and the thin 100 nm slices were studied without staining. Diamond knife was used for microtoming and nicks on the knife forms the long scratches on the samples. All images recorded at 13.5 kX magnifications using a Tecnai G2 microscope operated at 120kV. Differential scanning calorimetric (DSC) studies of the blend were carried out using DSC-Q200 (TA Instruments). Programmed heating cycles were used to heat the samples at a heating rate of 10°C/min under nitrogen atmosphere. The second heating cycles were considered for analysis.

RESULTS AND DISCUSSION

Tensile Properties

The tensile strength of PVC/TPU-1, PVC/TPU-2 blends with variable weight ratio, prepared using single screw and twin screw extruder, is compared in figure 1. The stress strain curves (not shown) of PVC (plasticized) and PVC (plasticized)/TPU blends showed profile characteristic of hard and tough materials, whereas the behavior of 100 TPU was soft and tough.

The tensile strength of T1-100 and T2-100 are 9.9 MPa and 18.9 MPa respectively. The tensile strength of plasticized PVC extruded in a single screw extruder (T1-0) and twin screw extruder (T2-0) is 3.5 MPa and 5.38 MPa respectively indicating 53.7% increase in the property. This indicates mixing of compounding ingredients in PVC has significant effect on mechanical properties PVC. The tensile strength of PVC/TPU-1 and of PVC/TPU-2 blends increases with an increase in TPU content up to 30% loading and shows a decreasing trend beyond 30% loading. The tensile strength of PVC/TPU-1 blends obtained from twin screw extruder is higher

by 39% to 98% than that obtained from single screw extruder, which indicates intimate mixing of two phases in twin screw extruder. The maximum tensile strength of 4.5 MPa and 6.42 MPa has been observed for T1-30 blend processed in single screw extruder and twin screw extruder respectively. A similar trend can be seen with PVC/TPU-2 blends too. The tensile strength of the PVC/TPU-2 blends obtained from twin screw extruder was always higher by 89% to 143% than that obtained from single screw extruder. The maximum tensile strength of 5.21 MPa and 10.36 MPa has been observed for T2-30 blend processed in single screw extruder and twin screw extruder respectively.

The elongation at break is relatively low in polymer blends processed in twin screw extruder in comparison with those processed in single screw extruder. This decrease is attributed to corresponding increase in tensile strength of blends as indicated in Fig. 2. In general, elongation at break increases with TPU content. However when processed in single screw extruder, elongation at break was found to decrease when the TPU content is more than 30%. This indicates inadequacy of single screw extruder in homogenizing the elastomer and PVC beyond a critical level of TPU (in this case \approx 30%). In other words, the blends prepared by twin screw extruder are intimately mixed compared to single screw extruder.

The increase in elongation at break of blends processed in single screw extruder and twin screw extruder is in the range of 12–45% and 2 – 60% for T1 series and T2 series blends respectively. The tensile modulus values of the T1 series and T2 series blends obtained by twin screw extruder (TSE) are presented in figure 3. As expected the addition of elastomer to PVC which is already plasticized with DOP further decreases the modulus of the blends. Up to 30% loading of TPU, the modulus of T1 series and T2 series blends is approximately same. Beyond 30% of TPU content, the blends of TPU-2 (high hardness grade) exhibit relatively high modulus compared to blends of TPU-1. As seen in figure 3, the modulus of T1 series and T2 series blends obtained by twin screw extruder is in the range of 10-20 MPa while that of T1-0, T1-100 and T2-100 are 46 MPa, 5.8 MPa and 14 MPa

respectively. The mechanical properties of PVC are known to be dependent on the degree of dipolar interaction. The interaction between plasticized PVC with TPU cause disruption to the PVC interchain interactions, by acting as specific barriers between PVC chains⁸. This disruption caused the lowering of the mechanical properties of the blends.

Hardness

The hardness of TPU-1 and TPU-2 as per the material data sheet is 66 and 85 Shore A. The Shore A hardness of the plasticized PVC obtained from single screw extruder and twin screw extruder were 50 and 94 respectively. The hardness of T1 and T2 series of blends with variable weight ratio, prepared by using single screw and twin screw extruder, is compared in Fig. 4. The Shore A hardness decreases with an increase TPU content in both PVC/TPU-1 and PVC/TPU-2. The plasticized PVC (T1-0 and T2-0) extruded in single screw extruder shows a Shore A hardness 50 whereas that extrudes in twin screw extruder shows a hardness value of 94 Shore A (88% increase). Compared to the blends prepared by single screw extruder, the blends prepared by twin screw extruder were much harder in case of both TPU-1 and TPU-2 blends. The increase in hardness is in the range of 75 – 124% and 86 – 178% for T1 and T2 series blends respectively. The decrease in hardness reduces stiffness and thus contributes flexibility to blends. Thus the increase in elongation at break and the decrease in hardness affect toughness enhancement.

Rebound resilience

The rebound resilience of plasticized PVC obtained from single screw extruder and twin screw extruder is 21% and 14% respectively. The rebound resilience of T1 and T2 series blends with variable weight ratio, prepared by using single screw and twin screw extruder, is compared in figure 5. Rebound resilience values of both the T1 and T2 series blends prepared by twin screw extruder showed higher values than the blends prepared by single screw extruder. The increase in property is in the range of 100 – 185% for T1 series blends and 50 – 107% for T2 series blends. The rebound resilience of T1 series blends is relatively higher for all the blend compositions, compared to T2 series blends due to more number of soft segments in

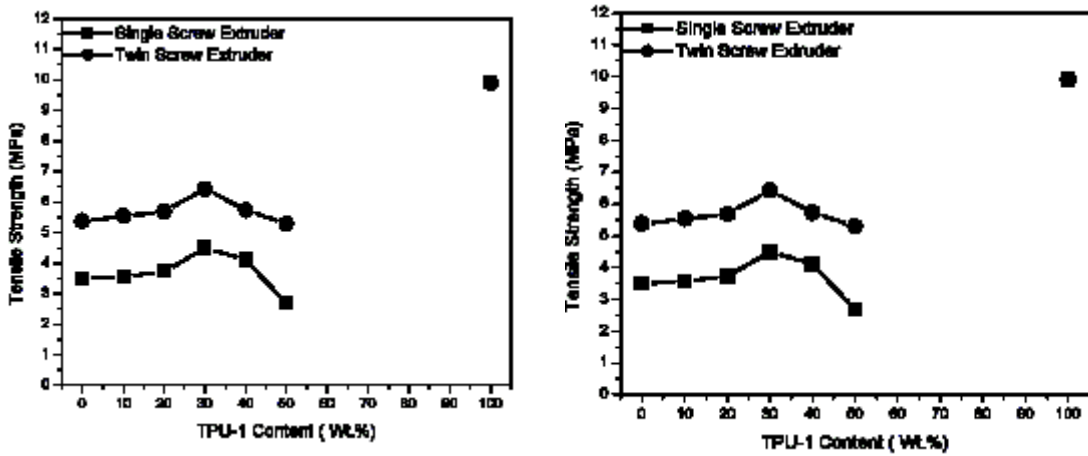


Fig 1: Variation of tensile strength with TPU content (a) PVC/TPU-1 blend (b) PVC/TPU-2 blend

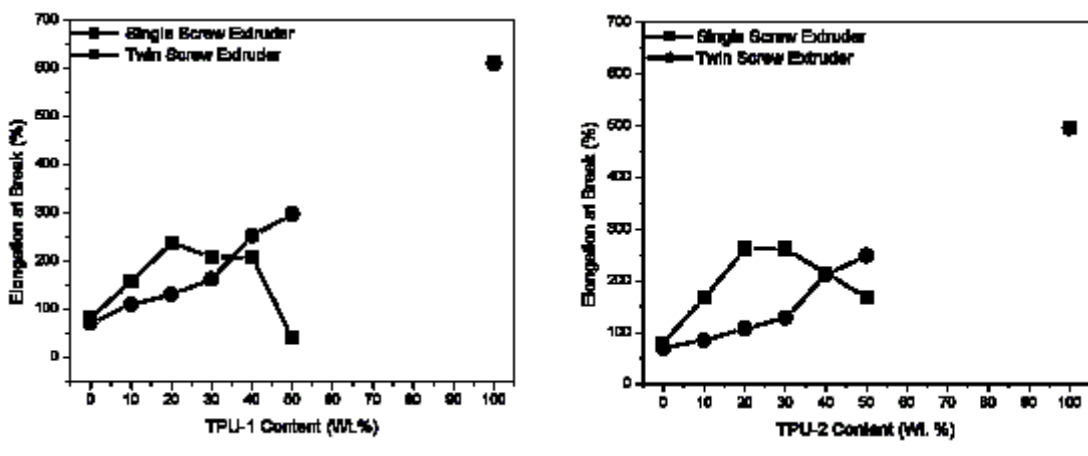


Fig 2: Variation of Elongation at Break with TPU content (a) PVC/TPU-1 blend (b) PVC/TPU-2 blend

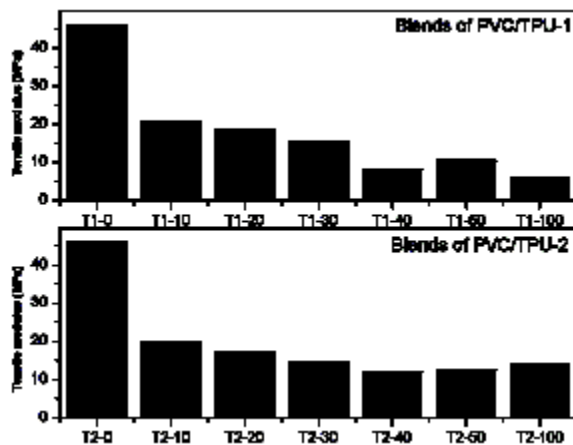


Fig. 3: Variation of tensile modulus with TPU content in blends (TSE)

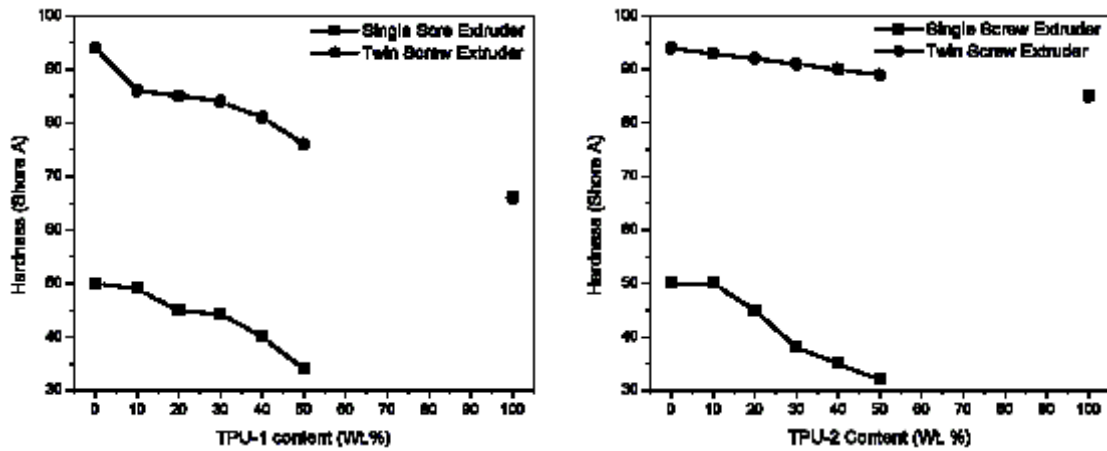


Fig 4: Variation of Hardness with TPU content (a) PVC/TPU-1 blend (b) PVC/TPU-2 blend

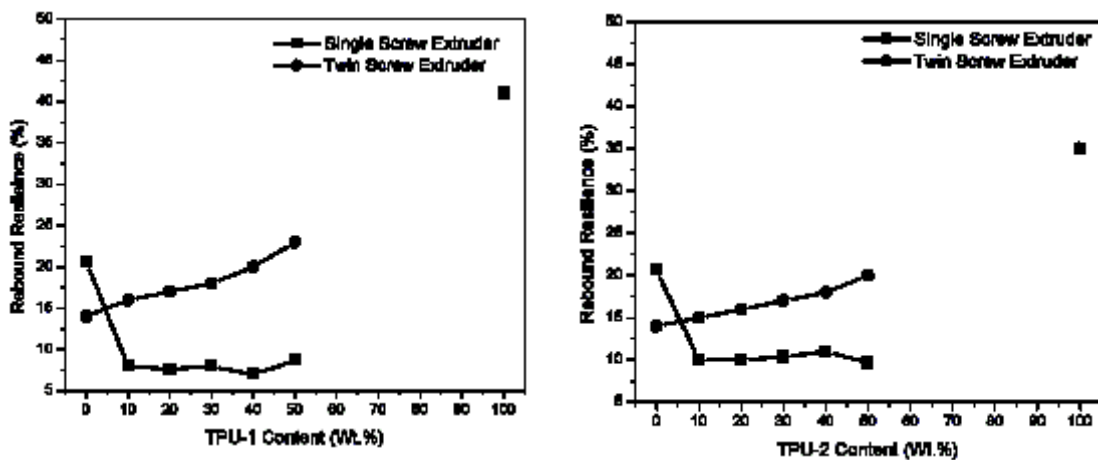


Fig 5: Variation of Rebound resilience with TPU content (a) PVC/TPU 1 blend (b) PVC/TPU 2 blend

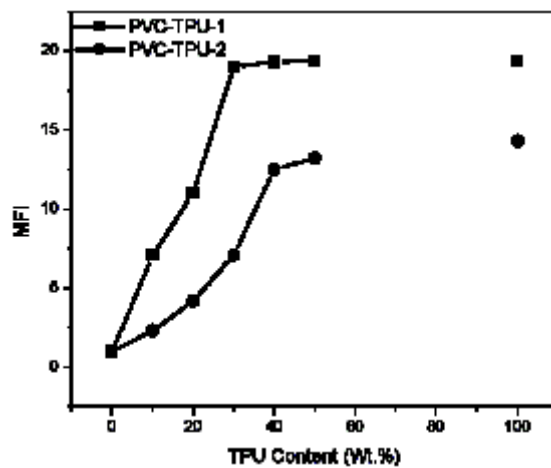


Fig. 6: Variation of melt index with TPU content

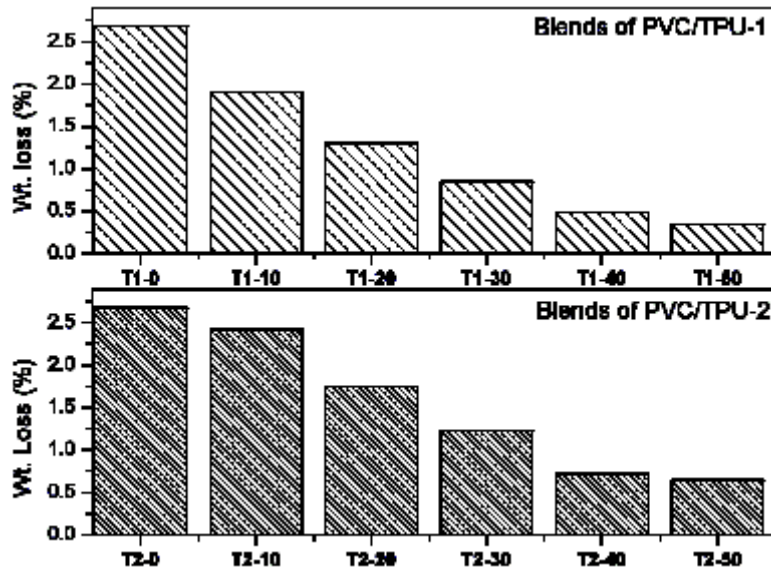


Fig 7: Variation of Abrasion resistance with TPU content (a) PVC/TPU-1 blend (b) PVC/TPU-2 blend

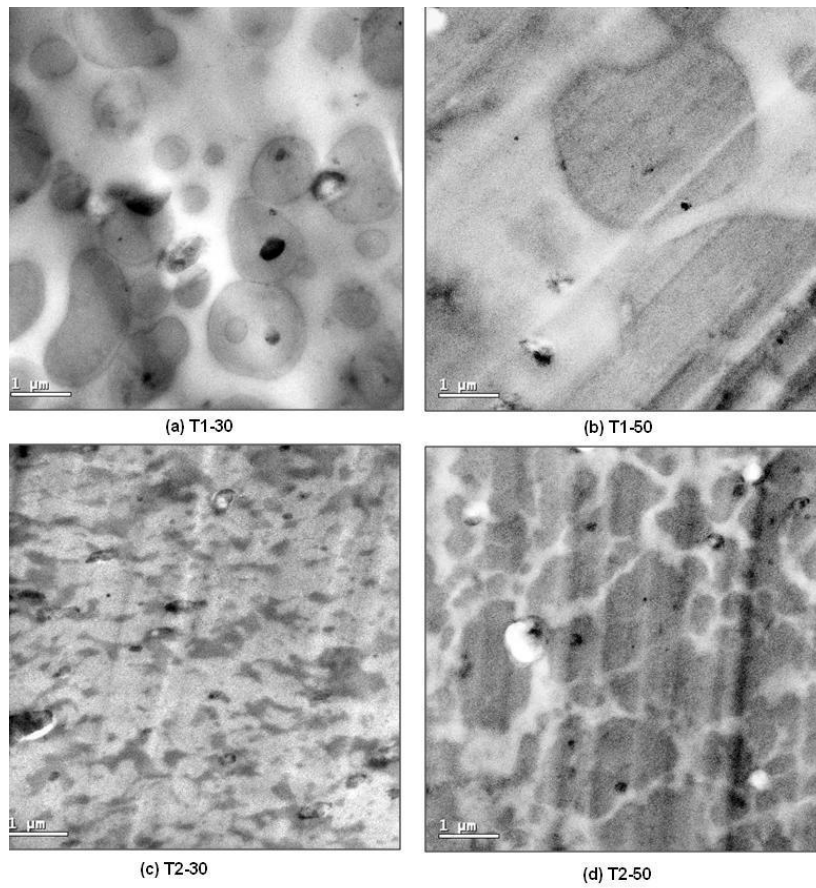


Fig. 8: TEM images; (a) and (b): 30/70 and 50/50 blends of PVC/TPU-1 (c) and (d): 30/70 and 50/50 blends of PVC/TPU-2

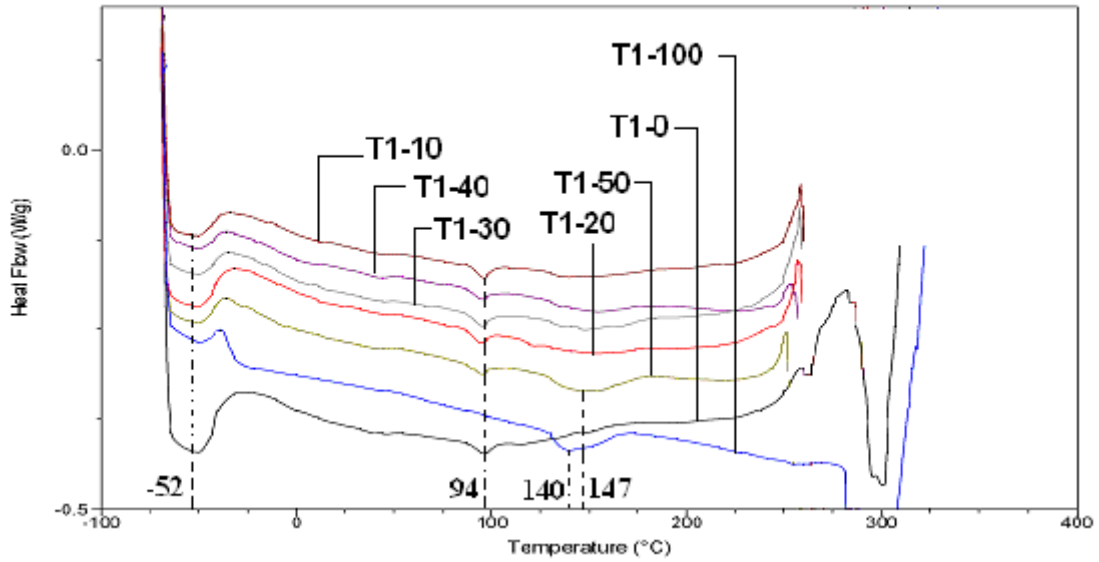


Fig 9: DSC thermograms of PVC/TPU-1 blends

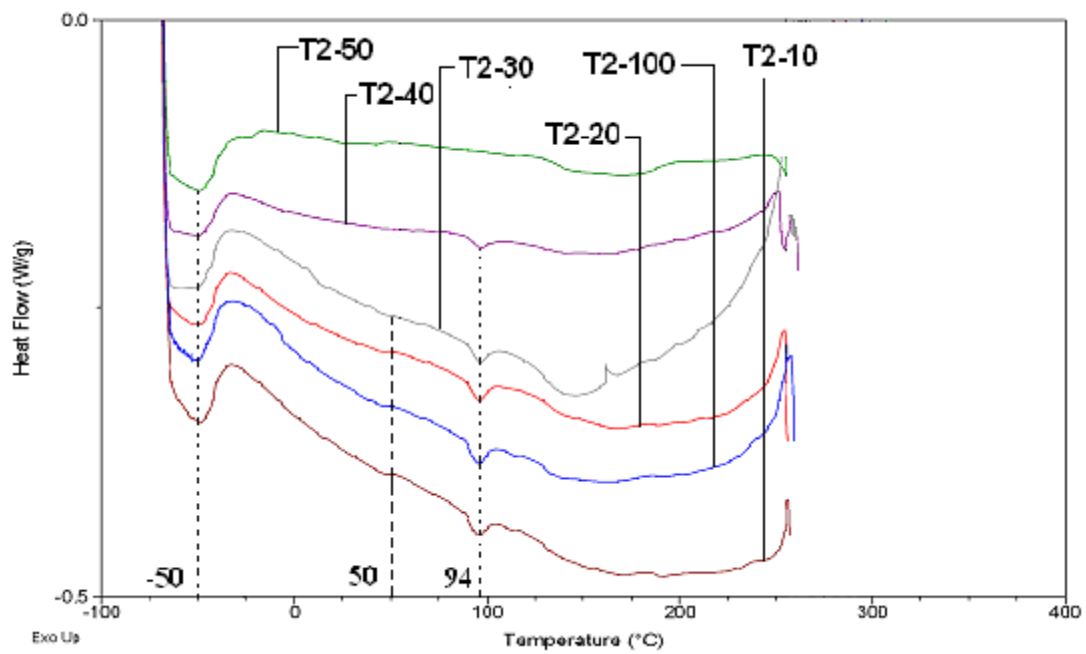


Fig 10: DSC thermograms of PVC/TPU-2 blends

TPU-1. All the above results indicate poor mixing of PVC and TPU when processed in single screw extruder. Hence, blends from single screw extruder were excluded for further studies.

Melt flow Index

The flow properties of TPUs are better than PVC. The MFI of T-1 blend series is always found to be higher than that of T-2 blend series as shown in figure 6. Addition of TPU results in better flow properties in both cases. However, MFI of the blends reached the values pure TPU at a TPU content of 30% in case of PVC/TPU-1, and 40% in case of PVC/TPU-2. Beyond these levels of MFI of blends seems to be less influenced by TPU content, indicating melt viscosity is mainly governed by TPU in blends.

Abrasion resistance

For both series of blends, the improvement in abrasion resistance can be seen with the addition of TPU (Fig. 7). Weight loss in T1 series of blends is less than T2 series of blends. Compared to plasticized PVC (T1-0), the weight loss in T1 series of blends is reduced by 29% to 87% while that in T2 series of blends is reduced by 9% to 76%. Thus relative improvement of abrasion resistance for the softer T1 series is greater than that for harder T2 series.

Transmission Electron Microscopy

The TEM images of the selected blends of TPU-1 and TPU-2 are shown in figure 8. The phases can be identified by mass thickness contrast. Hence the denser phase is dark in the images and lighter phase appear white. It is well known that the phase structures of the blends are mainly controlled by the components of the blends. When the concentration of the minor component increases, the particles begin to coalesce and form bigger structures. Further addition extends the continuous structure until the minor phase is continuous throughout the whole sample¹⁵. For the 70/30 blend of PVC-TPU-1 (figure 8a), PVC forms a dispersed phase and TPU-1 is a matrix. The morphology changes from discrete kind to co-continuous kind when TPU-1 content is increased from 30% to 50%. (Fig. 8b). However in case of PVC-TPU-2 blends, an intimate mixing is achieved at 30% loading of TPU-2, resulting in co-continuous

morphology (Fig. 8c). Further addition of TPU-2 leads transformation of co-continuous morphology tending to discrete morphology (Fig. 8d).

Differential Scanning Calorimetric results

DSC studies on PVC/TPU blends were carried out to examine the miscibility of these components. The Tg values reported in the literature are -10°C [9-10], -23°C [11], -60°C [12] for TPU and 78 °C [11], 80-84 °C [7, 13] for PVC. DSC thermograms of blends obtained from a twin screw extruder are shown in figure 9. The Tg of PVC was found to be 94°C. We can observe exothermal decomposition of PVC around 280°C. The soft segments of TPU are characterized by Tg of -50 to -52°C. T1-100 and T1-50 exhibit a broad endotherm in the range 140 -145°C that can be attributed to the softening temperature of TPU. It is clear from figure 9 that at all blend compositions, the Tg of soft segments of TPU-1 and that of PVC essentially remains constant at -52°C and 94°C respectively. TPU-2 shows two Tgs at -50°C and 50°C which corresponds to soft and hard segments (figure 10). The 50/50 blend of PVC/TPU-2 shows a single Tg at -50°C. However, it should be borne in mind that the use of Tg in determination of polymer/ polymer miscibility is based on the premise that a single Tg indicates that the domain size is below $2 < d < 15$ nm. A single Tg is not a measure of miscibility but only of the state of dispersion¹⁴.

The tensile strength of PVC/TPU-1 and of PVC/TPU-2 blends increases with an increase in TPU content up to 30% loading and shows a decreasing trend beyond 30% loading. The tensile strength of PVC/TPU-1 and PVC/TPU-2 blends obtained from twin screw extruder is higher by 39% - 98% and 89% - 143% than that obtained from single screw extruder, which indicates intimate mixing of two phases in twin screw extruder. The elongation at break is relatively low in polymer blends processed in twin screw extruder in comparison with those processed in single screw extruder. Up to 30% loading of TPU, the modulus of T1 series and T2 series blends is approximately same. Beyond 30% of TPU content, the blends of TPU-2 (high hardness grade) exhibit relatively high modulus compared to blends of TPU-1. Compared to the blends prepared by single screw extruder,

the blends prepared by twin screw extruder were much harder in case of both TPU-1 and TPU-2 blends. The increase in hardness is in the range of 75 – 124% and 86 – 178% for T1 and T2 series blends respectively. The rebound resilience of both T1 and T2 series blends prepared by twin screw extruder has been found to be always more. The rebound resilience of T1 series blends is relatively higher for all the blend compositions, compared to T2 series blends due to more number of soft segments in TPU-1. The MFI of T-1 blend series is always found to be higher than that of T-2 series. Addition of TPU resulted in better flow properties in both cases. Beyond 30% TPU-1 in case of T1 series and 40% TPU-2 in case of T2 series, the melt

viscosity is mainly governed by TPU. For both series of blends, the improvement in abrasion resistance was observed with the addition of TPU [29% - 87% improvement in T1 series and 9% - 76% improvement in T2 series of blends]. Thus relative improvement of abrasion resistance for the softer T1 series is greater than that for harder T2 series. The morphology seems to transform from discrete to co-continuous form when TPU-1 content is increased from 30% to 50%. In case of PVC-TPU-2 blends, an intimate mixing is achieved at 30% loading of TPU-2, resulting in co-continuous morphology. The DSC studies show that the 50/50 blend of PVC/TPU-2 shows a single Tg at -50°C indicating miscibility of the components.

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