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Preparing thermoplastic polyurethane/thermoplastic starch with high mechanical and biodegradable properties

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Abstract

This work focused on achieving a high mechanical properties and biodegradable thermoplastic polyurethane (TPU) blends by the corporation of starch. Thermoplastic starch (TPS) was developed by means of plasticizing corn starch in a twin screws. Polyolefin elastomer (POE) was used as the compatibilizer in order to improve the flexibility of TPU/TPS system. The miscibility of blends was investigated by fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and Differential Scanning Calorimeter (DSC). Mechanical analysis (impact, tensile, folding endurance tests), dynamic mechanical analysis (DMA), degradation and contact angle (CA) tests were employed to study mechanical properties and hydrophilic sensitivity of TPU/TPS blends. The results showed that POE improved the miscibility of blends by enhancing the interfacial effects of TPU/TPS blend, decreasing the interfacial tension between TPS and TPU, as well as increasing the inter-hydrogen bonds between TPU and TPS. The hydrophilicity of TPU blends such as water adsorption and CA increased with the increase of TPS content, resulting in improving the biodegradation ability. TPU/TPS (20 wt%)/POE(10 wt%) endowed

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good folding endurance (>30.0×10^3), notched impact strength (no break), elongation at break (>800%) and 6.2% biodegradation rate for 7 week. These improved properties of TPU/TPS showed that they have high potential for use in environmentally friendly materials.

Keywords

Thermoplastic polyurethane (TPU); thermoplastic starch (TPS); polyolefin elastomer (POE); mechanical and degradable properties

Introduction

Nowadays, thermoplastic polyurethane (TPU) has been widely applied in the fields of automotives, screens, roller systems films, medical, sports products, aerospace and electronics, etc. On the molecular chain of TPU, hard and soft segments alternated which endow it to show good mechanical properties, such as higher impact toughness and abrasive resistance. However, the defects of TPU such as high price, non-biodegradation and low water sensitivity, limit its further application. Therefore, developing reinforced TPU composites is one of effective method to improve the properties of TPU. Generally, fibers and nano-particles are used commonly into TPU. Layered silicates,[2-6] mica[7,8] and MMT[9] have been reported to improve mechanical, thermal, and barrier properties of TPU.

Recently, starch has attracted more and more attention from researchers and industrial companies due to its properties of renewable, biodegradable, abundantly nature sources. During the thermal process, thermoplastic starch (TPS) is formed by incorporating plasticizers into corn starch, such as glycerol, urea, formamide[10] and water. [11] Some researchers used polyurethane to react with TPS in order to improve the mechanical and hydrophobic performance of TPS[12-17], while the thermoplastic properties of PU/TPS were poor. Seidenstückert[18,19] developed a thermoplastic and biodegradable materials based on TPU/TPS with good hydrolysis and biodegradation. They surveyed effects of TPU and TPS types, process designs as well as their impact on material properties. However, with the increase of starch content, the toughness of TPU/TPS blends decreased, drastically. Considering eco-friendly and economic requirements the preparation of TPU/TPS with high performance is necessary. However, the hydrophobicity of TPU and the hydrophilicity of TPS causes problems such as adhesives and wettability of TPU/TPS blends. Furthermore, when TPS is blended with TPU, the introduction of rigid TPS will destroy the balance of microphase segregation and decrease TPU mechanical properties. Therefore compatibilizers are necessary to be used in the starch-TPU matrix interface to improve the adhesion and compatibility. Chiu et al[20] demonstrated that POE-g-MA improved the low viscosity and compatibility of PA and TPU during the blending process. POE-g-MA significantly improved the impact strength of PA to super-toughness grade (> 800 J/m). TPU could obtain better mechanical properties because the micro-phase segregation occurred between hard and soft segments.[12] It had no any reports whether POE could rehabilitate the balance of microphase segregation of TPU/TPS due to its excellent flexibility. The variation of mechanical properties and biodegradable of TPU/TPS had not been investigated when POE was employed as toughening agent.

In this work, TPU/TPS blends were prepared by extrusion processing in order to obtain economically biodegradable materials with high mechanical properties. POE was used as compatibilizer. Here this study about the effect of POE loading on the performances of TPU/TPS blends was also described. The FTIR test, SEM and DSC were employed to study the interfacial interaction of TPU/TPS blends. Dynamic mechanical analysis, tensile, impact and folding endurance tests were used to analyze the effect of TPS and POE content on the mechanical properties of TPU. Water adsorption, contact angle (CA) and degradation tests were operated to illuminate the relationship between the water sensitivity and degradation ability of TPU/TPS blends.

Experiment

Materials

Corn starch (CS, amylose: 23-26 wt %; moisture: 12 wt %) was obtained from Wuhan Corn Starch CO. Ltd. (Wuhan, China). Thermoplastic polyurethane (TPU), Utechllan UE-95A, was purchased from Bayer AG (Leverkusen, Germany). Polyolefin elastomers (POE) were obtained from Guangzhou Honest Chemical Co., Ltd (Guangzhou, China). Nitrile rubber (NBR) powder was purchased from Beijing Yudahang Industry & Trade Co., Ltd (Beijing, China). Disodium hydrogen phosphate (analytical grade, 99.5%) was purchased from China Specialty Products CO., Ltd (Jiangsu, China). Sodium dihydrogen phosphate (analytical grade, 99.5%) was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Glycerol and other regents were of analytical grade (99.5%) and purchased from Longxi Chemical Reagent (Shantou, China). All the mentioned materials were used as received.

Preparation of TPS and TPU/TPS blends

Prior to processing, mixed dried corn starch, glycerol and water for 5 min in a mixer and then stood 30 min at 80℃. The ratio of corn starch: glycerol: water was 70:20:10. TPS was prepared by thermal process used a twin-screw extruder (L/D=40:1, Nanjing Chenmeng Machinery Co., Ltd., Jiangsu, China). The temperature profile along the extruder barrel was controlled to be 80-100-120-130-130-140-140-130 ^{o}C (from feed to die), respectively, with 100 rpm screw rotation speed, then the product was dried at 80 ℃ for 8h.

The formulation of TPU/TPS blends in this work was shown in Tab.1. The mixtures of each formulation were fed into the same twin-screw extruder and extruded into strand followed by being pelletized. The temperature profile along the extruder barrel was controlled to be 120-140-145-150-150-150-150-150 ^{o}C (from feed to die), respectively. The screw rotation speed was 200 rpm. The products were dried at 80℃ for 4h in a blast drying oven. Tensile strength (63.5×12.7×3.2 mm) and notched impact strength (127×13×4 mm) tests specimens were injected (Germany, ARBUR 420M, ø =25 mm, L/D = 28) with 2-plate mold at 160-165-165-170-175℃, respectively. The folding endurance (100×15×0.5) mm, dynamic mechanical thermal analyzer (DTMA)(30×6×0.5mm) and water resistance (100×100×1.5 mm) tests sheets were done by hot press machine . Besides the specimens for degradation test were also obtained by compression-molding and cut into 40×40×0.1 mm sized sheets.

Before various characterizations, the extruded products were conditioned at 52%

relative humidity (RH) for at least 10 days at ambient temperature, in a closed chamber containing a $Mg(NO_3)_2{\cdot}6H_2O$ saturated solution of distilled water [21].

Characterizations

Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra were obtained from samples in potassium bromide pellets using a 170SX FTIR spectrophotometer (Nicolet, Madison, WI, USA).

Differential scanning calorimetry (DSC). DSC measurements were performed on a Netzsch DSC204 instrument under a nitrogen atmosphere. For every test, the sample was heated from -60 to 120 ºC in the first scan and the second heating scan was performed after cooling to -60 ºC. Both the heating and cooling rates were 10ºC /min. The glass transition temperature (T_g) was recorded from the second heating curve to minimize the thermal history effect.

Scanning electron microscopy (SEM). Morphology of the film cross-sections fractured under liquid nitrogen was investigated by an analysis scanning electron microscopy (S-3700, Hitachi).

Mechanical analysis. After samples were injection molded as standard bars, tensile properties were measured on a Universal test machine (Reger, RGT-20A) according to ASTM D638-03. The notched impact strength was performed by ASTM D256 using an impact tester (Sans Tested, ZBC1400-2). The folding endurance tests were obtained using folding endurance tester (PN-NZ135) according to ISO5626, the test temperature was 20℃ and the folding angle was 50°±1°. In all cases, a minimum of five specimens were tested for determining an average value.

Dynamic mechanical thermal analysis (DMA). Dynamic mechanical behavior of the specimens, kept at a conditioning cabinet of 25℃ and 35% RH, were determined with a dynamic mechanical thermal analyzer (TA instrument DMA 2980-USA) with tensile mode at 1 Hz with a strain of 30 μm and a heating rate of 3℃/min in the temperature range from -70 to 100℃.

Contact angle (CA) test. The surface energy was calculated by measuring contact angle (CA) measurement with a CA meter (Contact Angle System OCA20, Germany). The testing liquids were purified water and diiodomethane. Five microliter of testing liquid was deposited on the solid sheet surface. The CAs were measured with a CCD camera and processed using an image analysis video card which calculated the CA automatically using an image analysis setup. Take the average value of five measurements. Surface energy was calculated according to Equation (1), (2) and (3):

$$\gamma_w(1+\cos\theta_w) = 2\sqrt{(\gamma^D \cdot \gamma_w{}^D)} + 2\sqrt{(\gamma^P \cdot \gamma_w{}^P)} \qquad (1)$$

$$\gamma_d(1+\cos\theta_d) = 2\sqrt{(\gamma^D \cdot \gamma_d{}^D)} + 2\sqrt{(\gamma^P \cdot \gamma_d{}^P)} \qquad (2)$$

$$\gamma_s = \gamma_s{}^D + \gamma_s{}^P \qquad (3)$$

Where γ_w is the surface energy of water, $\gamma_w{}^D$ and $\gamma_w{}^P$ are its dispersion force one and the polar force one, respectively. γ_d is the surface energy of diiodomethane, $\gamma_d{}^D$ and $\gamma_d{}^P$ are its dispersion force one and the polar force one, respectively. γ_s is the surface energy of the solid and θ is the CA.

Water resistance tests. Samples were dried at 100℃ for 24 h, then cooled to 25℃ in a desiccators, then weighed immediately (M_0). All the samples were immersed in deionised water for 72h. They were then removed at specific intervals and gently blotted with tissue paper to remove the excess of water on the surface. Finally the samples were subsequently weighed (M_x). Five specimens were tested for determining an average value. The amount of water absorbed by the samples was calculated by Equation (4):

$$\text{Water absorption}(\%) = \frac{M_x - M_0}{M_0} \times 100\% \qquad (4)$$

Degradation property. Firstly 0.2 mol/L Na_2HPO_4 solution and 0.3 mol/L NaH_2PO_4 solution was formulated. Then degradation solution which pH was 7.4 were controlled to form the formulation of Na_2HPO_4:NaH_2PO_4=81:19. Before the tests degradation samples were dried at 100℃ for 36 h, then cooled to 25℃ in a desiccators, then weighed immediately (M_0). Finally the samples were immersed in the degradation solution for seven weeks. Each week they were took out from the solution followed by removing the water adhered to the surface of them and weighted quickly as M_X. The amount of weight loss ratio by the samples was calculated by Equation (5):

$$\text{Degradation ratio}(\%) = \frac{M_0 - M_x}{M_0} \times 100\% \qquad (5)$$

where M_x was the weight of sample x at time t in the degradation solution.

Results and discussions

Interfacial interaction of TPU/TPS blends. Fourier transform infrared spectroscopy (FT-IR) was a useful tool to characterize the changes of functional groups during chemical reactions. In this segment, FT-IR spectra of TPS, TPU and the blends are presented in Fig1.

In the curve 1 and 2, both CS and TPS had a characteristic peak around 1645 cm^{-1} which was attributed to *v-OH*.[21] Another band at 2927 cm^{-1} was attributed to the asymmetric stretching vibration of -CH_2- in the glucose unit.[22] As to TPU (presented in curve 3), the peak around at 3334 cm^{-1} was assigned to the inter- and intra-molecular bound hydrogen bond of NH groups (*v-NH*, H-bonded) in urethane carbonyl groups. Besides, two peaks present at 1732 cm^{-1} and 1701 cm^{-1} were assigned to the stretching of the free carbonyl groups (*v-C=O*, free) and hydrogen bond one (*v-C=O*, H-bonded),[22] respectively. Comparing with FT-IR spectra of TPU and TPU/TPS, it was found that the peak intensity at 1702 cm^{-1} of TPU/20TPS was stronger than that of TPU. This was attributed to the formation of hydrogen bond between TPS and TPU. When POE was added into the TPU/20TPS blend, the peak at 3334 cm^{-1} was weaker and broader than that of TPU/20TPS blend. Furthermore, the hydrogen bond band shifted to 1706 cm^{-1} and a slight decrease in peak intensity was observed. Compared with TPU and TPS, the flexibility of POE molecular chain was higher and it acted as compatibilizer in the TPU/20TPS blend. As a result, the inter- and intra-molecular bound hydrogen bond of NH groups and OH group decreased, respectively. Therefore POE improved the compatibility between TPU and TPS, which was attributed to the increase of the inter-hydrogen bond bands of TPU and TPS. Curve 6, 7 and 8 present that the peak intensity at 3334, 1732 and 1706 cm^{-1} decreased with the increase of POE content, respectively. It might that POE could act as soft segment in the TPU/TPS blends and dilute the intensity of hydrogen bond. Moreover, the addition of POE would shield the hydrogen bond. These two reason were respondent to the decrease of peak intensity at 1706 cm^{-1}. However, when NBR was mixed with TPU/20TPS, the peak at 3321cm^{-1} in curve 9 was sharper than that of TPU/20TPS/10POE. It meant that the hydrogen bond formed by NH groups in hard segment of TPU increased, and the addition of NBR was respondent to the decrease in miscibility of TPU and TPS.

Morphology. In this segment, the influence of TPS and POE loadings on the micro structures was characterized by scanning electron microscopy (SEM). The morphology for the fractured surface of TPU, TPU/CS and TPU/TPS samples are presented in Fig. 2.

It could be seen that TPU displayed a continuous and smooth fractured surface with a slightly coarse as shown in Fig. 2 (A), which was attributed to the microphase segregation occurred between hard and soft segments.[12] Fig. 2 (B) presents that there was significant phase separation appeared at the surface of TPU/20C. Because the corn starch could not achieve thermoplastic properties during the thermal process, they dispersed in the TPU matrix in particles form. A clear interface and gaps were found between corn starch particles and TPU matrix, indicating that the miscibility of TPU/20CS was poor. The results also could be confirmed by FTIR spectra (Fig. 1, curve 4, there was no bond formed between TPU and CS). When corn starch was plasticized by glycerol at the thermal process, the corn starch granules would be destroyed and TPS displayed a homogenous morphology.[13] In the Fig. 2(C), no starch granules could be found in the fractured surface indicating that TPS was well embedded into the TPU matrix with some cracks. Compared with that of TPU/20CS, it could be concluded that the TPS better dispersed in TPU matrix, and the compatibility and interfacial adhesion between TPU and starch phases improved.

Fig. 2(D), (E) and (F) present a miscible morphology that no crack in the TPU/TPS blend appeared after the corporation of POE with different content. Moreover, TPS was well dispersed in TPU matrix and the “sea-sea” structure was formed, which was favorable for the delivery and dispersion of stress. [24] Fig.2 (G) reveals that no distinct interface was found between TPU and TPS phase, even the TPS content was up to 30 wt%. In the morphology of TPU/30TPS/10POE, it indicated that TPS could well disperse and embed in TPU matrix. It was hard to find crack in the boundary of TPS/TPU. However, TPU/40TPS/10POE presented a deformed morphology with TPS aggregation as shown by Fig.2 (H). The reason was attributed to decrease of the compatibility and interfacial adhesion between TPU and starch phases with the increase of TPS content. The morphology of TPU/20TPS/10NBR (I) was disconnected and TPU matrix was in high deformed. The spherical domains of the dispersed TPS phase were large and the interface between TPU and TPS was smooth and clear. It indicated a poor interfacial adhesion between the two phases. The reason was that the addition of NBR decreased miscibility of TPU/TPS blends.

Thermal analysis. DSC is an effective tool to investigate the effect of compatibilizer on the miscibility of blends. The DSC thermograms of TPU, TPS and TPU/TPU blend systems are shown in Fig. 3, and the T_g values are summarized in Table 2. The glass transition temperatures (T_g) of TPU and TPS are -33.6^{o}C and 82.2 ^{o}C, respectively. TPU/CS only displayed one T_g at 34.1 ^{o}C because the CS could not show thermoplastic properties. Two distinct T_g at -28.9 ^{o}C and 79.6 ^{o}C for TPU/TPS, compared with those of TPU and TPS, its T_g move toward each other. It indicated the miscibility of the two components and it coincided with the results of FTIR and SEM. When POE was added to TPU/20TPS blend, the two T_g corresponding to the blend components shitted toward each other. So the compatibility of TPU and TPS was enhanced through interpenetration of TPU and TPS at the interface.[25] The reason was that the addition of POE could cause a decrease in interfacial tension of TPU/TPS, an increase in thickness of the interface of TPS/TPU.[26] When NBR was added to TPU/20TPS blend, the two T_g was -36.4 ^{o}C and 85.9 ^{o}C, compared with those of TPU/TPS, they move away each other. The result indicated the miscibility of TPU and TPS components could not be improved by the NBR.

Based on the results of FTIR, SEM and DSC, they demonstrated that the addition of POE enhanced the miscibility of TPU and TPS through interpenetration of TPU and TPS.

Mechanical properties. The effects of TPS content and compatibilizer on the mechanical properties of TPU/TPS blends were studied by tensile, impact and folding endurance tests and data are listed in the Table 3. First of all, TPU exhibited excellent mechanical performances. Its notched impact strength was too high to determine as well as the folding number could be higher than 30.0×10^3. When corn starch was blended with TPU, the decrease in mechanical properties was observed. The notched impact strength and folding number of TPU/20CS drastic decreased to 376.3J/m and 0.58×10^3, respectively. The deteriorated mechanical properties of TPU/20CS were caused by the poor compatibility between TPU and corn starch. Compared with those of TPU/20CS, the notched impact strength and folding number of TPU/20TPS increased significantly, the value was 872.5J/m and 4.5×10^3, respectively**.** It was attributed to the increase in the compatibility and interfacial adhesion between TPU and starch**,** though there were far lower than that of TPU.

The introduction of POE could play an important role to increase the flexibility of TPU/TPS. It was respondent to the increase of the interfacial force of TPS and TPU and resulted in increasing the mechanical properties. The notched impact strength of TPU/TPS/10POE depended on the TPS loading. With the increase of TPS content, the mechanical properties of blends decreased. When the TPS content was lower than 30%, the notched impact strength was too high to be measured. While when the loading of TPS arrived to 30%, the deteriorated mechanical properties of blends occurred**.** The interfacial adhesion between TPU and starch phases decreased when TPS was at higher content. As a result, the over loading of TPS reduced the flexibility of TPU and lowered the folding endurance due to the brittleness of TPS. However, it was clear that flexibility of TPU/TPS was greatly improved after its compositing with POE. The flexibility of TPU/20TPS/10POE and TPU/20TPS/15POE increased, the notched impact strength, elongation and folding number was comparable to those of TPU, respectively. Therefore TPU/20TPS/10POE was considered as the potential material for substituting the TPU. When NBR was added, all the mechanical properties of TPU/20TPS/NBR blends decreased, however. Their folding number reduced from 1.7×10^3 to 0.8×10^3 when NBR content ranged from 10% to 20%. It revealed that the addition of NBR into the TPU would decrease the flexibility. The reason was that NBR exhibited more rigid than that of the soft segments in TPU. Furthermore, NBR could not achieve thermoplastic properties, which restricted it to reduce the interfacial tension through interpenetration of TPU and TPS at the interface. It was respondent to the drastic reduction in folding endurance and notched impact strength. Moreover, by the results of FTIR, SEM and DSC, the incorporating NBR would lead to weaken the interfacial force of TPU and TPS, resulting from the severe phase separation and caused the mechanical properties deterioration of TPU/20TPS.

Dynamic mechanical thermal analysis (DMA). Dynamic mechanical thermal analysis (DMA) measures the mechanical properties (storage modulus, loss modulus and tan σ) as a function of temperature. In this segment, Fig. 4 describes the DMA analysis results of TPU/TPS blends. Fig. 4(a) presents storage modulus ($E^{'}$) vs temperature curve of TPU/TPS blends. A plateau was found when the temperature ranged from -60 ^{o}C to -30^{o}C. Then $E^{'}$ of TPU suffered a sharp decrease around its glass transition temperature (T_g), which was attributed to thermoplastic nature of TPU.[27] Because TPU resin was dominated by amorphous part, it could not obtain rubbery plateau when heated from T_g to 80 ^{o}C . $E^{'}$ of TPU decreased to a rather low value when the temperature increased to 100 ^{o}C. It was noted that when TPS was introduced into the TPU matrix, the storage modulus of TPU/TPS blends increased significantly at the glass stage. It could not be found a rubbery plateau when the temperature extended up to 10 ^{o}C to 80 ^{o}C, but $E^{'}$ of TPU/TPS obtained a rather stable value when the temperature ranged from 80 ^{o}C to 100 ^{o}C. This behavior was attributed to the stiffness and amorphous domain of TPS. When POE was added into the TPU/TPS blends, $E^{'}$ of TPU/20TPS/10POE was comparable to that of TPU/20TPS at lower temperature. The reason was attributed to the stiffness of TPS dominated $E^{'}$ of the blend at low temperature. The storage modulus decreased when the temperature ranged from -20 ^{o}C to 100 ^{o}C, significantly. The penetration degree of POE at the interface of TPU and TPS increased with the increase of temperature. As a result, the soft compatibilizer could increase the compatibility and interfacial adhesion, decrease $E^{'}$ of TPU/TPS, however. Fig. 4(a) also reveals that $E^{'}$ of TPU/TPS decreased with the TPS content increased from 10% to 40% below -30 ^{o}C when POE fixed at 10%. Fig. 4(b) shows tan δ curves of TPU/TPS blends. It revealed that TPU achieved T_g at the tan δ peak for -3.1 ^{o}C, it was attributed to the soft segment of TPU. There were two T_g in TPU/20TPS, T_{g1} shitted to lower temperature (about -11.4 ^{o}C) than that of TPU, while T_{g2} was about 64.5 ^{o}C (attributed to TPS). After the incorporation of POE, T_{g1} and T_{g2} of TPU/20TPS/10POE increased to -6.48 ^{o}C and 71.5, compared with TPU/20TPS. The increase in T_g of the blends resulted from the penetration of the TPS into the TPU domains promoted by POE. [25, 26] As a result, the TPS could restrict the molecular motion of soft segment of TPU, and the hard segment may retard the molecular motion of TPS. The introduction of POE would increase the compatibility and interfacial adhesion, increase the formation of inter-hydrogen bonding of TPU and TPS. When the TPS content ranged from 20% to

40%, there were no significant differ in tan δ curves of TPU/TPS/10POE. It also was attributed to POE acted as soft compatibilizer and improved the miscibility of TPU and TPS.

Water resistance. One of the fatal defects of TPS is that it imbibes water at high humidity and decreases the mechanical properties.[28] In this segment, the effect of TPS content on the hydrogenhobic ability of TPU/TPS/10POE blends was evaluated by contant angel (CA) test. In order to study the hydrophilicity of TPU/TPS in detail, CA and surface energy (SE) of TPU/TPS/10POE blends were measured. Fig. 5 presents the effect of TPS content on the CA of blends and the data are listed in Table 4.

Compared with that of TPU, water CA of TPU/20TPS decreased significantly from 85.6° to 57.1°, while its SE increased from 42.5 to 44.5 nN/m. The presence of polar OH groups (by both starch and glycerol) increased the hydrogen bonding interactions and therefore the hydrophilicity of TPU/TPS increased. When POE was added, CA of TPU/20TPS/10POE increased, while its SE decreased. The addition of POE could improve the miscibility of TPU and TPS through enhancing the interpenetration of TPS into the TPU matrix.[26] Part of hydroxyl groups in the starch would be shielded and result in increment of CA. When POE was added into TPU/TPS blends, it caused a decrease in interfacial tension of TPU/TPS, which was respondent to the decrease of SE. The results of FTIR, SEM and DSC revealed that POE could eliminate the interfacial cracks of the TPU/TPS, shield the inter-hydrogen bonding of TPU and TPS. With the increase of TPS content, CA of TPU/TPS/10POE decreased to 65.6 ° and SE increased to 38.7. This result also could be ascribed to the introduction of higher amount hydroxyl groups by starch and glycerol into TPU, which led to an increase in hydrophilicity. The increase of surface energy can be explained by the introduction of polar functional groups. Variations in surface chemical composition and surface structure were responded in the varied CA of TPU/TPS/10POE.

Fig.6 shows the water absorption in different time of the blends after samples submerged in water for 72h. TPU exhibited a good hydrophobicity and its WA at 72h was 0.6%. WA of TPU/20TPS increased to 12.5%, due to the hydrophilicity of TPS. When POE was added to TPU/20TPS, WA of TPU/20TPS/10POE decreased to 8.3%. With the increase of TPS content, water absorption ratio of TPU/TPS/10POE blends increased from 4.8% to 17.0%. Fig.6 displayed the water absorption of blends with different TPS content after 72h submerged in the water. The dashed line is the theoretical values of equilibrium water uptake, WA (theory) could be calculated by the Equation (6) (water absorption of POE was neglect):

$$\mathrm{WA(theory)} = \emptyset_{\mathrm{TPS}} \cdot \mathrm{WA}_{\mathrm{TPS}} + \emptyset_{\mathrm{TPU}} \cdot \mathrm{WA}_{\mathrm{TPU}} \tag{6}$$

where WA and $\emptyset$ are the equilibrium water absorption and mass fraction in the blends, respectively. WA of TPS was 50.5% achieved by the moisture test because it would dissolve in the water.[26] By the Equation (6) and Fig. 7, it could reveal that the test WA value of TPU/TPS blends was lower than that of the theoretical values. In case of TPU/TPS/POE blends, TPS could well disperse in TPU matrix, a decrease in interfacial tension of TPU/TPS and the crack at the interface was eliminated by POE. As a result, TPS was isolated with water by TPU and POE and it retarded TPS to uptake water. Moreover, due to hydrogen bonding interaction between TPU and

TPS[13] could be shield by POE, CA of TPU/20TPS/10POE increased and led to decrease of the water absorption ability.

Degradation property. Fig.8 showed the weight loss of the TPU and TPU/TPS/10POE blends under degradation solution for 7 weeks. The weight loss of TPU in 7 weeks was only 0.887%, which meant that TPU was different to degrade at the test condition. It has reported that the biodegradable properties were dependent on the hard segment of TPU[18]. However, the hard segment of TPU was mostly consisted by aromatic group, which was hard to hydrolyze. As a result, TPU was hardly the affected by the hydrolysis and could not obtain biodegradable properties. In pH 7.4 solution, starch started hydrolysis from the ether linkages on its polysaccharide chains [27] and starch is sensitivity to hydrolysis. Fig.8 presents that the degradation rate of TPU/TPS/10POE increased significantly, compared with TPU, and the degradation rate was dependent on the TPS content. The weight loss of TPU/30TPS /10POE and TPU/40TPS /10POE in 7 weeks arrived to 9.8% and 11.3%, respectively. There is no plateau listed in all the curves within the test period indicating that the biodegradation was not complete and it could be expected that with prolonged tests and with powder instead of sheets the criteria. With the increase of TPS content, the morphology of TPU/TPS/POE (10%) exhibited a “sea-island” construct and holes in the interface. Moreover, the hydrophobicity of TPU/TPS/POE (10%) decreased and resulted in a decreased of CA. It meant that the pH 7.4 solution was easy contact with starch and improved its hydrolysis rate. Moreover, the biodegradable position by starch hydrolysis would induce spontaneous attack and adhesion by fungi on the TPU/TPS blends.[18, 29] This result demonstrated that TPS improved the degradation rate of TPU/TPS and it could be controlled by varying of TPS content. To achieve the systemic biodegradation of TPU/TPS blends, it expected that the test time should be prolonged. Due to it biodegradable properties, TPU/TPS blends were favor to fabricating these products, such as sports shoes, disposable diapers, sanitary towels, and sheets used for agricultural purposes. They could degrade in the natural environment once they were used up and discarded. The motive for the development of biodegradable TPU/TPS blends lies in their potential to contribute to modern waste.

Conclusions

In this work, TPU/TPS blends were prepared to improve the degradation ability of TPU and decrease it price. To achieve high mechanical properties, POE was chosen to be the optimized compatibilizer. The results of FTIR, SEM and DSC demonstrated that compared with TPU/TPS, TPU/TPS/10POE blends exhibited the improved physical properties. The reason was attributed that POE could enhance the interfacial effects of TPU/TPS blend, improve miscibility and decrease the interfacial tension between TPS and TPU. As a result, the TPU/TPS blends kept the high mechanical properties, the degradable properties improved a lot, meanwhile. In addition, the mechanical properties of TPU/TPS/10POE blends were strongly influenced by the TPS content. The hydrophilicity and hydrolysis properties of starch in pH 7.4 solution could induce the TPU/TPS blends to degrade, and increased the biodegradable properties of TPU/TPS blends. In summary, incorporating TPS of 20 wt% and 10wt%

POE in TPU resulted in the blends with good folding endurance (>3.0×10^4), notched impact strength (no break), elongation at break (>800%) and 6.2% biodegradation rate for 7 week. These improved properties of TPU/TPS showed that they have high potential for being used in environmentally friendly materials.

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Table 1. Composition and content of different samples

Samples	TPU	TPS	POE	NBR
TPU/20CS	80	20(Corn Starch)	0	0
TPU/20TPS	80	20	0	0
TPU/10TPS/10POE	90	10	10	0
TPU/20TPS/10POE	80	20	10	0
TPU/30TPS/10POE	70	30	10	0
TPU/40TPS/10POE	60	40	10	0
TPU/20TPS/5POE	80	20	5	0
TPU/20TPS/15POE	80	20	15	0
TPU/20TPS/10NBR	80	20	0	10
TPU/20TPS/15NBR	80	20	0	15
TPU/20TPS/20NBR	80	20	0	20

Table 2 T_g of TPU, TPS and TPU/TPS blends

Samples	TPU	TPS	TPU/20CS	TPU/20TPS	TPU/20TPS/10POE	TPU/20TPS/10NBR
T_{g1} (℃)	-33.6	-	-34.1	-28.9	-23.5	-36.4
T_{g2} (℃)	-	82.2	-	79.6	69	85.9

Table 3. Notched impact strength, tensile strength, elongation at break and folding endurance for samples.

Sample	Notched Impact Strength (J/m^2)	Elongation at break (%)	Tensile Strength (MPa)	Folding Endurance (Times($\times 10^3$))
TPU	No break	>800	12.5	>30.0
TPU/20CS	376.3	575.6	12.2	0.58
TPU/20TPS	872.5	>800	12.2	4.5
TPU/10TPS/10POE	No break	>800	11.5	>30.0
TPU/20TPS/10POE	No break	>800	11.2	>30.0
TPU/30TPS/10POE	587.3	>800	9.5	16.0
TPU/40TPS/10POE	432.1	>800	8.5	8.6
TPU/20TPS/5POE	No break	>800	11.2	15.0
TPU/20TPS/15POE	No break	>800	11.0	>30.0
TPU/20TPS/10NBR	575.4	422.3	8.2	1.7
TPU/20TPS/15NBR	632.3	434.5	8.6	1.5
TPU/20TPS/20NBR	786.4	572.1	9.0	0.8

Table 4. Effect of TPS content on water adsorption and contact angle test of TPU

Samples	Water adsorption(%)	Contact angle(°)	Surface energy (nN/m)
TPU	0.53	85.6	42.5
TPU/20TPS	10.3	57.1	44.5
TPU/10TPS/10POE	3.5	79.6	31.4
TPU/20TPS/10POE	6.5	77.2	33.6
TPU/30TPS/10POE	13.1	71.6	36.1
TPU/40TPS/10POE	15.7	65.6	38.8

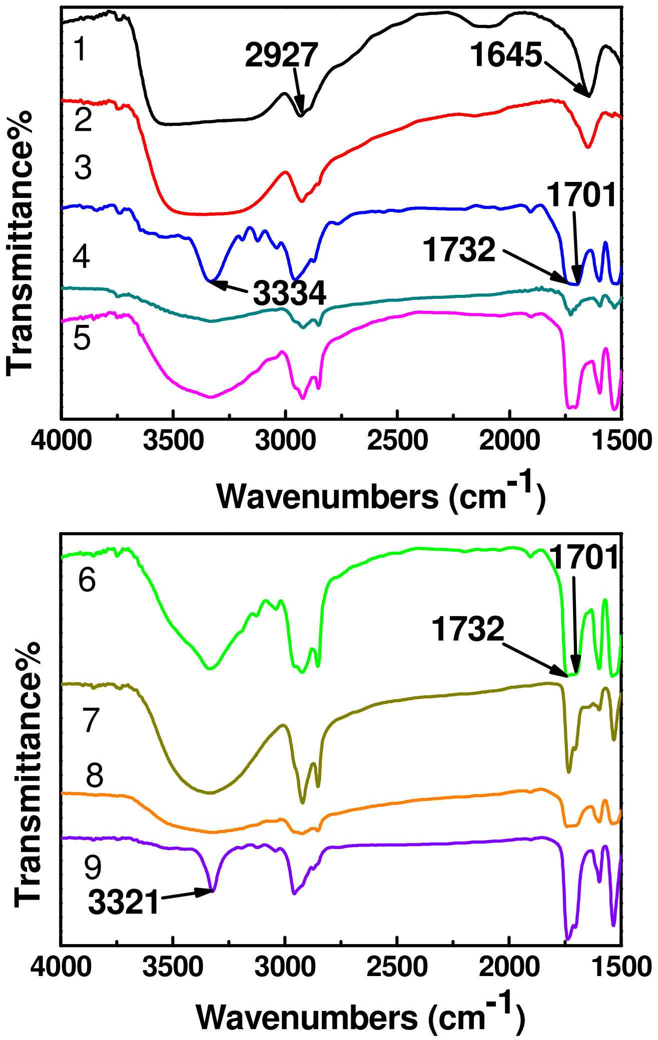

Figure. 1. FT-IR spectra of: 1:CS, 2:TPS, 3:TPU, 4:TPU/20CS, 5:TPU/20TPS, 6:TPU/20TPS/10POE, 7:TPU/20TPS/5POE, 8:TPU/20TPS/15POE, 9:TPU/20TPS/10NBR

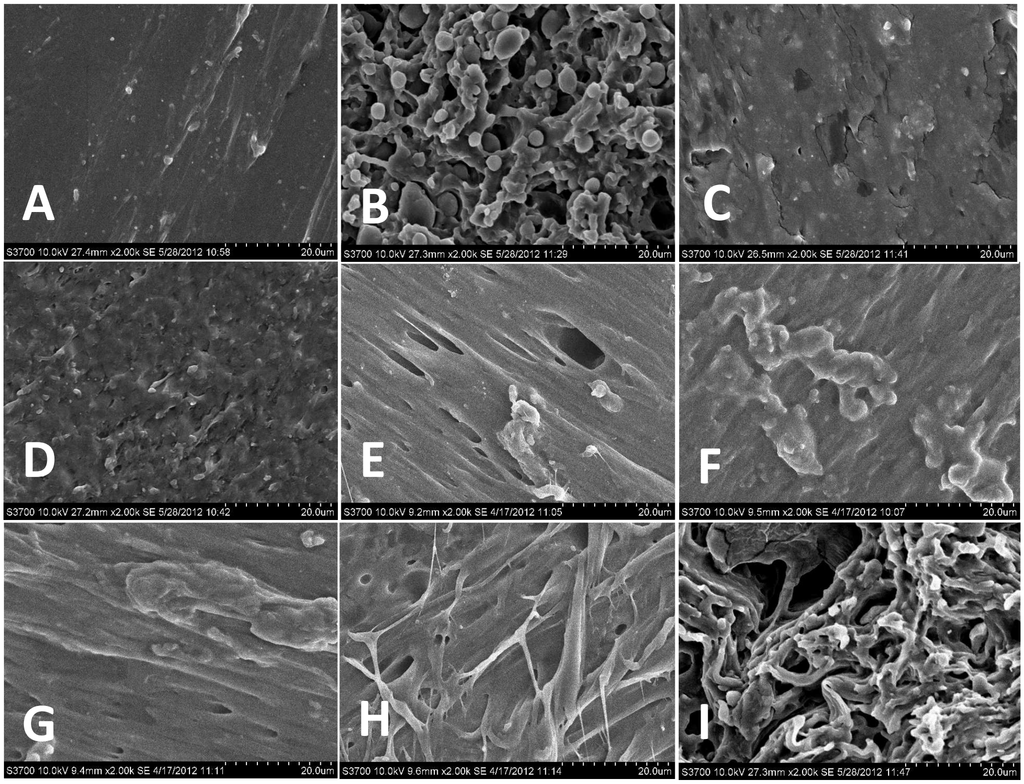

Figure.2. SEM Images(2.0K×) of (A) TPU; （B）TPU/20CS; (C) TPU/20TPS; (D) TPU/20TPS/5POE; (E) TPU/20TPS/10POE; (F)TPU/20TPS/15POE; (G)TPU/30TPS/10POE; (H) TPU/40TPS/10POE; (I) TPU/20TPS/10NBR.

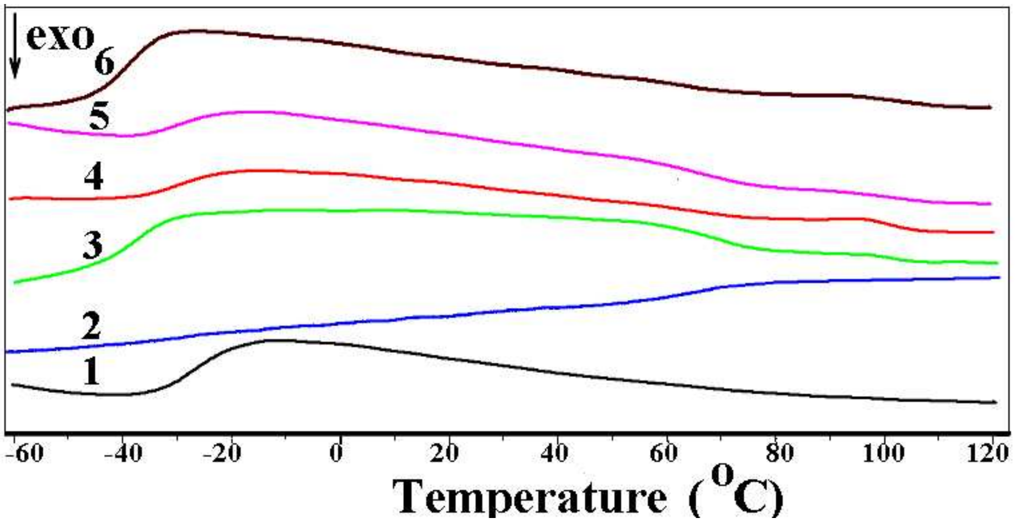

Figure.3. DSC thermograms of TPU and TPU/TPS blends. 1:TPU; 2:TPS; 3: TPU/20CS; 4:TPU/20TPS; 5: TPU/20TPS/10POE; 6:TPU/20TPS/10NBR.

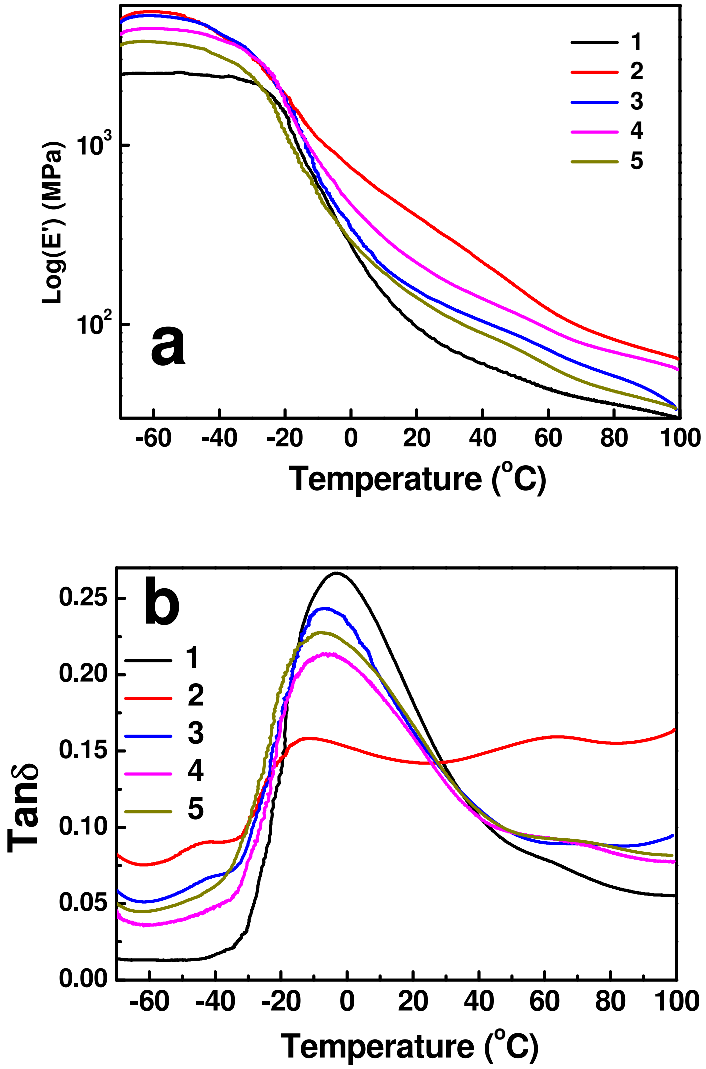

Figure. 4. DMA curves of TPU/TPS/POE with various TPS content, (a)storage modulus (E’) and (b)dissipation factor (tan δ) as a function of temperature: 1:TPU, 2:TPU/20TPS, 3:TPU/20TPS/10POE,4: TPU/30TPS/10POE 5: TPU/40TPS/10POE.

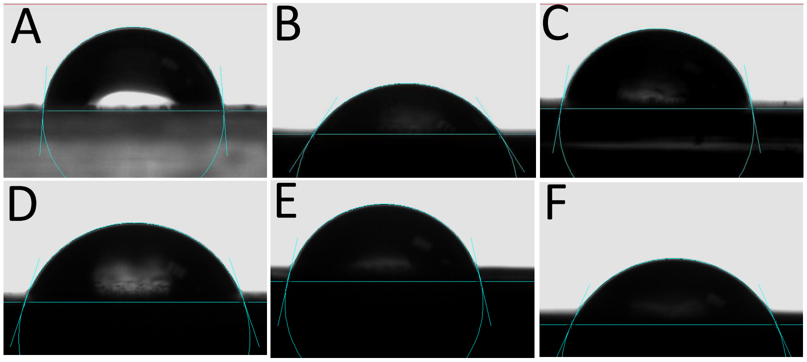

Figure. 5. Dependence of water contract angle on TPS content for TPU/TPS blends. A: TPU, B:TPU/20TPS, C:TPU/10TPS/10POE, D:TPU/20TPS/10POE, E:TPU/30TPS/10POE, F:TPU/40TPS/10POE.

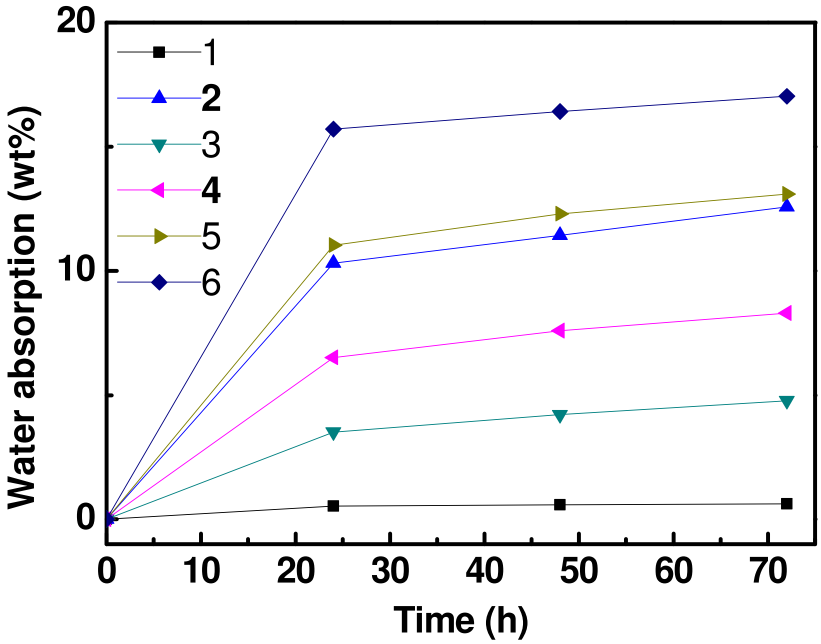

Figure.6. Dependence of water absorption on TPS content for TPU/TPS blends. 1:TPU, 2:TPU/20TPS, 3:TPU/10TPS/10POE, 4:TPU/20TPS/10POE， 5:TPU/30TPS/10POE， 6:TPU/40TPS/10POE.

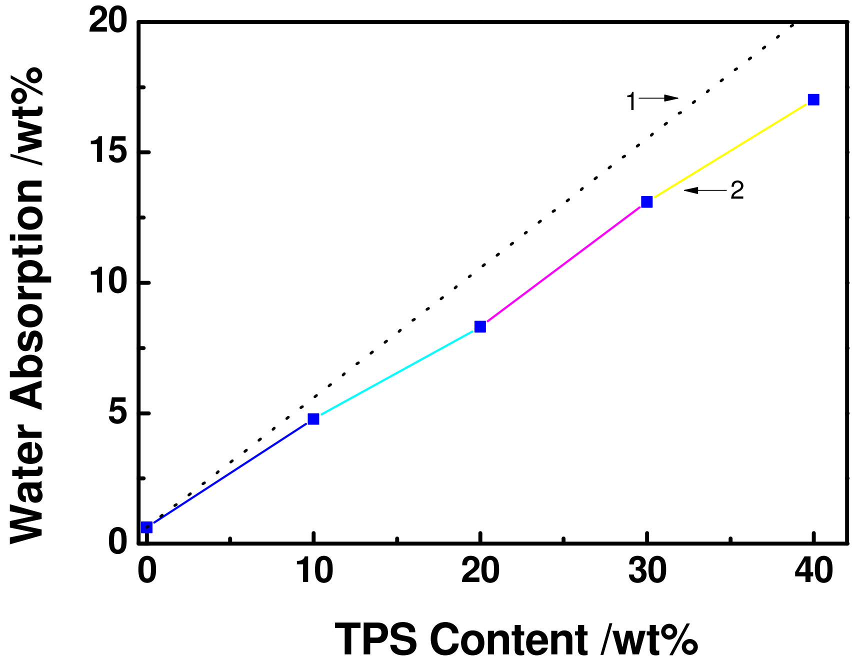

Figure.7. Dependence of water absorption after submerged in water for 72h on TPS content for TPU/TPS/10POE blends: 1: theoretical value; 2: measured values.

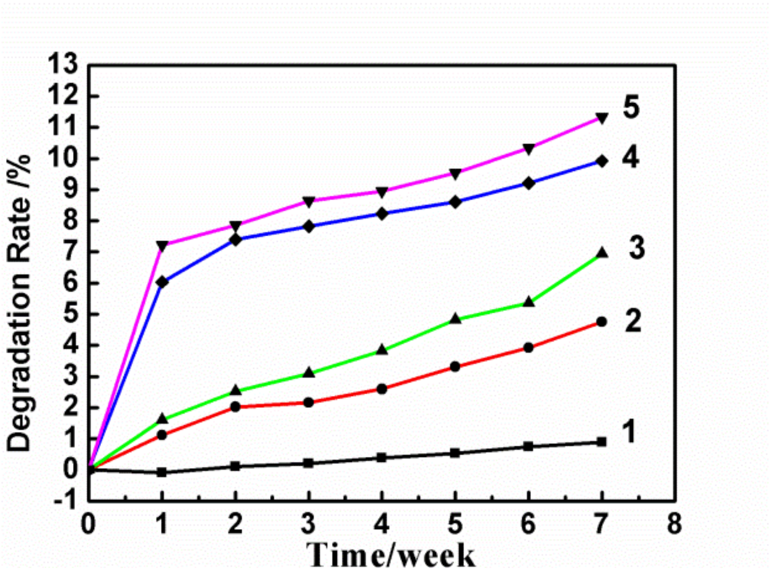

Figure.8. Effect of TPS content on weight loss ratio in different weeks of TPU/TPS/10POE blends: 1:TPU, 2:TPU/10TPS/10POE, 3:TPU/20TPS/10POE, 4:TPU/30TPS/10POE, 5:TPU/40TPS/10POE.