A Recent blend of thermoplastic polyurethane (TPU)

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Abstract. Polymer blending is a well-developed manufacturing process with features of efficient production, ease of processing and good controllability. It can effectively modify and adjust the properties of polymer in order to have greater mechanical, thermal and physical properties, and thus has been commonly used to make functional polymer materials. However, the differences in polarity as well as poor interfacial between each polymer in the blend will promote the difference in polarity between the immiscible and incompatible polymers, and then the blends did not succeed as a good blend. The blending of thermoplastic polyurethane (TPU) with other polymer has been widely study with focus on the improvement of mechanical properties, wear resistance, thermal stability, toughness and other related properties. This review only focuses on the latest studies on blending TPU with other polymer, just in the range of 3 years from 2017 to 2019.

1 Introduction

The polymer blend method using commercial existing polymers is generally believed to be the most effective way to develop new with high flexibility and versatility, compared with the synthesis of a new functional polymer, based on the practical and economical viewpoints. The blending of TPU with other polymers has been widely studied with different focus. It can effectively modify and adjust properties of the polymer in order to have greater mechanical, thermal and physical properties, as well as used to make functional materials.

Thermoplastic polyurethane is a thermoplastic elastomer (TPE) that consists of micro-phase separated blocks of amorphous and crystalline segments in the molecules. Pondong [1] reported that, the soft segments of TPU consist of either polyether or polyester long-chain macro molecules. The hard segments are combinations of isocyanate-based aromatic or aliphatic structures with short-chained diols. Typically, the crystallization in the hard segments of TPU acts as physical crosslinking and reinforcement that promotes excellent performance properties, while the soft segments contribute to high flexibility of the TPU. The first commercial thermoplastic polyurethane was manufactured by Bayer-Farbenfabriken and B.F. Goodrich. The blending of TPU with other polymer has been widely study with focus on the improvement of mechanical properties, wear resistance, thermal stability, toughness and other related properties.

This review only focuses on the latest studies on blending TPU with other polymer, just in the range of 3 years which only about TPU with nine polymers.

2 TPU and its blend

2.1 Natural rubber

Previously, the author has started the research on thermoplastic polyurethane and natural rubber (TPU/NR) blends [2], which are investigated with two different mixing temperature; 180°C and 190°C. With the increasing of NR, tensile strength also decreased because this will leading to the formation of a softer blend which exhibits lower tensile strength. Though the blends of TPU/NR are believed to be compatible, further improvement with respect to miscibility can be achieved by incorporating LNR to the blend. The tensile properties of the blend are determined by the homogeneity of mixing; the properties are better with higher homogeneity. The tensile strength decreased with temperature 190°C. In blending two or more polymer, too high a processing temperature also causes the materials (especially the NR) to degrade from oxidation. The higher temperatures are undesirable due to the possibility of oxidation of NR. For the swelling test

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in toluene, the equilibrium swelling degree of TPU and its blend increase with increasing of NR (Fig. 1). Swelling degree reduces with the increase of network because of the difficulty for solvent to diffuse into the gap between rubber molecules.

![Graph of Tensile Strength vs Weight % of TPU at 180°C and 190°C](image)

**Fig. 1.** Variation of tensile strength with weight % of TPU at 180°C and 190°C [2].

### 2.2 Acrylonitrile-butadienestyrene (ABS)

De Leon [3] was prepared a novel material suitable for additive manufacturing using ABS and. They decided to set printing temperature to 230°C which led to printable object for all material used ABS and TPU. From FTIR result, it can be observed that TPU characteristic peaks increase proportionally with the TPU content in the blends. This is the first indication of good compatibility between ABS and TPU, since cannot identify separated regions of ABS and TPU. The blends also present a homogeneous distribution of ABS and TPU. For the mechanical properties; it can be observed that Young’s modulus and yield strength, decreasing gradually when TPU content increased. Elongation at break was decreasing slightly at 10wt% of TPU, but then increasing gradually for higher TPU content. It was shown that blends containing 10-20wt% TPU led to enhanced adhesion between layers without loss in yield strength, while 30wt% TPU led to good adhesion between layers. SEM of the fracture surface has showed the roughness of the surface rises when TPU content is increased (Fig. 2). The roughness seems confirm a better interaction, as well as compatibility of ABS and TPU is high.

![SEM images of TPU/ABS blends](image)

**Fig. 2.** TPU/ABS blends in various composition (a) 10TPU (b) 20TPU (c) 30TPU [3]

### 2.3 Poly(ethylene oxide) (PEO)

Solid polymer electrolyte (SPE) membranes composed of TPU, PEO and lithium bis (trifluorimethane sulfonamide) (LiTfS) are prepared and investigated in Tao’s work [4]. The preparation step is represented in Fig. 3. With the increase of TPU amount in the blend polymer, the SPE membranes become more homogeneous.
Fig. 3. The preparation of TPU/PEO blends [4]

From FTIR spectra in Fig. 4, it can be easily found the characteristic absorption peak of TPU and PEO. The –CO stretching vibration of the blend SPEs were more pronounced with the increasing of TPU amount, however these stretching vibrations were slightly shifting to higher frequency compared to TPU. This may be attributed to the hydrogen bonding among the hard segments are weakened by the blending of PEO.

Fig. 4. FTIR spectra of TPU, PEO and TPU/PEO blend film [4]

From the DSC curves, a single $T_g$ showed in all the blend polymer, indicating that TPU and PEO were thermodynamically miscible. The tensile strength and elongation at break were enhanced with the increase of TPU content. The physical crosslinked network could be formed with the addition of TPU. When blending TPU to PEO, the hydrogen bond interaction can be formed by the –NH group in TPU chains and the –C-O-C- group in PEO chain. This interaction weakened the crystallinity and enhanced the mechanical strength of PEO effectively.

2.4 Poly(butylene terephthalate) PBT

The blends were prepared by melt blending technique. Hao [5] presented, PBT was immiscible with TPU and the crystallinity of PBT decreased with increasing of TPU content, as well as blending with TPU did not modify the crystal of PBT. But, an obvious improvement in toughness of PBT was achieved with addition of TPU.
Neat PBT was very rigid and brittle, with tensile strength around 52.8 MPa (Fig. 5). The blend sample has very drastically increased elongation and the elongation continuously increased with increasing of TPU. On the other hand, the tensile strength and modulus of the PBT/TPU blends decreased with increasing TPU content, as shown in Table 1. This attributed to the lower yield stress and tensile modulus of the TPU elastomer as compared to those of PBT. The presence of TPU elastomer domains in PBT, acting as stress concentrator, resulted in yielding at an overall stress lower than that of neat PBT.

Table 1. Mechanical properties of TPU and TPU/PBT blends [5]

| PBT/TPU (w/w) | Young’s modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Impact strength (kJ/m²) |
|---------------|----------------------|-----------------------|-------------------------|------------------------|
| 100/0         | 1340±37              | 52.8±5.6              | 15±0.8                  | 2.9±0.1                |
| 90/10         | 1227±30              | 46.7±3.0              | 27±1.5                  | 4.4±0.4                |
| 80/20         | 1066±19              | 42.3±2.6              | 159±5.1                 | 10.9±1.2               |
| 70/30         | 811±11               | 36.9±1.9              | 410±10.6                | 62.9±6.1               |

2.5 Polymethylmethacrylate (PMMA)

An increasing content of TPU in combination with PMMA leads to decreasing tensile strength and tensile modulus. These phenomena have been observed by Seeger [6]. The blends with 10 wt% TPU shows a four time higher elongation at break and the blends with 20 wt% TPU shows approximately eight times elongation at break compared to the neat PMMA as well as 5 wt% TPU blends. We can conclude that, bending PMMA and TPU resulted in an enhanced impact strength and elongation at break. This blend also changed the behavior, from brittle towards ductile break up.

Blending PMMA with TPU resulted in an enhanced impact strength and elasticity, although decreased the tensile properties. The enhancement on elasticity prevented it from cracking and from material removal. Unfortunately, adding more TPU led to a changed in opacity making it impossible to compare the scratch visibility.
The scratch behavior of the tested blend indentation depth of the scratch tip was recorded as in Fig. 6. Since the PMMA/TPU blend is a two phase system, the content of TPU plays an important role for the elasticity of the whole blend. With an increasing of the surface, an increasing of indentation depth can be measured.

### 2.6 Polylactic acid (PLA)

The TPU/PLA blends which have reported by Liu [7] could possess unique properties, including excellent shape memory performance. The viscosity properties of PLA/TPU blends were enhanced as the TPU content increased (range are between 5% to 20%), due to the interfacial interaction between PLA phase and TPU phase were strengthen with the hydrogen bond effect. The binary TPU/PLA show two transition peaks (refer to Fig. 7), with little shifts towards each other demonstrate the immiscibility between TPU and PLA.

![Fig. 6. The scratch behavior of the tested blend indentation depth [6](#)](image)

Consequently, TPU/PLA blends exhibited typical phase-separated morphologies controlled by the content of PLA. In the wake of the increment content of PLA, the phase morphology of PLA represented the following variation trend. Firstly; a droplet-like dispersion phase, followed by a continuous phase and finally, the matrix. Qu [8] also suggesting that PLA/TPU blends had much elasticity with increasing TPU content. But the compatibility between PLA and TPU became poor gradually. The phase morphology could provide useful information about the blends. The sea-island structure appeared with the introduction of TPU into PLA matrix. Also the roughness increased evidently, compared with in pure PLA. TPU dispersion phase was spherically dispersed in PLA matrix.

![Fig. 7. tan δ versus temperature for TPU/PLA blends [7](#)](image)

Others, the biodegradable pure PLA were exhibited degraded around 20 days. However it degrades almost 100% after 70 days. Jaso [9] reported that, pure TPU takes early and rapid degradation than PLA. By looking for the rate of degradation, the concentration of PLA in TPU/PLA blends are not depending on this behavior, but the degradation rate are rapidly after 20 days. PLA at higher percentage above 50% showed higher rate. After 60 days, PLA at 80% presented the highest degradation rate among other, which is 20%, 40% 50% and 60%, as refer to Fig. 8.
2.7 Polytetrafluoroethylene (PTFE)

An approach to produce PTFE in TPU has been developed by Huang [10]. PTFE is a white powder and under SEM examination, the shape of the PTFE particles was oval or rounded with the individual particles could be separated and had different diameter. The virgin PTFE powder did not have fibril morphology. The TPU/PTFE blends showed the amount of fibrils increased with PTFE concentration. Many of fibrils were entangled and intertwined, as can be seen in Fig. 9.

The formation of the fibrilled PTFE during melt compounding resulted from the low yield strength of PTFE at elevated temperature and plastic deformation. For the mechanical, all TPU/PTFE blends exhibited extremely high tensile strains. Also, because of PTFEs high modulus compared with that of neat TPU thus indicated that PTFE had reinforcing effect.

The rheological properties of the neat TPU showed liquid-like melt and a typical homopolymer-like terminal behavior at low frequency range. On the other hand, the blends presented a different rheological behavior. The liquid-like changed to solid-like. Huang [10] also investigate the cross section of the blends in foam form. They were found that neat TPU foam exhibited large, elliptical pores, which showed in Fig. 10. The foam exhibited better pore and more uniform structures. The pore size decreased and the density increased after PTFE fibrillation.
The presence of PTFE fibrils dramatically improved the foamed structure, resulting in pore density in comparison to neat TPU. The fibrillar of PTFE dramatically enhanced the hydrophobicity, by investigate the contact angle. These behaviors are necessary as competitive materials for shoe sole, food packaging and also automotive interiors.

2.8 Polypropylene (PP)

For the study of Ting & research team [11], they broadened their focus on previous PP to impact-resistant PP with TPU. However, the differences in polarity as well as poor interfacial compatibility between these modified PP and TPU provide PP/TPU blends with less comparable functionalities to that of pure PP or TPU. Both are immiscible and incompatible. 30% and 40% of TPU also intrigue the apparent presence of voids, which is evidence that the poor adhesion triggers TPU granule to detach from the PP matrix. The modified PP has improvement in impact resistance and reduced arrangement of crystallinity. The crystallization temperature of the blends is not dependent on the content of TPU, because TPU is non-crystalline polymer. PP has relatively higher thermal stability and helps postpone decomposition of urethane bonds of TPU hard segments and the high crystallization of PPs molecular chains have damaged the molecular chain of TPU’s soft segments. Although PP and TPU are incompatible, PP still distinctively improves the thermal stability of TPU. The thermal degradation data showed in Table 2 below, describe the three stage of degradation temperature for pure TPU and PP, also the blends from TPU10, TPU20, TPU30 and TPU40 [11].

| Pure TPU | Pure PP | TPU10/PP90 | TPU20/PP80 | TPU30/PP70 | TPU40/PP20 |
|----------|---------|------------|------------|------------|------------|
| 302.59   | -       | 338.77     | 314.28     | 321.08     | 329.05     |
| 395.29   | -       | 352.11     | 352.11     | 365.59     | 377.45     |
| -        | 441.09  | 456.94     | 459.62     | 467.06     | 470.56     |

2.9 Polycarbonate (PC)

Surface hydrophilicity and roughness of TPU/PC membranes have been investigate [12]. With addition of TPU content, the hydrophilicity decreased and membranes roughness decreased. SEM image showed the TPU/PC membranes exhibited the fully developed asymmetric membranes including of a dense skin layer, a porous sub-layer and macro-pores with typical sponge-like structure at the bottom. With increasing of TPU content, the sponge-like structure gradually increased at porous sub-layer of asymmetric structure as shown in Fig. 11 below.
TPU mechanism of pore formation differs since the TPU is a kind of hydrophobic polymer. The more TPU content, the more nascent pore formed in the sub layer. In general, hydrophobic polymer developed sponge-like structure through delayed phase separation. Lastly, the TPU blended in PC matrix improved the pure water flux to be used as membranes in wastewater treatment.

3.0 Conclusions

The blending of various polymers with TPU will provide more advantages in diverse aspects, especially in the desired property modification. The preferred blend properties will meet the requirement of some application such as biomaterial, medical, food packaging, furniture, shape memory foam, transportation, water treatment or others. However, the compatibility of certain polymers with TPU is very important to assess. Incompatible, immiscible and poor interface between them will cause the blends to have diminished in mechanical properties. The blending method also plays an important role. The mixing temperature very important to produce the best blends with good properties.

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