# RSC Advances

# Investigation on Morphology, Mechanical, Dynamic mechanical and Thermal Behaviour of Blends Based on Ethylene Vinyl Acetate (EVA) and Thermoplastic Polyurethane (TPU)

Joyeeta Dutta and Kinsuk Naskar*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur, Kharagpur 721302, West Bengal, India

**Abstract:** Novel blends based on Ethylene vinyl acetate/Thermoplastic Polyurethane (EVA/TPU) at different ratios were prepared via melt blending technique. Scanning electron microscopy (SEM) study revealed primarily a two phase morphology in which the minor TPU phase was dispersed in the major continuous EVA matrix. However in the 50/50 blend EVA and TPU appear as co-continuous phase. The influence of blend ratio on mechanical properties and hardness were investigated. 80/20 EVA/TPU blend was observed to exhibit optimum tensile strength and elongation at break. Various models have been applied to predict the change in modulus with blend composition. Veenstra B model was found the best to correlate the experimental modulus values. All the blends show a single Tg and a shift in Tg with change in blend composition was observed through Differential scanning calorimetry (DSC) and Dynamic mechanical analysis (DMA), indicating technological compatibility. Thermogravimetric analysis (TGA) was performed to study the thermal stability of the EVA/TPU blends. Incorporation of TPU has also been found to improve the oil resistance property of the blend system.

**Key words:** Polymer blends and alloys, EVA, TPU, Morphology, Modeling and Thermal properties

**\*Corresponding author, e-mail: knaskar@rtc.iitkgp.ernet.in**

## Introduction:

Blending of two or more structurally and functionally different polymers with suitable proportion have been found to be an important and emerging field for the last few decades to the scientific as well as industrial community. Blending offers unique, improved and desired properties to a newly developed material that the blending components lack, leading to immense and useful applications to revolutionize the polymer technology. While synthesizing a solely new material with all desired properties is a daunting task and consumes high cost, long time and huge efforts, effective blending provides a low cost alternative with improved properties playing a key role in polymer and elastomer industries meeting specific purposes. Voluminous literature reports are there which show that blended polymers do provide unusual combination of mechanical, thermal, chemical, and morphological properties by compensating the deficiencies of the individual precursors.[1, 2] Polymer blends are often broadly categorized into miscible, immiscible and compatible blends among which occurrence of miscible blends are very few in number. Miscible blends result in single phase morphology characterized by single glass transition temperature ($T_g$). On the other hand, immiscible blends do not satisfy the thermodynamic criteria of miscibility resulting in multiphase morphology causing multiple $T_g$ s. Therefore, the mechanical behavior of immiscible blends become more complicated and hence, is an intriguing area of research. However, in case of partially miscible blends, conditional miscibility is exhibited by the corresponding blends depending on the relative proportions of the constituent polymers, mixing temperature and so on.

Ethylene vinyl acetate (EVA) is a random copolymer synthesized from ethylene and vinyl acetate (VA) monomers where the weight percent of VA usually varies from 10 to 45%. Numerous desired features of EVA such as, high polarity (due to polar nature of the acetoxy side group), excellent aging resistance, weather resistance, good mechanical properties, resistance to colour change and relatively low cost have turned EVA to a candidate of choice for blending with other polymers. In addition, they can provide easier melt processability to the corresponding blends. EVA blends with low density Polyethylene (LDPE) [3, 4], High density Polyethylene (HDPE) [5], Polypropylene (PP) [6, 7], Natural rubber (NR) [8] and acrylonitrile butadiene rubber (NBR) [9, 10] etc have been extensively studied by several group of researchers. Blends of EVA/Polybutadiener rubber [11] have been successfully used for the manufacture of microcellular

solings and EVA/PE blends find their application mainly in cable industries. Naskar et al. studied the miscibility, morphology, crystallization and mechanical properties of EVA/Engage blends and successfully used the blend to develop cable insulation and fire resistant low smoke (FRLS) sheathing compound.[12]

Thermoplastic polyurethane elastomer (TPU) is one of the most versatile polymers that bridge the gap between rubbers and plastics. They can be used in a wide range of properties, from hard rubbers to soft engineering thermoplastics as they are elastic and melt-processable.[13] TPU is a linear segmented block copolymer containing alternating hard (adduct of di-isocyanate and small glycols) and soft (e.g. polyester, polyether etc.) segments connected to each other by the urethane groups (–NH–COO–). By varying the amounts of the hard and soft segment, the properties can be varied over a wide range, and it also influences the properties of their blends. TPUs exhibit a considerable number of superior physical properties like high tensile modulus, resilience, abrasion resistance, wear and tear resistance, good compression set, good chemical and solvent resistance along with low-temperature elasticity.[14-17] Such materials can offer flexibility even without the use of plasticizers. However, TPU is relatively more expensive material. Therefore, attempts have been made to blend TPU with other polar polymers. Maity et al. discussed about the effect of blending techniques on the properties of peroxide cured EVA/PU rubber blend.[18] Poomalai et al. reported that the impact strength of the PMMA/TPU blends increase significantly with an increase in the percentage of TPU up to 20%, by retaining the tensile strength of PMMA and a drastic reduction in percentage elongation at break and tensile modulus of the blends were observed after exposure in different chemical reagents.[19] Santra et al. revealed that polyether based TPU and poly(ethylene-co-methyl acrylate) (EMA) blends are miscible throughout the entire composition range via hydrogen bond formation.[20] Wang et al. studied morphology, mechanical properties and rheological behavior of TPU/EPDM blend and improved their compatibility by adding maleic anhydride grafted polyethylene oxide (PEO-g-MA) as a compatibilizer.[21] Palanivelu et al. investigated TPU/Poly(butylene terephthalate) blends at various compositions and reported that addition of small amount of TPU to Poly(butylene terephthalate) increases the impact strength while tensile and flexural properties decrease.[22]

It is already mentioned before that TPUs provide a number of remarkable physical properties like, high tensile modulus, excellent abrasion resistance, good compression set, good chemical

and solvent resistance etc. On the other hand, EVA copolymer with 28% VA contents is widely used as an insulating and sheathing material for medium to high voltage cables, shrinkable films, multilayer packaging and also in the footwear and toy industries due to its high flexibility, good heat resistance and chemical inertness. Since TPU is relatively more expensive than many other polymers, there has been a growing interest in blending TPU with various other polymers in recent years to make it cost effective. This motivates the authors to study the influence of the blending of TPU with EVA to develop a novel cost effective material. This particular blend system can be used as a new material for footwear industries and can also find its application as a potential candidate for cable sheathing material with good oil resistance, heat stability and low temperature flexibility. Hence, the objective of this research work is to study the morphology, mechanical, thermal, and dynamic mechanical properties of the blend system in detail and to develop an economically viable useful blend system. However to the best of our knowledge no systematic study has been made so far to develop the blend of EVA and TPU. The present investigation explores our observations on the blends of EVA and TPU prepared by melt blending process in internal mixer. Attempts have also been made to correlate the mechanical properties with various theoretical models.

## EXPERIMENTAL

### Materials

Thermoplastic Polyurethane (TPU) Desmopan 385 S, composed of 4,4′-diphenylmethane diisocyanate hard segment and polyester based soft segment was procured from Bayer Chemicals, India. The density of TPU is 1.2 g/cm$^3$ with a Shore-A hardness of 84 and melting temperature is around 170 °C. Ethylene vinyl acetate copolymer (EVA) containing 28% vinyl acetate, grade Elvax 265, with a melt flow index (MFI) of 1.7 g/10 min and a density of 0.95 g/cm$^3$, was obtained from Dupont, India.

### Preparation of Blends

EVA and TPU were mixed in Haake Rheomix OS (Germany) 600 internal mixer, having a mixing chamber volume of 85 cm$^3$ at 180 °C for 7 min. At first TPU was added and it was allowed to melt for 2 min. After that EVA was added and the mixing was continued for another 5 min. The mixes so obtained were sheeted under hot conditions in an open mill set at 2 mm nip gap. The sheets were compression molded between Teflon sheets for 4 min at 190 °C at a

pressure of 5 MPa in an electrically heated hydraulic press (Moore Hydraulic Press, England). The moulded sheets were cooled under pressure to maintain the overall dimensional stability of the moulded articles. Table 1 shows the various blends prepared for this study having different blend ratio of EVA and TPU.

## Characterization of blends

**Mechanical tests:** Tensile test was carried out using a universal testing machine Hounsfield H10KS at room temperature at a crosshead speed of 200 mm/min. Tensile specimens as per ASTM D 412 were punched from the molded sheets using ASTM Die-C. The tensile strength for all of the samples was the maximum stress of the tensile stress–strain curves before they were broken. All results reported were based on the average values of three measurements.

**Stress relaxation and tension set**

For stress relaxation and tension set measurement, the dumbbell specimens were extended upto 100% in the tensile direction at a rate of 200 mm/min and kept at that position for 10 min at room temperature and the value of stress was noted after each 30 sec interval upto 10 min for stress relaxation measurement. It was then relaxed back to unstressed condition and the percentage change in dimension in tensile direction was measured after 15 min and reported as tension set.

$$\text{Tension set } (\%) = \left( \frac{\text{Change in length}}{\text{Original length}} \right) \times 100 \, \% \tag{1}$$

**Hardness test**

Hardness of the samples was measured in both Shore-A and Shore-D scale. Shore D hardness of samples were obtained by a Shore-D hardness-testing machine (Bowers Mertrology, UK) as per ASTM D2240 standard at room temperature. Hardness reported in Shore A scale were measured in Rex Durometers (as per ASTM D2240 method) Model 2000, Buffalo Grove, UK. The hardness value is determined by the penetration of the Durometer indenter foot into the sample.

**Morphological Study**

Surface morphology of the blends was examined by using JEOL JSM 5800 Digital Scanning Electron Microscope (SEM). The accelerating potential 20 kV was used for the analysis of samples. All the blends were cryofractured in liquid nitrogen to avoid any possibility of phase

deformation during cracking process. The cryofractured surface of the blends was etched in tetrahydrofuran (THF) solvent for 4 days in order to remove TPU phase of the blends. The EVA component of the blend remained unaffected while TPU dissolves in the solvent, appearing as black holes in the SEM photomicrographs. The etched surface after adequate drying for 24 hours at room temperature was gold sputtered and then observed under SEM. From the SEM results particle size determination was done by measuring the domain diameter. The number average ($D_n$), weight average ($D_w$) were calculate using the following equations:

$$D_n = \frac{\sum n_i d_i}{\sum n_i} \tag{2}$$

$$D_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \tag{3}$$

**Differential scanning calorimetry (DSC)**

Differential Scanning Calorimetry studies of the pure polymers and the blends were carried out using a DSC Q2000 V24.10 (TA Instruments, USA) at a heating and cooling rate of 10 °C/ min in an inert atmosphere ($N_2$ atmosphere). Standard aluminum pans were used to analyze the sample. The experiment was conducted from -80 °C to 230 °C for all the samples. Glass transition temperatures (Tg) and melting behaviour were observed from the second heating run of DSC plot. The data of second heating cycle was used to eliminate thermal history.

**Thermogravimetric analysis (TGA)**

Thermogravimetric analyses (TGA) and derivative thermogravimetry (DTG) of the neat components as well as EVA/TPU blends were measured by using a thermogravimetric analyzer (TGA Q5000, TA Instruments, USA). The sample weight was 8–10 mg and the heating rate was 10 °C/min. Tests were performed from ambient temperature to 800 °C under $N_2$ atmosphere.

**Dynamic mechanical thermal analysis (DMTA)**

Dynamic mechanical thermal analyses of the samples were carried out using an Eplexor 150N DMTA (Gabo Qualimeter, Ahlden, Germany). Tests were carried out at a frequency of 10 Hz under a static strain of 0.50% and a dynamic strain of 0.001%. The samples were first cooled to −100 °C and then subsequently heated at a rate of 2 K/min. The range of temperature under which the tests were carried out was −100 °C to 80 °C. The sheets were cut into approximately

$35 \times 10 \times 2 \ \text{mm}^3$ rectangles. The nitrogen flow rate was 200 ml/min. The temperature corresponding to the peak in tan δ versus temperature plot was taken as the Tg.

**Oil swelling study:**

The test specimens were immersed in ASTM 3 oil at room temperature for 7days. After the required period of time the specimens were removed from the oil, quickly dipped in acetone, and blotted lightly with a clean blotting paper to eliminate the excess oil on the specimen surfaces and the final weight was taken. For every single composition three specimens were tested and their average values have been reported. Swelling % was measured as follows:

$$\% \ \text{swell} = \frac{M_2 - M_1}{M_1} \times 100 \tag{4}$$

where, $M_1$ = initial mass of specimen in air and

$\qquad M_2$ = mass of specimen in air after immersion

**RESULTS AND DISCUSSION**

**Mechanical properties:** Mechanical properties like tensile strength, elongation at break, modulus at various strains and hardness are summarized in table 2. Neat EVA shows a tensile strength of 16.9 MPa and elongation at break of 1061 %, whereas TPU exhibits a tensile strength of 35.1 MPa and elongation at break of 805%. However, the tensile strength of 80/20 EVA/TPU blend is found to be 17.5 MPa with a good elongation at break of 1067%. Thus it is observed that with addition of only 20% of TPU tensile strength is improved by 4%. With further addition of TPU in the blend tensile strength gradually decrease to 9.3 MPa at 50 wt% of TPU (Figure 1) Although the value of elongation at break also continuously decreases from 1067% to 494% with increasing TPU in the blend over the entire composition range, ET 80 exhibits almost similar elongation at break value as that of neat EVA retaining the excellent elastic property of the pure polymer.

In figure 2 the stress-strain curve of EVA and all the blends are shown. It is to be noted that all the EVA/TPU blends have higher modulus than EVA. Figure 3 clearly shows that the modulus at 100%, 200% and 300% becomes gradually higher with increasing TPU content in the blend. It is found that in ET 80, ET 70, ET 60 and ET 50 the modulus at 300% show an increase by 8%, 15%, 18% and 43% respectively. However, a small variation has been observed at higher

strain level (> 300% strain) where the modulus of pure EVA becomes slightly higher than 80/20 and 70/30 EVA/TPU blend. It has been observed that after 450% elongation EVA shows crazing phenomena (sample undergoes yielding and strain hardening due to strain induced crystallization of amorphous phase). This phenomenon may be attributed to the orientation of the crystalline polyethylene hard segments present in EVA.[3, 9] In case of ET 60 and ET 50, as the amount of EVA reduces in the blend the crazing phenomenon becomes somewhat restricted. That is why it is observed that the modulus of EVA at higher strain is slightly higher for 80/20 and 70/30 EVA/TPU blend.

Hardness of the TPU/EVA and the blends has been reported in Shore A and Shore D scale. EVA has a hardness of 25 shore D and Hardness of the blend varies from 25.2 to 31.4 Shore D. Thus it is found that the hardness of the blend system increases with increasing TPU content.

**Mechanical modeling:** Mechanical properties of the blend system are found to depend on the relative proportion of the components in the blend. Different theoretical models such as series, parallel and Veenstra model have been used to describe the change of modulus with composition. The modulus of polymer blends generally range between an upper limit given by the parallel model (Reuss model) and a lower limit given by the series model (Voigt model).[23, 24] The parallel coupling of polymer components means that the strains of all elements are equal and each of them contribute to the final mechanical property according to the mixing rule. Here the resulting mechanical properties of the blends become independent of interfacial adhesion. Mathematically parallel model is given by the following equation:

$$M = M_1\phi_1 + M_2\phi_2 \tag{5}$$

Where, M is the mechanical property of the blend under consideration and $M_1$ and $M_2$ are the particular property of the component 1 and 2 respectively. $\Phi_1$ and $\Phi_2$ indicates the volume fractions of component 1 and 2 respectively.

On the other hand, in the lowest lower bound series model contribution of the constituent to the blend system are expressed by the inverted rule of mixing. Here it is assumed that the components are arranged in series with the applied stress. Since in this model all the stress is

transmitted through the present interface, interfacial adhesion plays the major role in determining the ultimate property. Series model is expressed as:

$$M = \frac{M_1}{\phi_1} + \frac{M_2}{\phi_2} \tag{6}$$

Veenstra model A and model B can be used for modeling of polymer blends with a droplet/matrix morphology when the dispersed particles are evenly distributed in the matrix. These two models have been mathematically expressed in Equation 5 and 6 respectively:

$$M(A) = M_1 \frac{\Psi^2 M_2 + \left(1 - \Psi^2\right) M_1}{\left(1 - \Psi\right)\Psi^2 M_2 + \left(1 - \Psi^2 + \Psi^3\right) M_1} \tag{7}$$

$$M(B) = \left(1 - \Psi^2\right) M_1 + \frac{\Psi^2 M_1 M_2}{\Psi M_1 + \left(1 - \Psi\right) M_2} \tag{8}$$

Where, $\psi 3 = 1 - \phi_1 = \phi_2$.

M(A) and M(B) indicate the properties obtained from Veenstra model A and model B respectively. Here $M_1$ is taken as the modulus of matrix phase which in this case is EVA and $M_2$ is the modulus of dispersed phase, that is TPU.[25]

These models have been applied by several researchers to characterize the compatibility of various blend systems. Furthermore, although the parallel and series models are valid only for simple and idealized structures, they are often used as limiting models irrespective of morphology. In Figure 4, the experimental values of 100% moduli of EVA/TPU blends are plotted as a function of wt % of EVA and compared with the theoretical values calculated using parallel, series, Veenstra A and B models. It is found that the experimental values of modulus lie very close to the Veenstra B model except ET 50. It indicates that for ET 80, ET 70 and ET 60 blends TPU particles are almost evenly dispersed in the EVA matrix which is further also supported by SEM images of the samples.

**Tension set and stress relaxation:** The results of tension set test are given in table 3. It clearly shows that pure EVA has somewhat better set property than TPU. The tension set % for the EVA/TPU blends gradually increase with increasing TPU content in the blends. During this tension set test the change of stress value after each 30 sec interval were also noted as the decay of stress upto 10 min. It is a well-known fact that when a constant strain is applied to a rubber sample, the force required for maintaining the strain decreases with time and this behaviour is called 'stress relaxation'. It has been found from table 3 and figure 5 that the decay of stress (stress relaxation) is relatively lower for EVA and EVA rich blends. As more TPU is added in the blend, the decay of stress slightly increases.

**Morphology:** The mechanical properties of the blends are strongly dependent on their morphology (i.e. size, shape and distribution of the blend components) and therefore, the control of morphology plays a significant role to modulate the ultimate performance properties of the blend system.[26, 27] Factors governing the morphology are composition, interfacial tension, processing conditions and rheological properties of the components. Here THF solvent has been used to preferentially remove TPU, the minor component of the blend and the black domains indicate the positions of extracted TPU phase. Figure 6 shows the morphology of ET 80, ET 70, ET 60, and ET 50 blends. SEM photomicrographs reveal that all the blends, except ET 50, have two phase morphology. The morphological observation correlates well with the mechanical behavior of the EVA/TPU blends.) Figure 6a shows that in ET 80 the fine, spherical TPU particles are almost homogeneously distributed in continuous EVA matrices leading to good mechanical properties due to better interfacial adhesion and effective stress transfer (from matrix to dispersed phase. The size of dispersed TPU particles becomes coarser in the 70/30 EVA/TPU blend than 80/20 counterpart. Similarly in 60/40 blend the particle size of TPU has been found to be even bigger. The number average ($D_n$) and weight average ($D_w$) domain diameter values of the blends were calculated for matrix dispersed morphologies and the values are given in Table 4. With increasing TPU content from 20% to 40%, the number average diameter of the dispersed TPU domains increases from 2.95 to 7.15 $\mu$m. In case of 50/50 EVA/TPU blend, both TPU and EVA exist as continuous phase and generate a co-continuous morphology. Fig. 6b and 6c indicate the presence of larger TPU domain that can be easily removed by THF, whereas in case

of ET 80/20 blend extraction of finer TPU particles are somewhat restricted indicating better compatibility and interfacial adhesion. Such composition dependent morphology is related to the mechanical behavior of the blend system and thus ET 80 with finer domain size provides the best combination of physico-mechanical properties than the other blends with coarser domain size.

**Differential scanning calorimetric (DSC) studies:** Figure 7 shows the second heating curve for different blends. TPU shows a glass transition at -37.7 °C whereas glass transition of EVA is observed at -27.7 °C ( Tg). However, for all the EVA/TPU blends a single broad peak appears in the DSC heating curve in between the Tg of pure polymers. On addition of TPU with EVA, there is a distinct reduction in Tg from -29.12 °C to -32.98 °C as the TPU content in the blend increases from 20 wt% to 50 wt %. Since there is very small difference between the Tg of neat EVA and neat TPU, a single Tg does not indicate that EVA and TPU are completely miscible in this composition range. Rather it can be said that there is technological compatibility to some extent between EVA and TPU. Tg of the various blend system have been also calculated theoretically using the Fox equation. The equation is mentioned below:

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{9}$$

It is also observed that there is not much difference between the experimental Tg (from DSC) and the Tg calculated using Fox equation (table 5). Pure EVA shows a melting endotherm ($T_m$) at around 78 °C and there is a slight depression of melting point of EVA component in all the blends. However, for different blend compositions melting temperature of the EVA does not change significantly with variation in TPU content. DSC cooling curves of the samples are shown in figure 8. It has been observed that neat EVA exhibits a sharp crystallization peak ( $T_c$ ) at around 54.9 °C. Although the crystallization peak temperature corresponding to EVA, do not change much in case of the EVA/TPU blends, the crystallization peak hight (exothermic peak) corresponding to EVA content gradually decreases with increasing TPU content. Table 4 represents the detailed DSC data of various samples.

**Thermogravimetric analysis (TGA):** TGA and DTG plots of EVA, TPU and their blends are shown in figure 9 and figure 10 respectively and the quantitative data are summerized in table 5. Neat EVA shows a two step degradation; the first decomposition at around 268 °C involves the evolution of acetic acid( along with) and the second decomposition which starts at about 379 °C corresponds to the transvinylene formation associated with main chain-scission.[28] TPU thermal degradation is also a two stage process. The first step involves the degradation of hard segments (decomposition of urethane group) and the latter is associated with the greatest rate of mass loss of soft segment.[29] In case of EVA thermal degradation starts at about 268°C and about 20.36% weight loss occurs at around 377 °C while for TPU thermal decomposition starts only at 258 °C and % weight loss in the first step is 40.19% upto 380 °C.T he result of thermogravimetric analysis show that EVA is thermally somewhat more stable than TPU and the thermal stability of all the blends lie in between. From the TGA curve it is observed that the 50% weight loss temperature for TPU is 392 °C whereas for EVA it is rather higher, 457 °C. But in case of ET 80, ET 70 and ET 60, the 50 % decomposition temperature has been shifted to 448 °, 443 °and 422 °C indicating an increase by 56 ° C, 51 ° C and 30 °C respectively. For the 50/50 EVA/TPU blend 50 % decomposition temperature is only 414 °C which is significantly higher than that of pure TPU. In case of all the blends with increasing TPU the 50 % decomposition temperature reduce and the maximum degradation temperature of the blends are higher indicating better thermal stability of the blends than that of TPU.

Similarly from the DTG plots (figure 10) it is clearly observed that EVA exhibits two major peaks at 353.4 and 470.2 °C due to deacetylation and main chain degradation respectively. TPU exhibits a first minor peak at 377.6 °C and a second major peak at 409.4 °C associated with its hard and soft segment decomposition respectively. In case ET 70, ET 60 and ET 50 initial weight loss occur in two minor steps at about 350 °C and 450 °C. The first DTG peak arises mainly due to deacetylation and the second one is probably related to the dissociation of TPU into diisocyanate and polyols. However for all the blends maximum rate of decomposition takes place at around 468 °C due to main chain decomposition of EVA component. It is also to be noted that the rate of weight loss in the main degradation region gradually decreases with increasing TPU content in the blends.

**Dynamic Mechanical Analysis:**  Figure 11 represents the variation of storage modulus (E') as a function of temperature in the range -100 °C to 80 °C. Initially the storage modulus of TPU is higher than EVA and all the EVA/TPU blends in the low temperature region. The E' value of the blends gradually goes up with addition of TPU. Then TPU shows a sharp and drastic fall in E' value at around -48.5 °C due to its glass to rubber transition. However in case of EVA, E' value starts to decrease at rather higher temperature -37.8 °C and also the storage modulus drops at comparatively slower rate than that of TPU. It is clearly seen that in this glass transition region E' value of TPU and TPU rich blends become relatively lower than EVA and EVA rich blends. Thus at -20 °C the E' values of ET 80, ET 70, ET 60 and ET 50 are 399.1, 352.1, 330.5 and 297.1 MPa respectively. However at about -9 °C a cross-over region is observed and thereafter again the storage modulus of EVA and EVA rich blends goes down. At ambient temperate TPU show much higher storage modulus than EVA and the E′ value of all the blends lie in between the pure components. The influences of temperature on the loss modulus of the samples are shown in figure 12. From table 7 it is observed that TPU exhibits a prominent loss peak at about -40.2 °C while for EVA the relaxation corresponding to the loss modulus occurs at -26.2 °C. With increasing TPU content in the blend the maximum loss peak gradually shift to lower temperature. While ET 80 shows the loss peak at -28.8 °C where the shift is marginal, the other blends show significant shifts to lower temperature as compared to ET 80. The corresponding peaks for ET 70, ET 60, and ET 50 are at -33.3 °C, -34.2 °C and -35.3 °C, respectively. It is also to be noted that the loss peak height takes intermediate values of the two pure components. Figure 13 illustrates the effect of temperature on tan δ of the neat polymers and their blends. In the above temperature region TPU shows a single sharp loss tangent peak at -29°C which is attributed to the glass to rubber transition of polyester based soft segments of TPU.[20] EVA exhibits one major peak at -14.6 °C corresponding to the crystal unconstrained glass-rubber relaxation. This tan δ peak can be assigned as the Tg of EVA and it is higher than the Tg obtained from DSC measurement which is shown by other researchers also. Another tiny peak at around 10°C associates this glass transition which is probably related to the segmental motion in amorphous zone and correspond to the crystal constrained glass rubber transition.[30] This α transition peak is mainly prominent in ET 80 and ET 70 due to the presence of higher EVA content. However the Tg values obtained from E" versus temperature plots are always higher

than those obtained from tan δ values.[9] $T_g$ of the all the blends is shifted to lower temperature by a few degrees from the $T_g$ of EVA and a single broad tan δ peak appears in between the tan δ peak of neat EVA and neat TPU. However, it is to be noted that the glass transition temperature (Tg) of pure TPU and pure EVA lie very close. Hence, in this case a single tan δ peak does not indicate miscibility in true sense. It can be said that there is technological compatibility to some extent between EVA and TPU. It is also seen that with increasing TPU content in the blend there is a shifting of relaxation peak towards the TPU region.

**Oil swelling study:** Oil resistance property of the blends is measured by immersing the samples in IRM 903 oil for 7 days at room temperature. The results of oil swell test are shown in figure 14. With increasing TPU content oil swell of the blends significantly reduces due to excellent oil resistance property of TPU. Neat EVA shows almost 45% swelling after 7 days. However as the amount of TPU increases from 20 wt % to 50 wt % the oil swell changes from 40% to 17.6% only. It is clearly seen that incorporation of even small amount of TPU causes a great improvement on oil resistance property of EVA.

**Conclusions:** The mechanical properties of the blends based on EVA and TPU are found to be strongly influenced by the blend ratio and the morphology of the blend system. The SEM observation revealed primarily a two phase morphology and the size of dispersed TPU particles increase with increasing TPU content. However, a 50/50 EVA/TPU blend generates co-continuous morphology. 80/20 EVA/TPU blend showed the optimum tensile strength and elongation at break may be due to finer dispersion of TPU particles in continuous EVA matrix. With further addition of TPU, tensile strength and elongation at break gradually reduce but modulus and hardness continuously improve. The tension set % and the decay of stress at constant strain are lower for EVA rich blends. The experimental modulus have been compared with relevant theoretical models and it was observed that except the 50/50 blend the experimental data fits the best with the Veenstra B model suggesting the droplet matrix morphology for rest of the blends which has also been confirmed through morphological analysis. All the blends exhibit single Tg in between the Tg of neat polymers as evidenced from DSC study. With addition of TPU, Tg of the blends gradually shift towards the Tg of TPU indicating that there is technological compatibility to some extent between the blend

components. Similar trend was observed from the loss modulus peak and the loss peak height also takes intermediate values between the pure components. Blends with higher TPU content show higher storage modulus as observed from DMA study throughout the entire temperature range excepting the glass transition region. Oil resistance property of the blend system significantly improves upon addition of TPU.

## Acknowledgement:

## References:

1.   J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.*, 1981, **21**, 985-996.
2.   F. B. D. Utracki L. A., ed., *Polymer alloys and blends-Thermodynamics and rheology.*, Hanser, Munich, 1990.
3.   I. Ray and D. Khastgir, *Polymer*, 1993, **34**, 2030-2037.
4.   M. Faker, M. K. Razavi Aghjeh, M. Ghaffari and S. A. Seyyedi, *Eur. Polym. J.*, 2008, **44**, 1834-1842.
5.   B. John, K. T. Varughese, Z. Oommen, P. Pötschke and S. Thomas, *J. Appl. Polym. Sci.*, 2003, **87**, 2083-2099.
6.   S. Thomas and A. George, *Eur. Polym. J.*, 1992, **28**, 1451-1458.
7.   D. G. Dikobe, *eXPRESS Polym. Lett.*, 2009, **3**, 190-199.
8.   A. T. Koshy, B. Kuriakose, S. Thomas and S. Varghese, *Polymer*, 1993, **34**, 3428-3436.
9.   H. Varghese, S. S. Bhagawan, S. S. Rao and S. Thomas, *Eur. Polym. J.*, 1995, **31**, 957-967.
10.  P. Kumari, C. K. Radhakrishnan, S. George and G. Unnikrishnan, *J. Polym. Res.*, 2007, **15**, 97-106.
11.  M. Maiti, R. V. Jasra, S. K. Kusum and T. K. Chaki, *Indus. Eng. Chem. Res.*, 2012, **51**, 10607-10612.
12.  K. Naskar, S. Mohanty and G. B. Nando, *J. Appl. Polym. Sci.*, 2007, **104**, 2839-2848.
13.  L. N. R. Holden G., Schroeders H. E., ed., *Thermoplastic elastomer: A comprehensive review*, Hanser, Munich, 1987.
14.  Q.-W. Lu and C. W. Macosko, *Polymer*, 2004, **45**, 1981-1991.
15.  K. Bagdi, *eXPRESS Polym. Lett.*, 2011, **5**, 417-427.
16.  Y. Kim, W.-J. Cho and C.-S. Ha, *J. Appl. Polym. Sci.*, 1999, **71**, 415-422.
17.  F. Feng and L. Ye, *J. Appl. Polym. Sci.*, 2011, **119**, 2778-2783.
18.  M. Maity, C. K. Das, K. N. Pandey and G. N. Mathur, *Int. J. Polym. Mater.*, 2000, **45**, 123-133.
19.  P. Poomalai and Siddaramaiah, *J. Macromol. Sci., Part A*, 2005, **42**, 1399-1407.
20.  R. N. Santra, T. K. Chaki, S. Roy and G. B. Nando, *Angew. Makromol. Chem*, 1993, **213**, 7-13.
21.  X. Wang and X. Luo, *Eur. Polym. J.*, 2004, **40**, 2391-2399.
22.  K. Palanivelu, P. Sivaraman and M. Dasaratha Reddy, *Polym. Test.*, 2002, **21**, 345-351.
23.  R. C. Willemse, A. Speijer, A. E. Langeraar and A. Posthuma de Boer, *Polymer*, 1999, **40**, 6645-6650.
24.  O. Martin and L. Avérous, *Polymer*, 2001, **42**, 6209-6219.

25.    H. Veenstra, P. C. J. Verkooijen, B. J. J. van Lent, J. van Dam, A. P. de Boer and A. P. H. J. Nijhof, *Polymer*, 2000, **41**, 1817-1826.

26.    M. Baer, *J. Appl. Polym. Sci.*, 1972, **16**, 1109-1123.

27.    L. A. Utracki and Z. H. Shi, *Polym. Eng. Sci.*, 1992, **32**, 1824-1833.

28.    S. K. Dutta, A. K. Bhowmick, P. G. Mukunda and T. K. Chaki, *Polym. Degrad. Stabil.*, 1995, **50**, 75-82.

29.    M. A. Hood, B. Wang, J. M. Sands, J. J. La Scala, F. L. Beyer and C. Y. Li, *Polymer*, 2010, **51**, 2191-2198.

30.    B. G. Soares, F. C. F. Alves, M. G. Oliveira and A. C. F. Moreira, *J. Appl. Polym. Sci.*, 2002, **86**, 239-249.

**Figure captions:**

*Fig 1. Variation of tensile strength with TPU content*

*Fig 2. Stress-strain curve of EVA and EVA/TPU blends*

*Fig 3. Modulus of the blends as a function of TPU content*

*Fig 4. Experimental and theoretical Modulus at 100% strain for various blends as a function of EVA content*

*Fig 5. Stress relaxation curves of neat polymers and different blends in tension mode*

*Fig 6. SEM photomicrographs of the THF extracted fractured surfaces of (a) ET 80 (b) ET 70 (c) ET60 and (d) ET50*

*Fig7. DSC second heating curve for neat polymers and their*

*Fig 8. DSC cooling curve for neat polymers and their blends*

*Fig 9. TGA thermograms of different blends*

*Fig 10. DTG thermograms of various blends*

*Fig 11.Variation of storage modulus with temperature for different blends*

*Fig 12. loss modulus versus temperature curve for various blends*
*Fig 13. tan δ versus temperature plots*

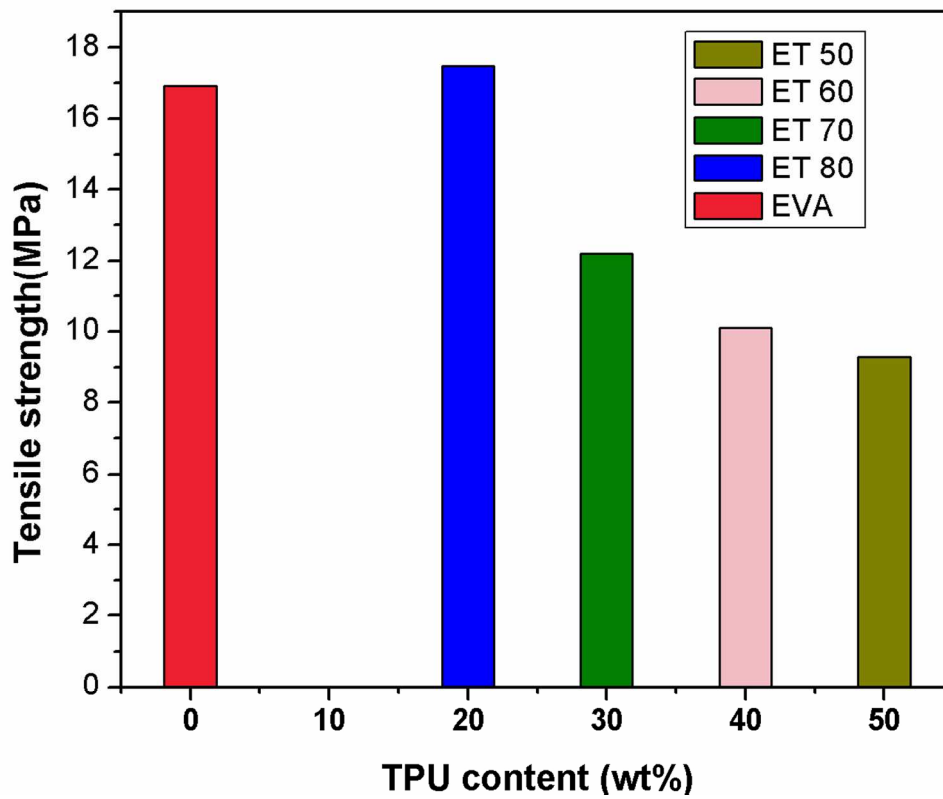*Fig 14. Oil swelling of different EVA/TPU blends*

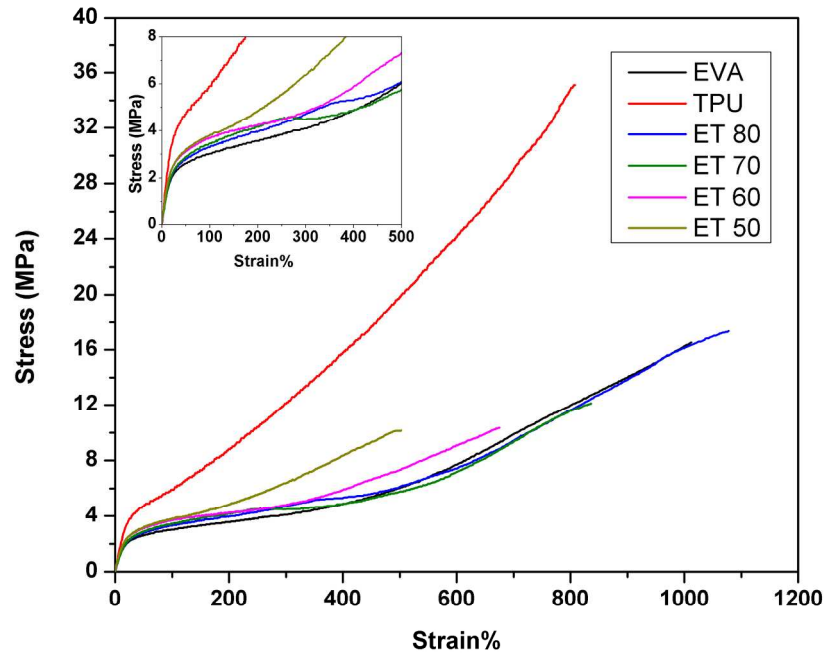Fig 1. Variation of tensile strength with TPU content
203x168mm (300 x 300 DPI)

Fig 2. Stress-strain curve of EVA and EVA/TPU blends
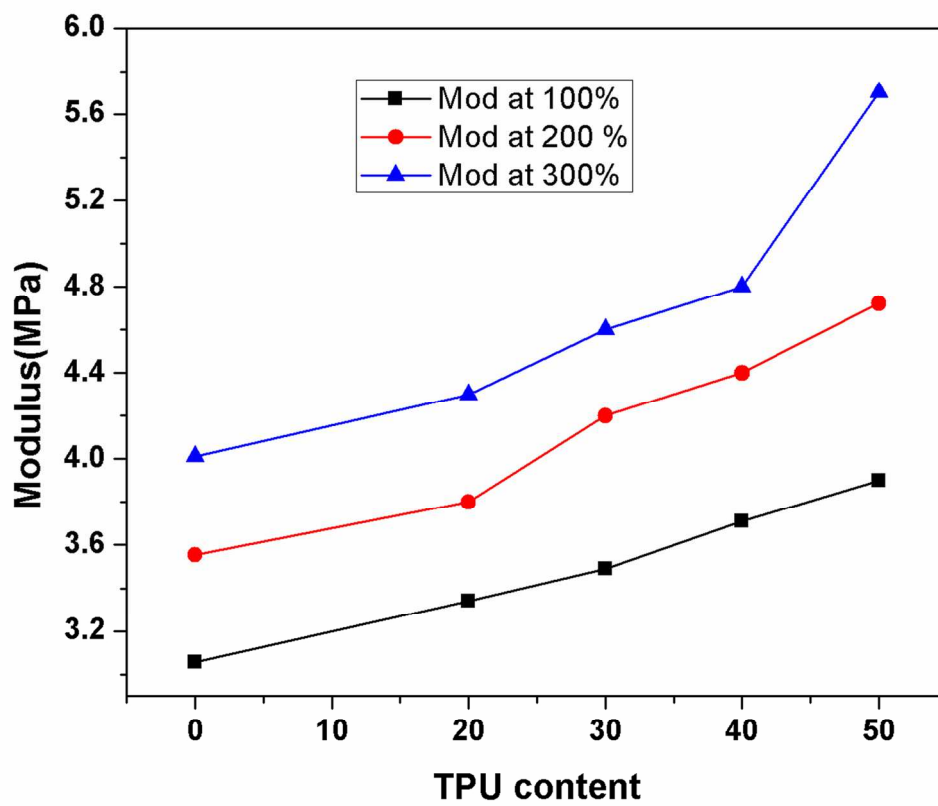215x166mm (300 x 300 DPI)

Fig 3. Modulus of the blends as a function of TPU content
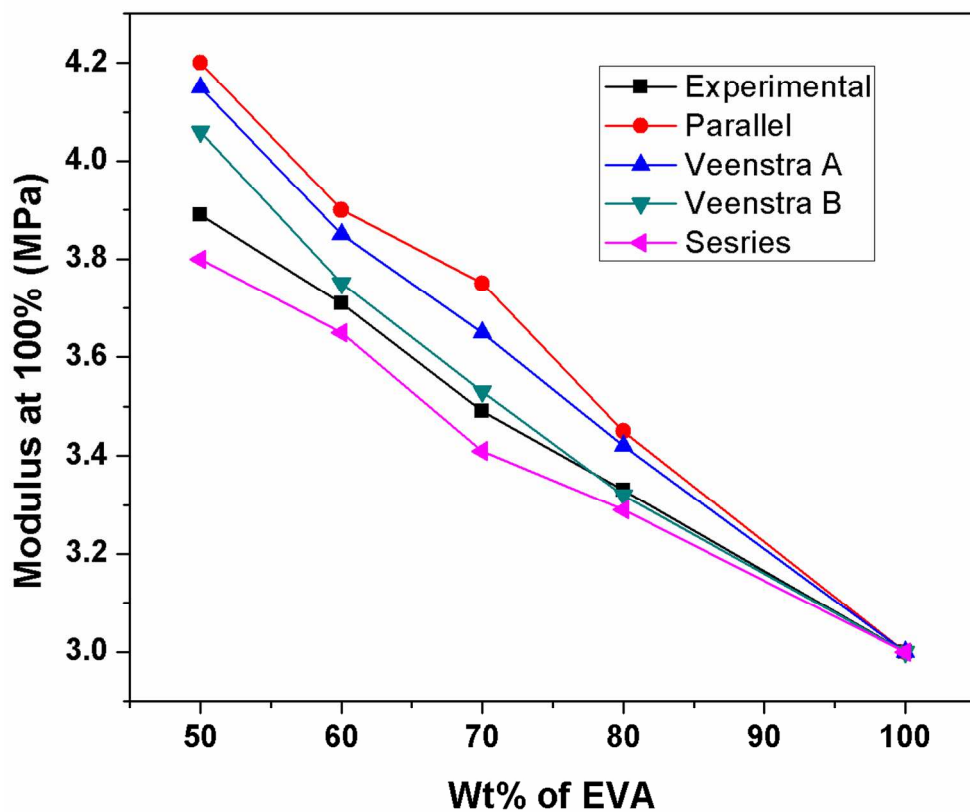171x145mm (300 x 300 DPI)

Fig 4. Experimental and theoretical Modulus at 100% strain for various blends as a function of EVA content
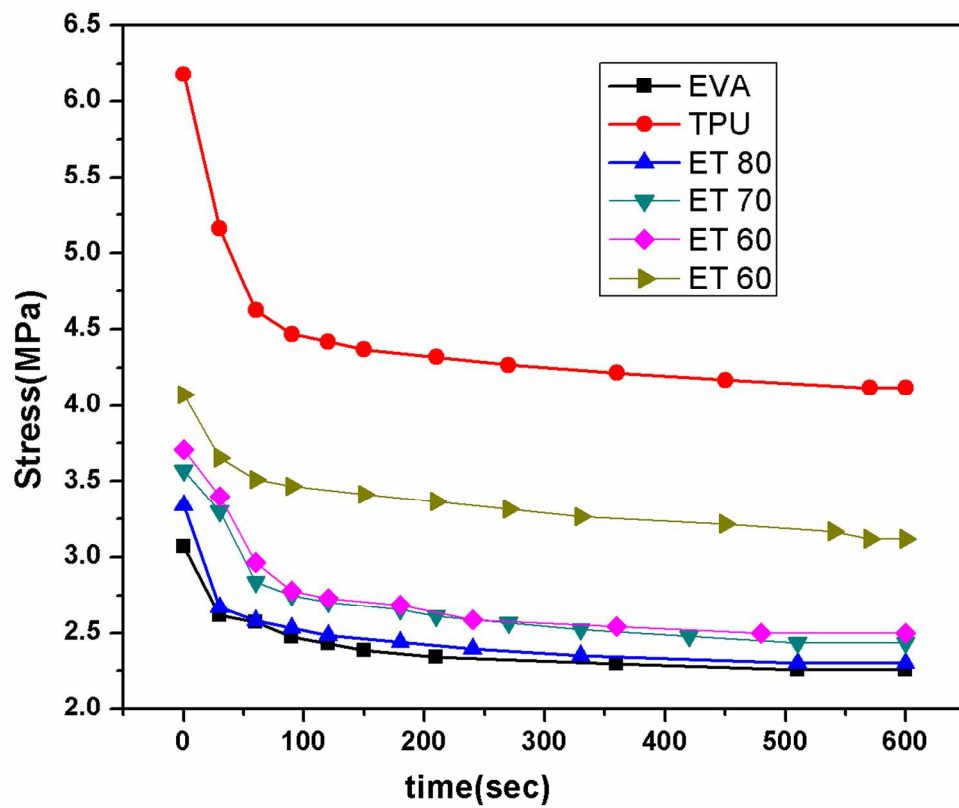203x169mm (300 x 300 DPI)

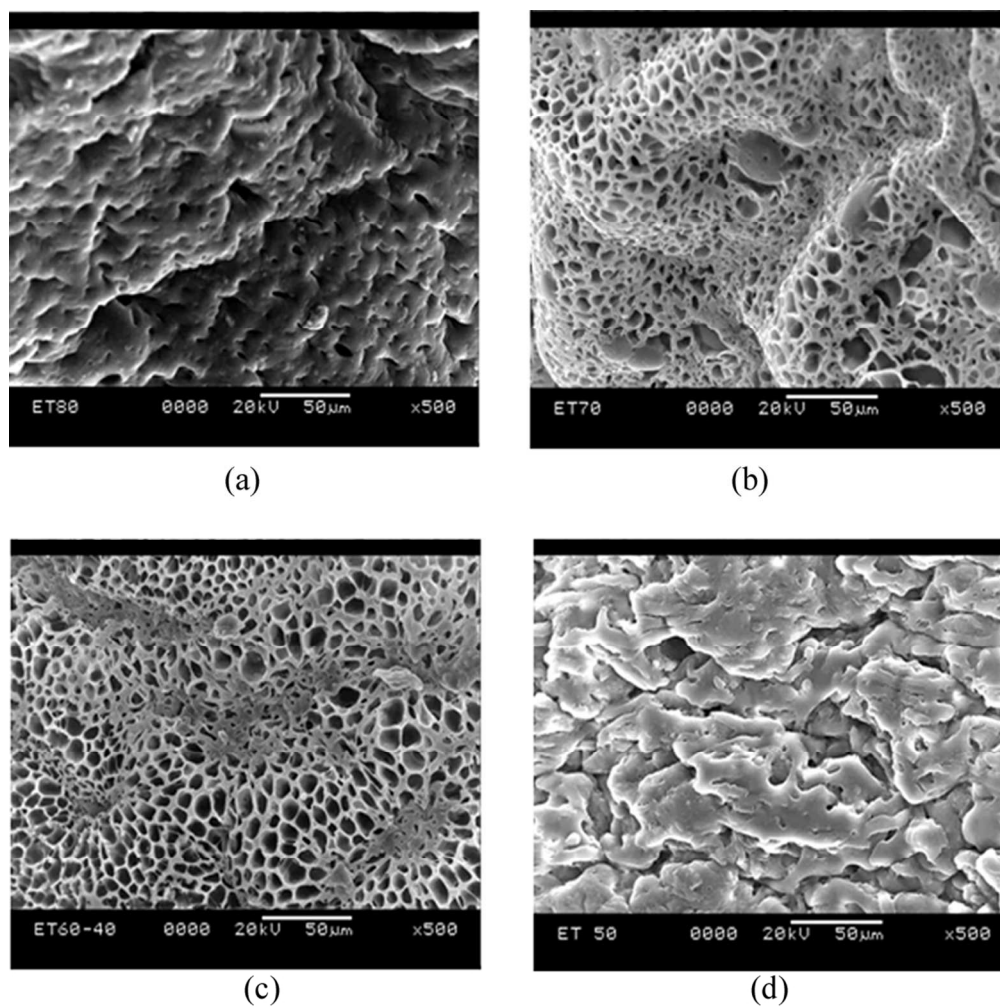Fig 5. Stress relaxation curves of neat polymers and different blends in tension mode
203x171mm (300 x 300 DPI)

Fig 6. SEM photomicrographs of the THF extracted fractured surfaces of (a) ET 80 (b) ET 70 (c) ET60 and (d) ET50
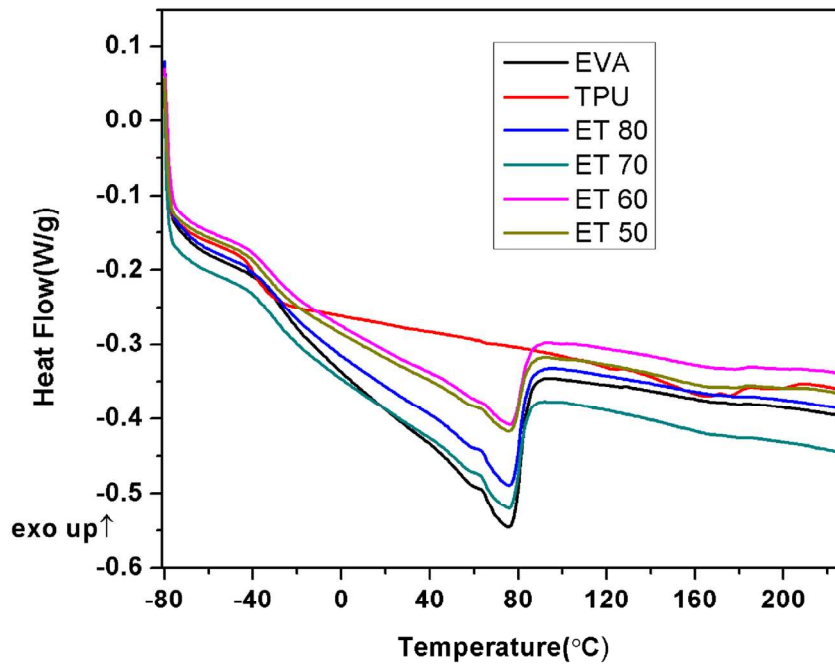151x160mm (200 x 200 DPI)

Fig7. DSC second heating curve for neat polymers and their blends
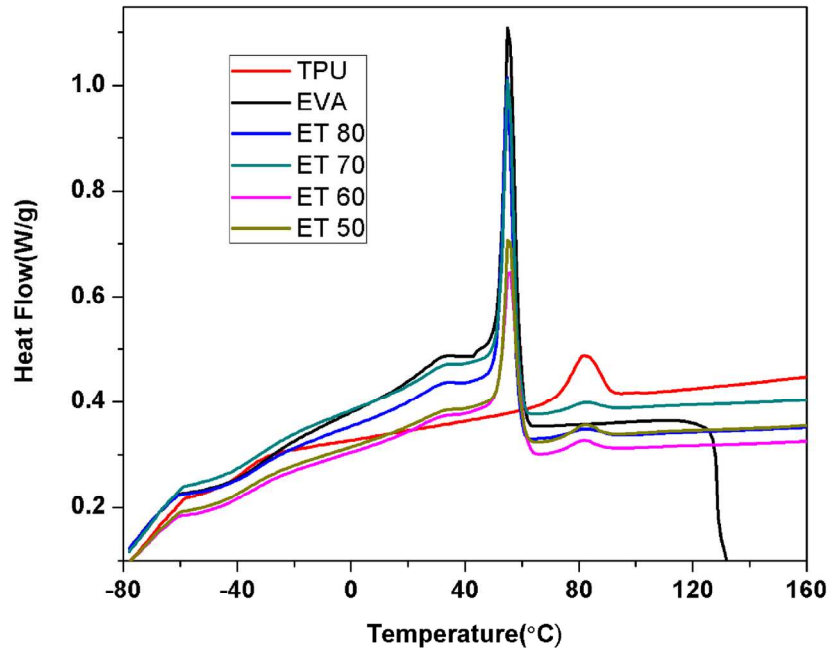79x61mm (600 x 600 DPI)

Fig 8. DSC cooling curve for neat polymers and their blends
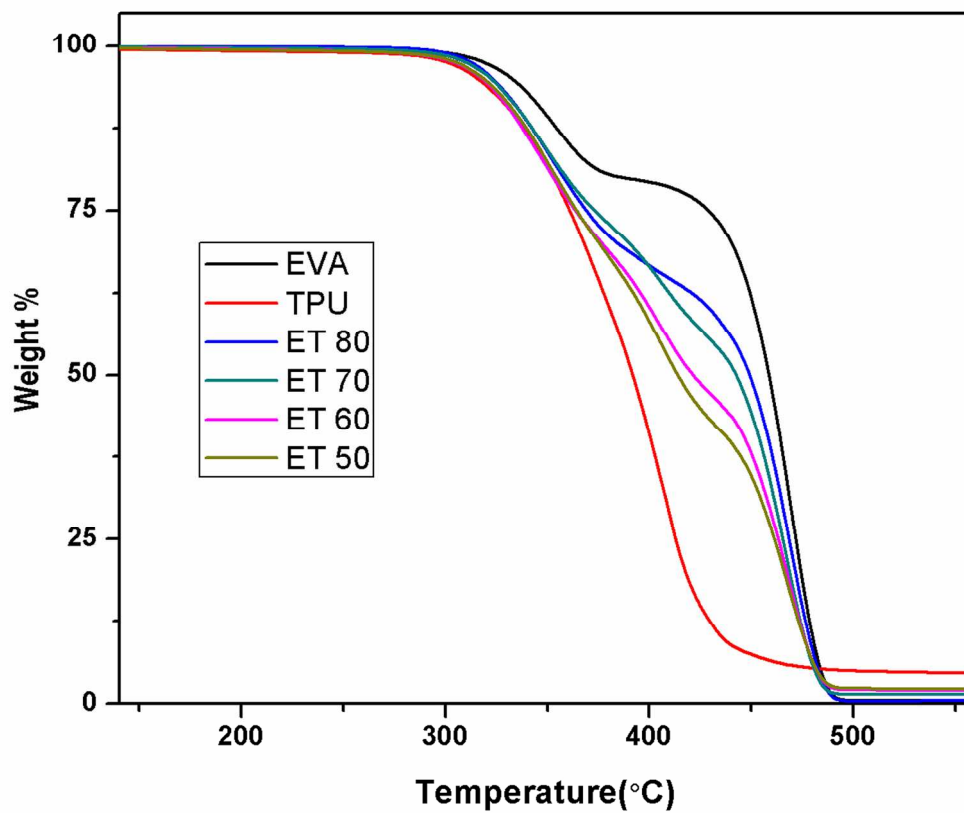78x60mm (600 x 600 DPI)

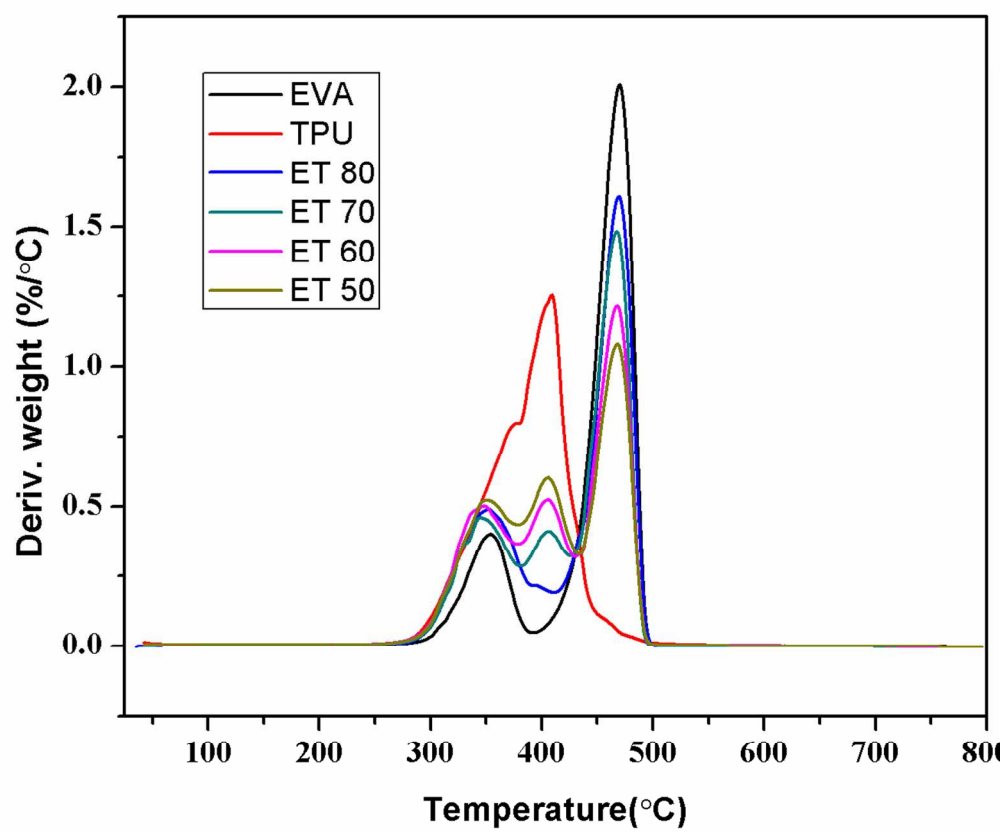Fig 9. TGA thermograms of different blends
203x178mm (300 x 300 DPI)

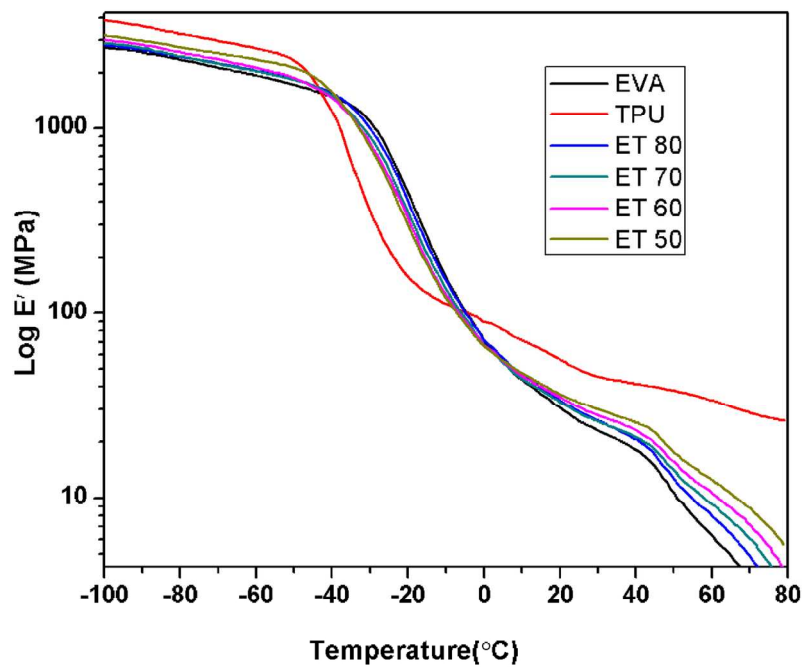Fig 10. DTG thermograms of various blends
176x152mm (300 x 300 DPI)

Fig 11.Variation of storage modulus with temperature for different blends
78x60mm (600 x 600 DPI)
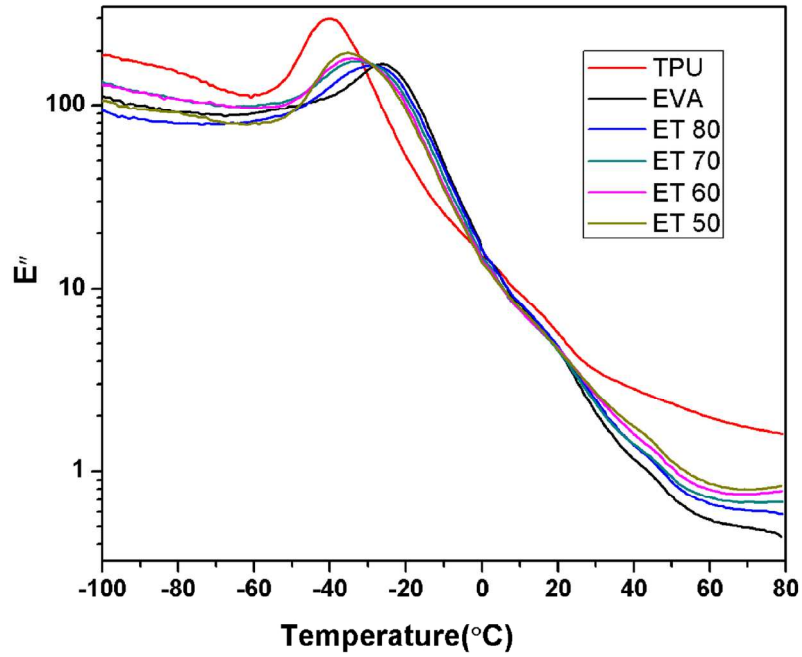
Fig 12. loss modulus versus temperature curve for various blends
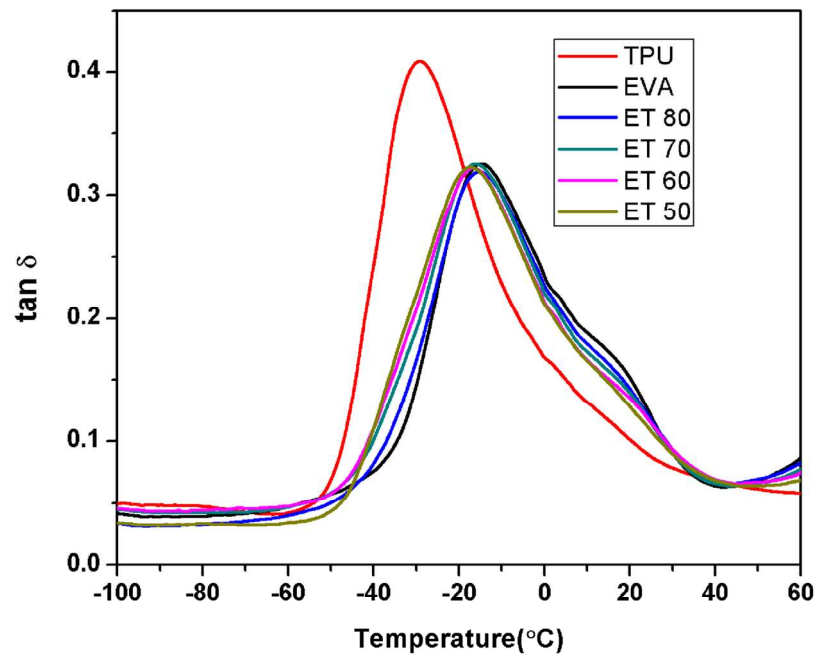
78x60mm (600 x 600 DPI)

Fig 13. tan δ versus temperature plots
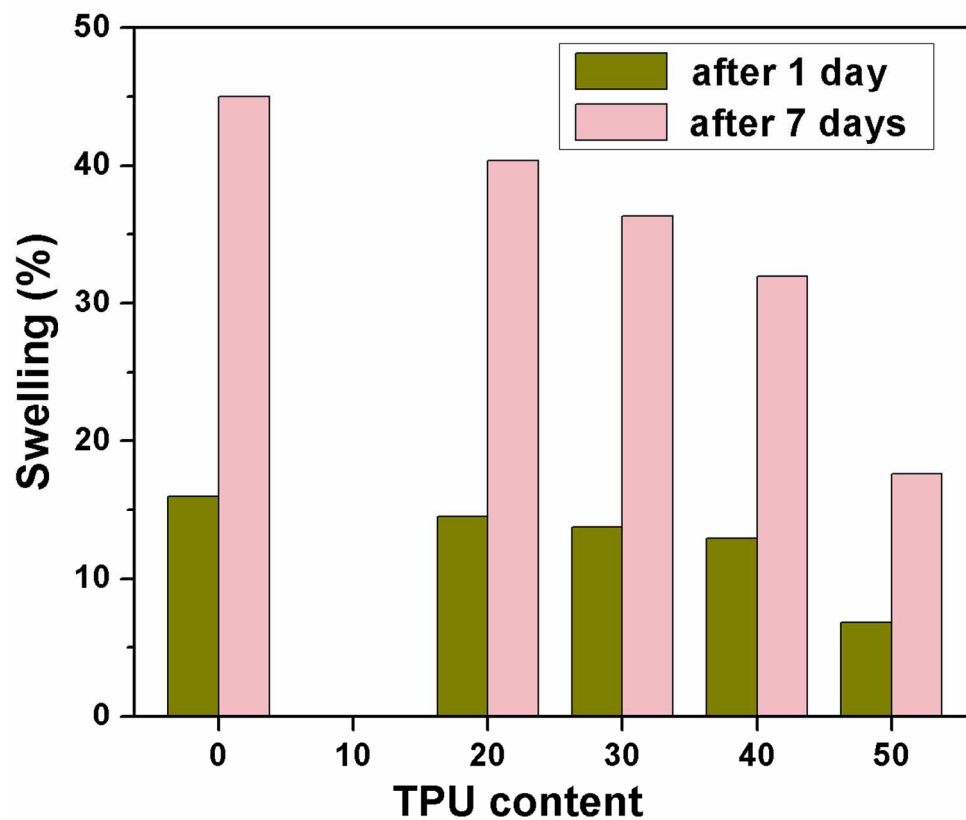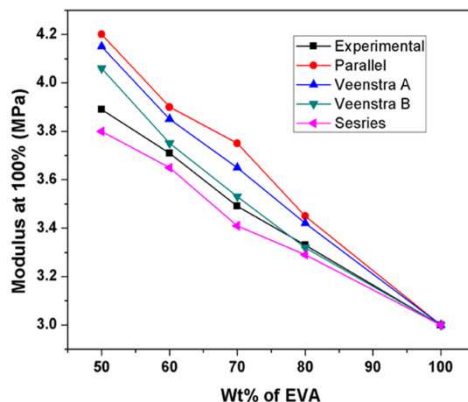78x60mm (600 x 600 DPI)

Fig 14. Oil swelling of different EVA/TPU blends
203x170mm (300 x 300 DPI)

## Table of contents



Novel blends based on EVA (Ethylene vinyl acetate) and TPU (Thermoplastic polyurethane) have been developed and characterized which may find potential application in cable and footwear industry.

**Table 1. Sample Designations with Composition**

| Sample designation | EVA (wt %) | TPU (wt %) |
|:---:|:---:|:---:|
| EVA | 100 | 0 |
| ET 80 | 80 | 20 |
| ET 70 | 70 | 30 |
| ET 60 | 60 | 40 |
| ET 50 | 50 | 50 |
| TPU | 0 | 100 |

**Table 2.  Mechanical Properties of the EVA/TPU blends**

| Sample designation | T.S.(MPa) | EB% | Mod at 100%(MPa) | Mod at 200%(MPa) | Mod at 300%(MPa) | Shore D Hardness |
|:---:|:---:|:---:|:---:|:---:|:---:|:---:|
| EVA | 16 .9±0.4 | 1061±48 | 3.0±0.3 | 3.5±0.3 | 4.0±0.3 | 25.0 (78) |
| ET 80 | 17.6±0.4 | 1067±45 | 3.3±0.2 | 3.9±0.3 | 4.3±0.2 | 25.2 (80) |
| ET 70 | 12.2±0.6 | 832±25 | 3.5±0.3 | 4.0±0.2 | 4.5±0.2 | 25.5 (80) |
| ET 60 | 10.4±0.7 | 722±37 | 3.7±0.3 | 4.1±0.3 | 4.6±0.3 | 29.5 (81) |
| ET 50 | 9.5±0.5 | 494±15 | 3.9±0.2 | 4.7±0.2 | 5.7±0.3 | 31.4 (83) |
| TPU | 35.1±1.1 | 805±32 | 5.9±0.3 | 8.7±0.2 | 11.5±0.4 | 33.5 (86) |

*The hardness values in the parenthesis indicate corresponding shore A hardness

**Table 3.  Tension set and stress relaxation of different blends**

| Sample designation | Initial stress (MPa) | Final stress (MPa) | Stress Relaxation (MPa) | Tension Set % |
|:---:|:---:|:---:|:---:|:---:|
| EVA | 3.11 | 2.29 | 0.82 | 16 |
| ET 80 | 3.34 | 2.30 | 1.04 | 17 |
| ET 70 | 3.57 | 2.43 | 1.14 | 18 |
| ET 60 | 3.71 | 2.50 | 1.21 | 20 |
| ET 50 | 4.07 | 2.74 | 1.33 | 20 |
| TPU | 6.10 | 4.12 | 1.98 | 21 |

**Table 4. Domain diameter of EVA/TPU blends**

| Sample designation | $D_n$ (µm) | $D_w$ (µm) | $\dfrac{D_w}{D_n}$ |
|---|---|---|---|
| ET 80 | 2.94 | 3.21 | 1.09 |
| ET 70 | 5.60 | 6.18 | 1.10 |
| ET 60 | 7.15 | 7.60 | 1.07 |

**Table 5. DSC data of various samples**

| Sample designation | $T_g$ ($^o$C) | Theoretical $T_g$ ($^o$C) | Melting temperature, $T_m$ ($^o$C) | Crystallization temperature, $T_C$ ($^o$C) | $\Delta Cp$ (J/g K) |
|---|---|---|---|---|---|
| EVA | -27.70 | -27.70 | 78.06 | 54.91 | 0.787 |
| ET 80 | -29.12 | -29.76 | 77.03 | 55.01 | 0.910 |
| ET 70 | -31.02 | -30.78 | 77.64 | 55.03 | 0.875 |
| ET 60 | -31.83 | -31.80 | 77.58 | 55.89 | 0.849 |
| ET 50 | -32.98 | -32.81 | 77.17 | 56.04 | 0.828 |
| TPU | -37.76 | -37.76 | 166.6 | 82.11 | 0.260 |

**Table 6. TGA and DTG data of neat polymers and their blends**

| Sample designation | Initial decomposition temperature, $T_i$ (°C) | Temperature corresponding to 5% decomposition $T_{95}$ (°C) | Temperature corresponding to 50% decomposition $T_{50}$ (°C) | Maximum decomposition temperature, $T_{max}$ (°C) |
|---|---|---|---|---|
| EVA | 267 | 332 | 457 | 470 |
| ET 80 | 262 | 323 | 447 | 467 |
| ET 70 | 262 | 322 | 443 | 466 |
| ET 60 | 260 | 318 | 422 | 466 |
| ET 50 | 258 | 317 | 414 | 465 |
| TPU | 258 | 315 | 392 | 409 |

**Table 7. Dynamic mechanical analysis of different blends**

| Sample designation | tan δ peak (°C) | Loss modulus peak (°C) | Storage modulus at -80°C (MPa) | Storage modulus at 30°C (MPa) |
|---|---|---|---|---|
| EVA | -14.61 | -26.2 | 2350.12 | 20.67 |
| ET 80 | -15.80 | -28.8 | 2450.23 | 23.39 |
| ET 70 | -16.68 | -33.3 | 2465.05 | 23.65 |
| ET 60 | -16.95 | -34.2 | 2584.69 | 25.68 |
| ET 50 | -17.45 | -35.3 | 2759.41 | 27.78 |
| TPU | -29.02 | -40.2 | 3251.69 | 43.29 |