

Synthesis and Characterization of Biodegradable Polyester/Polyether WPU As The Environmental Protection Coating

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Abstract

Polyester diol PCL and PBA, polyether diol PTMG and polycarbonate diol PCDL were used as components of WPU soft segment, respectively. Polyether PTMG-WPU has the worst hydrolytic property and the highest thermal stability. The maximum degradation rate temperature T_{max} is 407.8°C, the water contact angle reaches 89.5°. Traditional polyester PCL-WPU shows the strongest hydrolysis performance, the smallest water contact angle, only 71.7°, the water absorption rate of 72 hours at room temperature is as high as 26.7%. However, the thermal stability of PCL-WPU is lower, the soft segment T_g is -52.3°C, and T_{max} is only 333.7°C, but the mechanical properties of which is the best, the tensile strength is 58.3 MPa, and the elongation at break reaches 857.9%. The most important thing is that the structure of polyester PCL-WPU is more easily destroyed by lipase and water molecules. The acidic products produced after hydrolysis will further promote the degradation of polyester. Therefore, compared with other WPU, PCL-WPU has the best biodegradability and the most obvious degradation effect under the same conditions. The degradation rate of PTMG-WPU after 30 days of degradation in 0.6% lipase PBS buffer solution and soil was only 4.2% and 2.3%, while the highest degradation rate of traditional polyester PCL-WPU reached 41.7% and 32.0%, respectively. In addition, polycarbonate PCDL-WPU has the highest hardness, reaching 95.5 HD. But its other performances are lower than PCL-WPU.

Introduction

Traditional WPU coatings have been unable to meet people's requirements for high-efficiency, energy-saving, environmentally friendly, and resource-recycling properties of new polymer materials^[1-4]. In the face of subsequent polymer waste treatment, the biodegradability of WPU becomes more and more important^[5-9]. Biodegradable WPU not only avoids all kinds of health problems caused by the volatilization of organic solvents of traditional WPU, but also has the properties of non-toxic and harmless degradation products in compliance with relevant laws and regulations^[10, 11].

According to the type of glycol of the soft segment, WPU can be divided into three types: polyether, traditional polyester and polycarbonate^[12, 13]. The cohesive energy of the ether bond in the polyether WPU is low, and the strength and oxidation resistance of the coating film are deviated^[14]. The ester group in polyester WPU shows high mechanical properties with strong polarity and cohesive energy^[15]. Besides, the carbonate group bond energy in polycarbonate WPU is larger, and the wear resistance and strength of the coating film are higher^[16]. However, there are few researches on the biodegradability of the three WPU and corresponding products, so there is a lot of research space and value^[17, 18].

Lin Y.Y. et al. used PEG, PEBA, and PLLA diols as soft segment materials to prepare three biodegradable WBPU coating films by spin coating. Compared with the other two types of WBPU, the PLLA-based WBPU showed the strongest degradability after hydration in the buffer solution, and the domain shape became more irregular. It showed that the type and structure of the soft segment glycol would affect the various properties of the biodegradable WPU^[19]. Samy A. M. et al. reviewed the biodegradable WPU and its solid

membranes of different soft segments such as PEG, PLA, PLLA, PCL, PBGA, PLGA, PHB, PEBA, chitosan, gelatin, castor oil, etc^[20]. It provided an important quantitative experimental basis and structural evolution for the development and synthesis of degradable WPU with new functions. Kateřina S. et al. used polyester and polyether as soft segments to prepare bio-based non-toxic polyurethane foam (PUF) that can be decomposed in the environment^[21]. However, the eco-toxicity test of biological PUF and its biodegradation products was still insufficient.

In this study, the polyester type polycaprolactone glycol (PCL), poly-1,4-butanediol adipate (PBA) and polyether type polytetrahydrofuran glycol (PTMG) and poly carbonate diol (PCDL) were used as the soft segment component, and four corresponding WPU water-based coatings were prepared by the prepolymer method. The differences and the pros and cons of the surface properties, thermal properties, mechanical properties and biodegradability of four WPU films with different soft-segment components were studied, and the soft-segment glycol type with the best biodegradability was selected through comparative analysis.

Experimental

Materials

Poly(ϵ -caprolactone) diol (PCL, Mn = 1000, Wanhua, China), poly(butylenes adipate) glycol (PBA, Mn = 1000, Huaxia, China), polycarbonate diol (PCDL, Mn = 1000, Hongming, China), polytetramethylene-oxide glycol (PTMG, Mn = 1000, Macklin, Shanghai) were degassed at 80 °C under vacuum for 4 hours before use. Isophorone diisocyanate (IPDI, 98% purity, Aladdin) was dried over 4A° molecular sieves before use. Dimethylol propionic acid (DMPA, 99% purity, China), triethylamine (TEA, AR grade, Lingfeng, China), lipase (200 U/ml, Amano Pharmaceutical, Japan), phosphate buffered saline (PBS, pH = 7, Qingdao, China), acetone and deionized water were used as received.

Preparation of biodegradable WPU dispersions and membranes

First, PCL(PBA, PCDL, PTMG), IPDI (dehydration) and 0.015 wt% DBTDL as catalyst were added and reacted for about 2.5 hours to obtain -NCO terminated potential ionomer segments. Then the hydrophilic chain extender DMPA was added and reacted for the next 2 hours to prepare -NCO terminated polyurethane prepolymer. Secondly, add a small amount of low molecule chain extender BDO to the system, keep the same temperature and speed, and react for 1.5 hours to further extend the WPU molecule. During the period, use acetone to adjust the reaction viscosity to prevent the reaction from being too high. With the phenomenon of complete and violent polymerization, the molecular chain length of WPU is basically determined at this time. The prepolymer was then cooled to 35 °C, and the neutralizer TEA in the same molar amount as DMPA was added to neutralize the -COOH groups in the reaction system for 0.5 h. Finally, deionized water was added to the WPU prepolymer, and the WPU water dispersion emulsion can be obtained after high-speed dispersion at a speed of 1000 r/min of the

mechanical stirrer for 1 h. The formulas and reaction schemes for synthesizing four WPUs with different soft segment components were shown in Table 1 and Scheme 1. In addition, the emulsions were evenly coated on the mold made of PTFE and dried at 35°C until they completely lost their fluidity and the surface was basically film-formed. The four WPU emulsions and films were labeled PCL-WPU, PBA-WPU, PCDL-WPU, and PTMG-WPU, respectively.

Table 1
Preparation formula of PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU

Samples	Ingredient					
	Glycol	IPDI	DMPA	BDO	TEA	Water
	(g)	(g)	(g)	(g)	(g)	(g)
PCL-WPU	19.820	11.120	1.012	1.000	0.763	77.000
PBA-WPU	19.820	11.120	1.012	1.000	0.763	77.000
PCDL-WPU	19.820	11.120	1.012	1.000	0.763	77.000
PTMG-WPU	19.820	11.120	1.012	1.000	0.763	77.000

Characterizations

Fourier transform infrared spectroscopy (FTIR)

Attenuated Total Reflectance/Fourier Transform Infrared (IS50, Nicolet, USA) was used to characterize the structure of PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU films. The films were scanned 32 times in transmission mode in the wave number range of 4000 cm^{-1} to 500 cm^{-1} at a resolution of 8 cm^{-1} .

Contact angle and hardness measurement

Water droplet contact angle of the films were measured with a contact angle goniometer (DSA 30, Kruss, Germany). The film with a thickness of 0.8 mm was placed horizontally on the test bench, each sample was measured three times. The Shore A hardness of the films were measured by an indentation durometer according to ASTM D 2240-75. Five splines with thickness of 0.8 mm were superimposed together to make the thickness reach 4mm, and the hardness of each film was measured for 3 times.

Water absorption measurement

The PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU films were cut into square slices of 10 mm×10 mm×1 mm and weighed (M_0). After soaking in deionized water at 25 °C for 24 hours, the residual water on the surface was wiped off with a filter paper and weighed (M_1). The test was in triplicate and the average was taken. The membrane water absorption rate (M) was calculated as follows:

$$\text{Water absorption } M (\%) = \frac{M_1 - M_0}{M_0} \times 100\% \quad (1)$$

After the soaked samples were washed with deionized water and dried to a constant weight (M_2), the water leaching rate (W) of the films were calculated as follows:

$$\text{Water absorption } W (\%) = \frac{M_0 - M_2}{M_0} \times 100\% \quad (2)$$

Differential scanning calorimetry (DSC)

The thermal performance of chemical hybrids films was measured by differential scanning calorimeter (Perkin Elmer, USA). A sample of a 9 mg was placed in an alumina crucible and measured at a heating rate of 10 °C/min in the presence of nitrogen. The measurement temperature is divided into four sections, first from 30 °C to 140 °C, then from 140 °C to -70 °C, again from -70 °C to 140 °C, and finally from 140 °C to 30 °C.

Thermal gravimetric analysis (TGA)

The tests were performed with pyris 1 TGA thermogravimetric analyzer (TGA4000 Perkin Elmer, USA). In the nitrogen environment, the sample was heated from 30 °C to 600 °C at a heating rate of 10 °C/min. Mechanical property measurement

The mechanical properties of the films were measured by tensile testing machine (Instron, USA) at room temperature. Each group of splines were tested by the dimensional shear of 30 mm×4 mm×1 mm, and the crosshead speed of 100 mm/min was measured. Tensile strength and elongation at break were tested three times and averaged.

Scanning electron microscopy (SEM)

The degradation structure changes of PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU films by soil microorganisms and lipase solution were characterized by JSM6510 instrument (JEOL, Japan). Testing voltage was 10 kV.

Biodegradation assessment

The films of PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU were cut into thin sheets of 20 mm×20 mm×8 mm and weighed and recorded (M_a). Groups of the same films were divided into two groups, one of which was buried in moist soil rich in microorganisms. The other group was put into PBS buffer solution

(pH = 7) containing lipase (200 u/ml, 0.6%), and the temperature was kept at 50 °C. Three of the same samples were taken from the two degradation systems at 1, 7, 14, 21, 28, 35 and 60 days respectively, and washed with distilled water for several times. Then, the washed samples were dried in a drying oven at 40 °C to constant weight and weighed (M_b). The degradation rate (ML) of the two degradation films were calculated according to the following formula:

$$\text{Degradation rate ML(\%)} = \frac{M_a - M_b}{M_a} \times 100\% \quad (3)$$

where, M_a represented the initial weight of the PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU films without degradation, M_b represented the the final weight of the films after degradation.

Results And Discussion

FTIR spectra analysis

It can be seen from Fig. 1 that the films of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU all showed -NH₂ absorption peak at 3300 cm⁻¹, and -CH₃/-CH₂ absorption peaks at 2750–3000 cm⁻¹. PTMG-WPU showed more methylene groups on the molecular chain, so the peak value was larger. There was no absorption peak in the four infrared spectrum curves at 2270 cm⁻¹, indicating that the -NCO groups in each WPU had been completely reacted^[22]. The curve of PCDL-WPU showed a clear absorption peak of carbonate carboxyl group at 1774 cm⁻¹, which proved that the preparation of PCDL-WPU was successful. The curve of PTMG-WPU showed a typical asymmetric stretching vibration peak of ether bond at 1162 cm⁻¹, and a typical symmetric stretching vibration peak of ether bond at 1020 cm⁻¹, which proved the successful preparation of PTMG-WPU. In addition, PCL-WPU and PBA-WPU curves showed typical ester C-O-C vibration absorption peaks at 1210 cm⁻¹, indicating the successful preparation of the two types of polyester WPU^[23].

Water contact angle and water resistance

Table 2
Surface properties of PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU films

Samples	Surface properties			
	water contact angle(°)	water absorption(%)	hardness(HD)	appearance change
PCL-WPU	71.7	26.7	91.5	colorless-milky
PBA-WPU	75.6	22.8	87.0	colorless- white
PCDL-WPU	82.8	17.3	96.5	colorless- pale
PTMG-WPU	89.5	7.5	75.5	no change

It can be seen from Table 2 and Fig. 2 that the water contact angles of polyester PCL-WPU, PBA-WPU and PCDL-WPU were 71.7°, 75.6°, 82.8°, and the water absorption rates reached 26.7%, 22.8%, and 17.3, respectively. Compared with polyether type PTMG-WPU (water contact angle was 89.5°, water absorption rate was 7.5%), the water contact angle value was lower, but the water absorption rate was higher, and the water resistance was relatively poor. This was because the molecular chain of polyester WPU was susceptible to the erosion of water molecules and breaks. The acid generated after the ester group was hydrolyzed would further catalyze the hydrolysis of the polyester, so the water absorption rate of the polyester was relatively high^[24]. For the polycarbonate PCDL-WPU, the carbonate group in the structure had greater strength, higher structural regularity, and strong hydrolysis resistance. Therefore, the water resistance of the polycarbonate PCDL-WPU was stronger than that of the two traditional polyesters PCL-WPU and PBA-WPU, which were consistent with the data obtained in this experiment^[25]. In addition, the changes in appearance, color and transparency of each component film before and after the water absorption test were also shown in Fig. 3 and Table 2. Among them, the polyester PCL-WPU film had the most obvious change, from colorless and transparent before hydrolysis to milky white, polyether type PTMG-WPU film basically did not change before and after the test, which also showed that the hydrolysis performance of polyester type WPU was stronger than that of polyether type WPU.

Surface hardness

Apart from analyzing the water contact angle and water resistance of polymer materials, the hardness of the material was also an important indicator of the surface performance of the WPU film^[26]. As Fig. 4. and Table 2 showed that the shore hardness of the four groups of polyester, polyether, and polycarbonate WPU films were significantly different due to the different types of soft segment components. The hardness of PCL-WPU was 91.5 HD. PBA-WPU was 87.0 HD, PCDL-WPU was 96.5 HD, and PTMG-WPU was 75.5 HD. The relationship between the strength of the surface hardness of the four groups of WPU was:

PCDL-WPU > PCL-WPU > PBA-WPU > PTMG-WPU

The test results showed that the surface hardness of the polycarbonate WPU film was higher than those of the traditional polyester WPU, and the surface hardness of the polyether WPU film was the lowest. This was because polyester PCL-WPU, PBA-WPU and polycarbonate PCDL-WPU contained a large number of ester groups and carbonate groups, and these three types of WPU could not only form hydrogen bonds between the hard segments, but also the groups on part of the soft segment could also form hydrogen bonds with the groups on the hard segment, which was conducive to the uniform distribution of the hard segment phase in the soft segment phase and enhance the surface hardness of the material^[27]. The polyether PTMG-WPU molecular chain contained a large number of ether bonds with low cohesive energy and easy rotation, and its surface hardness was the lowest. In addition, the strength and molecular weight of the carbonate base were higher than the traditional polyester base, so the surface hardness of the polycarbonate type PCDL-WPU was higher than that of the polyester type PCL-WPU and PBA-WPU^[28].

Based on the above, the test and analysis of the water resistance and hardness of the four groups of films of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU showed that the hydrolysis performance of the polyether PTMG-WPU film was the worst. The water contact angle was the largest at 89.5°, the water absorption was the lowest at only 7.5%, and the surface hardness was the lowest at 75.5 HD. The polyester PCI-WPU film had the best hydrolysis performance, the highest water absorption rate was 22.7%, the water contact angle was the lowest, only 71.7°, the surface hardness was relatively high, 91.5 HD, the surface of the polycarbonate PCDL-WPU film hardness was the highest, reaching 96.5 HD.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to test and study the soft segment glass transition temperature (T_g) of the four groups of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films. As shown in Fig. 5., the T_g of the soft segment of the traditional polyester PCL-WPU and PBA-WPU were -52.3°C and -41.8°C , respectively while polycarbonate PCDL-WPU was -20.2°C . This was due to the higher strength of the carbonate base compared with the traditional polyester base, so the T_g of the soft segment moved to the high temperature direction and the glass transition temperature plateau area was larger^[29]. The soft segment T_g of the polyether PTMG-WPU appeared at -58.5°C , which was lower than the other three polyester WPU. This was because the cohesive energy of the ether bond in PTMG-WPU was relatively low and the bond rotation barrier was relatively small, the overall material was soft, the flexibility of the molecular chain was higher than those of polyester WPU. Therefore, the T_g temperature of the soft segment of PTMG-WPU film was the lowest, and the temperature range of the glass transition temperature plateau region was the smallest^[30].

Thermal weight loss

The thermal weight loss test (TGA) of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU four groups of films was carried out to study the thermodynamic properties of each component of WPU. The thermogravimetric curve of each sample was shown in Fig. 6., and the derivative thermogravimetric curve (DTG) was shown in Fig. 7. In addition, the thermal weight loss data of each component WPU was shown in Table 3. As can be seen from Fig. 6., Fig. 7. and Table 3, the thermal stability of polyether PTMG-WPU film was significantly higher than that of the three polyester WPU films. The highest thermal degradation rate T_{max} of PTMG-WPU film reached 411.3°C , and the temperature of $T_{5\%}$ (282.3°C), $T_{10\%}$ (313.4°C) and $T_{70\%}$ (407.8°C) were also significantly higher than that of polyester WPU. This was because the ether bond cohesion energy in polyether type PTMG-WPU was relatively low and the rotational barrier of the bond was small, so the thermal weight loss temperature of polyether type WPU films at each stage was higher and the thermal stability was stronger^[31]. In addition, compared with traditional polyester PCL-WPU, polycarbonate PCDL-WPU showed only a slightly lower temperature of $T_{5\%}$, which was 267.5°C . This was because PCDL-WPU had smaller relative molecular weight compounds and trace moisture after being heated. It was caused by volatilization, but the carbonate bond has a higher bond energy, so its $T_{10\%}$ (302.2°C), $T_{70\%}$ (348.5°C) and T_{max} (346.0°C) temperatures were slightly higher than PCI-WPU^[32]. PCL-WPU showed the worst thermal stability with a T_{max} of only 333.7°C , and its thermal decomposition temperature at each stage was the lowest.

Table 3
Thermal weight loss rates of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

Samples	T5% ^a (°C)	T10% ^b (°C)	T70% ^c (°C)	Tmax ^d (°C)
PCL-WPU	272.2	291.7	341.0	333.7
PBA-WPU	276.7	299.3	384.8	394.7
PCDL-WPU	267.5	302.2	348.5	346.0
PTMG-WPU	282.3	313.4	407.8	411.3
^a Temperature corresponding to 5% weight loss.				
^b Temperature corresponding to 10% weight loss.				
^c Temperature corresponding to 70% weight loss.				
^d Temperature corresponding to maximum decomposition rate.				

Mechanical properties

The mechanical properties of WPU with different soft segment composition were studied by tensile test. The tensile curve of each component sample was shown in Fig. 8., and the mechanical properties of the material were shown in Table 4. As can be seen from Fig. 8. and Table 4, the elongation at break of polyether PTMG-WPU was the highest, reached 943.5%, while the tensile strength was the lowest, only 42.3 MPa. Compared with the other three polyester WPU, the mechanical properties were the worst. This was due to the soft segment accounts for more than the hard segment in the WPU structure, and the ether bond was lower and weaker than the ester bond. The polyester WPU contained ester groups with stronger bond energy, and the interior of the matrix could not only be hard hydrogen bonds were formed between the segments, and part of the groups on the soft segment could also form hydrogen bonds with specific groups on the hard segment, so that the hard segment phase of WPU was more uniformly dispersed in the soft segment phase and elastic crosslinking^[33]. Therefore, when comparing polyether WPU and polyester WPU, the overall structure was soft, with high elongation at break but low tensile strength. The carbonate groups in the polycarbonate PCDL-WPU had a high strength and a large modulus while the WPU molecular chain showed a relatively short chain length and a complex side chain structure with dense groups. Compared with traditional polyester WPU, it showed poor flexibility, the elongation at break and the tensile strength of which were lower, only 480.1%, 55.1 MPa^[34]. In addition, polyester PCL-WPU had the characteristics of soft-segment crystallization at room temperature, so the elongation at break and tensile strength of PCL-WPU were higher than those of PBA-WPU by 764.3% and 57.8 MPa, reaching 857.9% and 58.3 MPa respectively^[35].

Table 4
Mechanical properties of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

Samples	Young's Modulus	Tensile Strength	Elongation of break	Hardness
	(MPa)	(MPa)	(%)	(HD)
PCL-WPU	22.9	58.3	857.9	91.5
PBA-WPU	18.3	57.8	764.3	87.0
PCDL-WPU	16.8	55.1	480.1	96.5
PTMG-WPU	14.1	42.3	943.5	75.5

Biodegradability

The relationship between the degradation rate and the degradation time of each group of samples in the PBS buffer solution dissolved with biological lipase and in a humid soil environment with sufficient oxygen was studied. The curves of the two degradation experiments were shown in Fig. 9. and Fig. 10., respectively. It could be seen that the degradation rate of polyether PTMG-WPU in 0.6% lipase PBS buffer solution and soil microorganisms was very low. The degradation rate in the first 3 days is basically zero, and then it began to slowly degrade. After the degradation reaction lasted for 15 days, the degradation effect basically reached the maximum degree. The degradation rate in the lipase solution and the soil was 4.2% and 2.3%. When the degradation time reached 30 days, the degradation rate changed little compared with 15 days, reached 4.4% and 2.4%. This was due to the ether bond on the main chain of the polyether WPU molecule had low cohesive energy and excellent hydrolysis resistance. The degradation effect of the polycarbonate PCDL-WPU was significantly lower than that of the two traditional polyester WPU. This was due to the high strength of the carbonate group in the PCDL-WPU, the relatively superior film surface performance, strong hydrophobicity, and effective reduction the corrosive action of water molecules and microorganisms, so that the 30-day degradation rate in the two degradation systems was only 12.7% and 7.0%^[36]. For traditional polyester PCL-WPU and PBA-WPU, the hydrolysis performance of PCL-WPU was higher than that of PBA-WPU. Therefore, under the same conditions, the biodegradation effect of PCL-WPU was significantly stronger than that of PBA-WPU. After testing and analysis, it was concluded that the degradation rate of PBA-WPU in the two degradation systems was 35.3% and 18.8%, respectively, while the degradation rate of PCL-WPU in the two degradation systems for 30 days was the highest, reached 41.7% and 32.0%. In addition, the maximum degradation rate of the four WPU films generally occurred within the 3rd to 15th days of degradation. This was because the degradation effect of each group of samples at this time has expanded from the breakage of the molecular chain side chain or partial degradation within the first 3 days to the destruction of the overall structure and the collapse of the main chain of the molecular chain^[37]. The degradation effect of each group of samples in the soil was lower than that in the 0.6% lipase PBS buffer solution, because the activity and degradation ability of

the biological enzymes in the solution were far stronger than the soil, which could more effectively and quickly cause the membrane corrosion, destroy the molecular structure of WPU^[38].

Scanning electron microscope

Scanning electron microscope (SEM) was used to observe and analyze the surface structure of the four groups of films of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU degraded by the above two biodegradation experiments. The specific results were shown in Fig. 11. and Shown in Fig. 12. Firstly, in the first 3 days of biodegradation in 0.6% lipase PBS buffer solution, the surface of the two groups of traditional polyester WPU sample films of PCL-WPU and PBA-WPU showed small holes and cracks in a local area, respectively. Corresponding to (a) and (b) in Fig. 11., while the surface of the polycarbonate PCDL-WPU and polyether PTMG-WPU films did not change significantly, and there were no holes and cracks, corresponding to (c) and (d) in Fig. 11. Secondly, when the biodegradation reached 7 days, it could be found that the number of holes on the surface of the two groups of PCL-WPU and PBA-WPU and the depth of the cracks further expanded, and the biodegradation effect spread to the entire sample surface, corresponding to the (e) and (f), and at this time, the PCDL-WPU and PTMG-WPU two sets of membranes showed holes and cracks in a local area, corresponding to (g) and (h) in Fig. 11., However, there was a huge gap between the number of holes and the size of the cracks compared with the two groups of polyester WPU, and the biodegradation effect was obviously low. Compared with polyether WPU, polyester WPU had lower biodegradation resistance under the same conditions, and the degradation effect was more obvious^[39]. Finally, when the biodegradation reached 15 days, the surface degradation of the PBA-WPU membrane continued to increase, and the number and size of pores increased significantly compared with the 7 days degradation, corresponding to (b) in Fig. 12. The surface morphology of the PCL-WPU film was completely changed. A large number of holes and ridges were distributed on the surface of the sample. The degradation degree and effect were more than that of the traditional polyester type PBA-WPU and the polycarbonate type PCDL-WPU, corresponding Fig. 12 (a). The surface degradation of the two groups of PCDL-WPU and PTMG-WPU films further deepened, and the size of the pores on the film surface and the depth of the cracks continued to increase, corresponding to (c) and (d) in Fig. 12., respectively. Compared with PCDL-WPU film, PTMG-WPU film had a lower number of holes and crack size after degradation, and its biodegradation effect was relatively poor. This was due to that compared with polyester WPU and polycarbonate WPU, polyether WPU had the best hydrolysis resistance and the lowest degree of degradation under the action of lipase and water^[40]. In addition, the four groups of films of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU were biodegraded in soil for 15 days. The surface degradation of the film was tested and analyzed, which corresponds to (e), (f), (g), (h) in Fig. 12. Compared with the degradation degree of each component sample in 0.6% lipase PBS buffer solution, the degradation effect of soil was lower.

Conclusion

Compared with polyether-based PTMG-WPU and polycarbonate PCDL-WPU, the molecular structure of traditional polyester-based PCL-WPU is more easily destroyed by the erosion of biological lipase and water

molecules, and the acidic products produced after hydrolysis will further promote polymerization. The degradation of esters, therefore, PCL-WPU has the best hydrolysis performance and biodegradability under the same conditions, and the degradation effect is the most obvious. The degradation rate of PTMG-WPU and PCDL-WPU after 30 days of degradation in 0.6% lipase PBS buffer solution and soil is only 4.2%, 2.3% and 11.2%, 6.5%, while the degradation rate of traditional polyester PCL-WPU is the Highest, reached 41.7% and 32.0% respectively. In addition, the cohesive energy of the polyester group and the bond energy of the ester bond are higher than those of the polyether group and the ether bond. Therefore, the mechanical properties of PCL-WPU are relatively high, with a tensile strength of 58.3 MPa and an elongation at break of 857.9 %. However, in terms of thermal performance, PCL-WPU shows poor thermal stability, the soft segment T_g is -52.3°C, and the maximum weight loss rate temperature T_{max} is only 333.7°C. Comprehensive analysis shows that polycaprolactone diol PCL is the best choice for preparing biodegradable WPU.

Declarations

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Figures

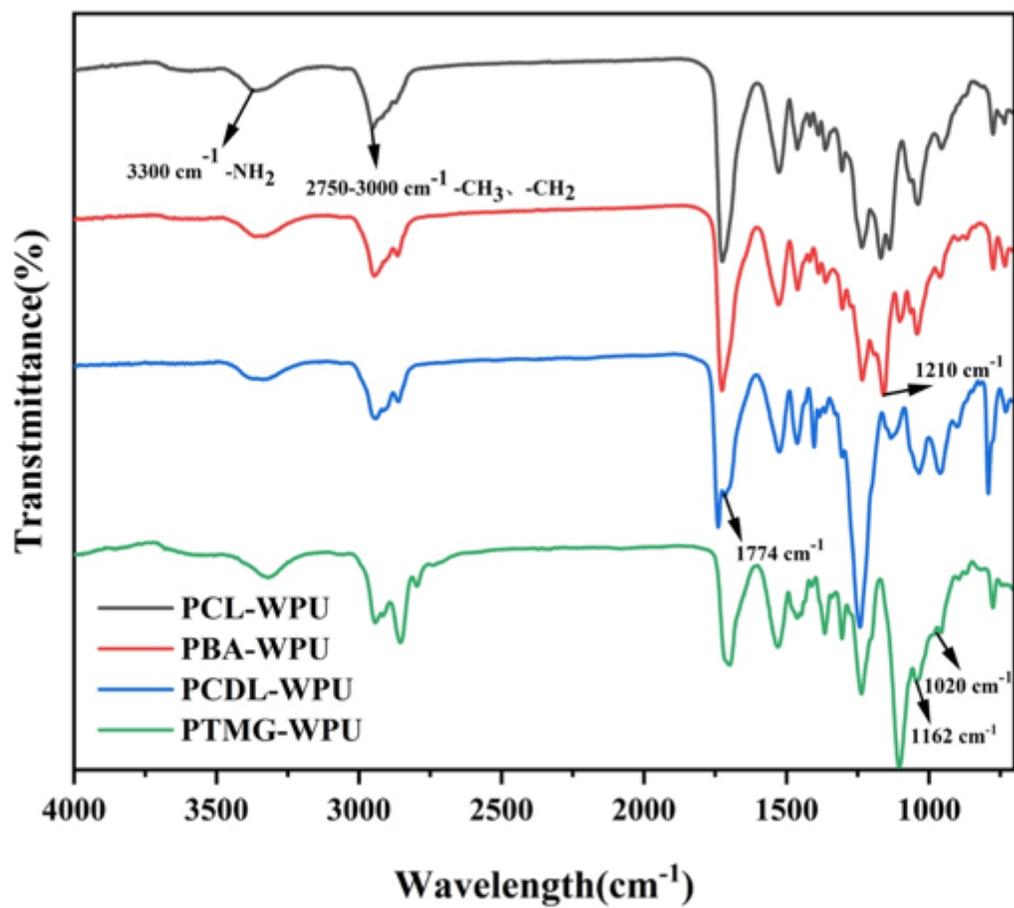


Figure 1

FTIR spectra for PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

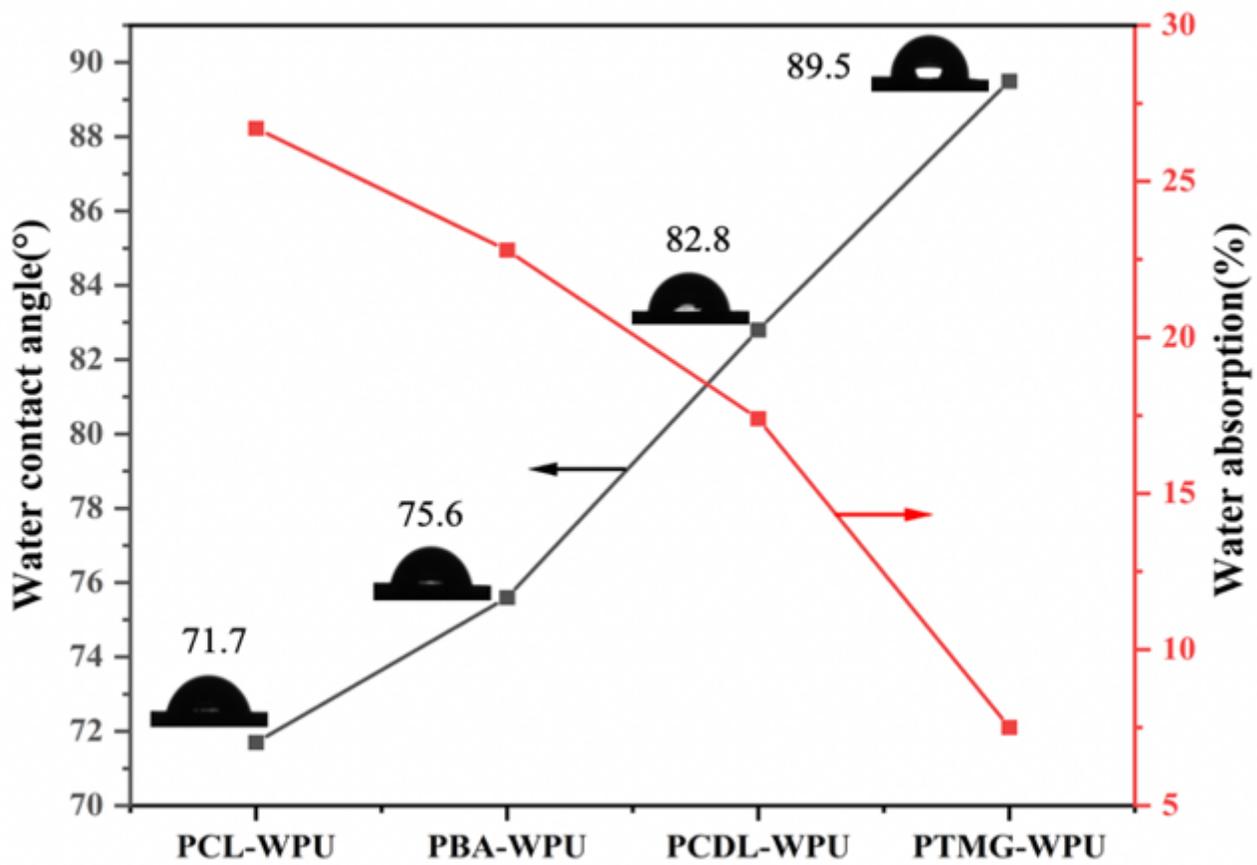


Figure 2

Contact angles and water absorption of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

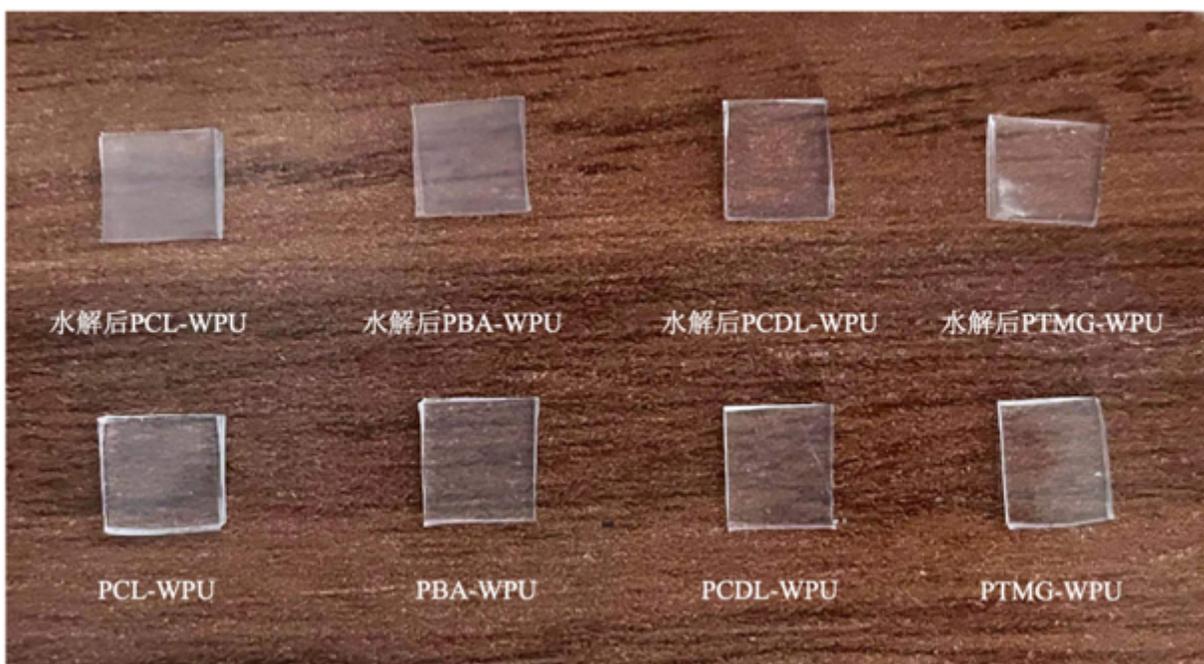


Figure 3

Comparison of appearance of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU before and after hydrolysis

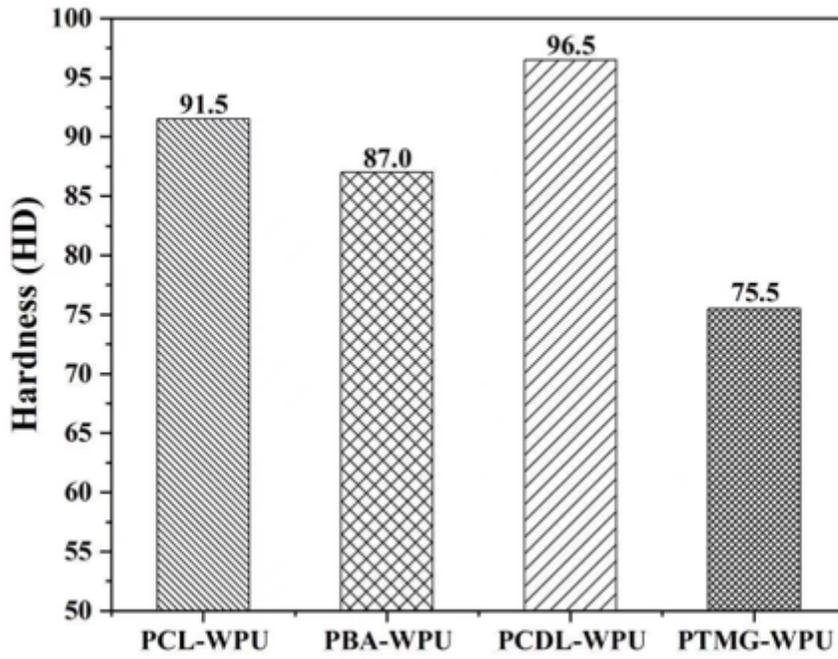


Figure 4

Hardness of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

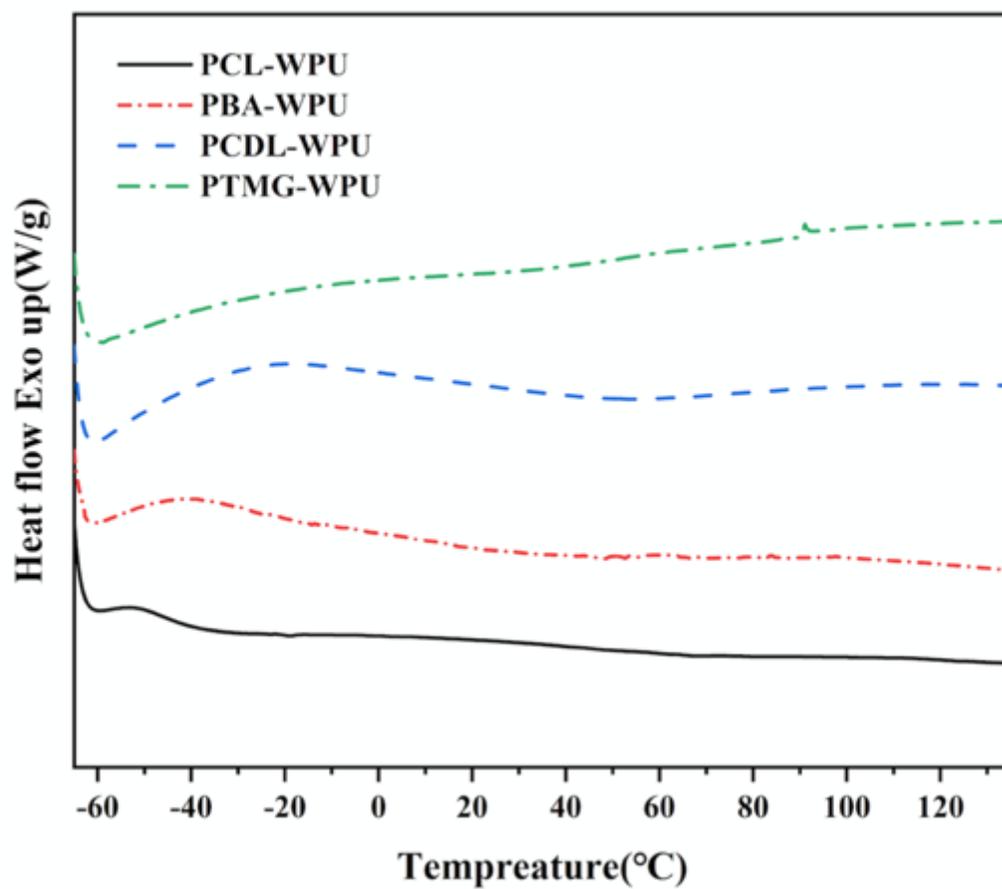


Figure 5

DSC of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

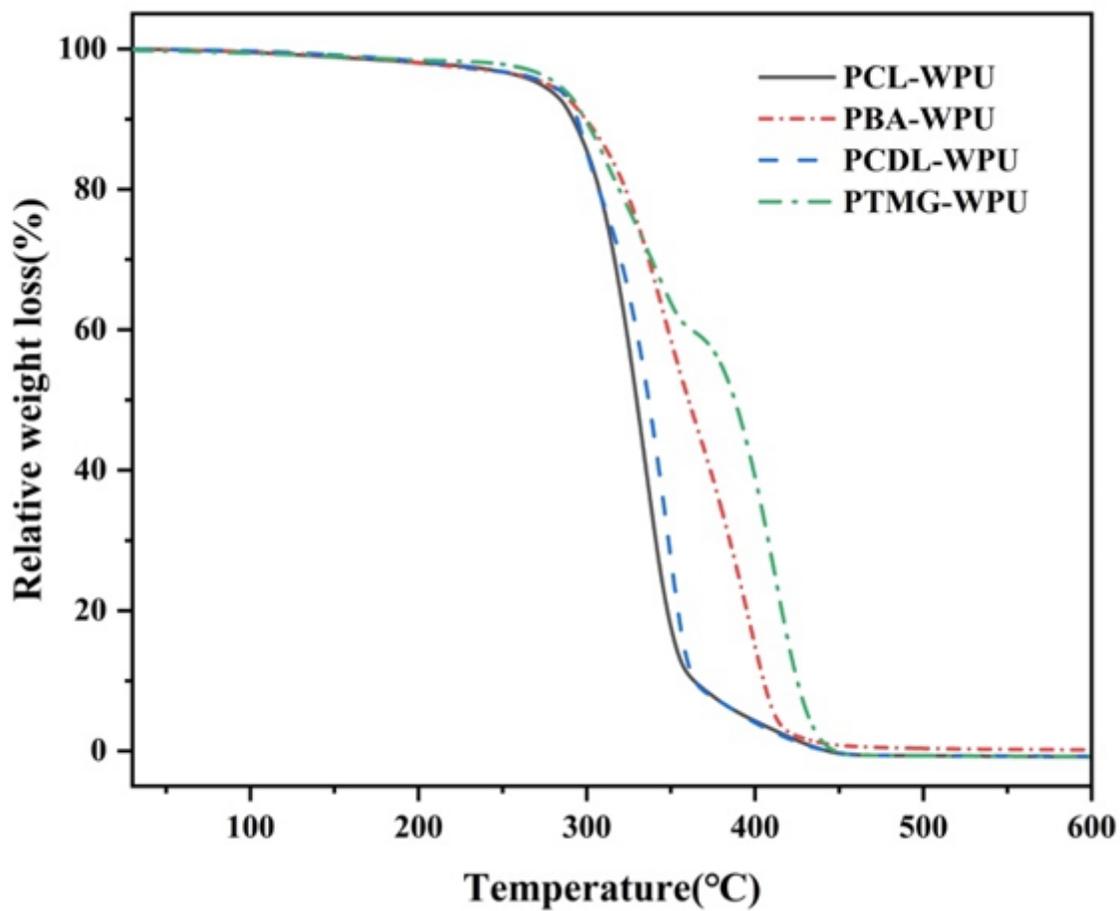


Figure 6

TGA of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

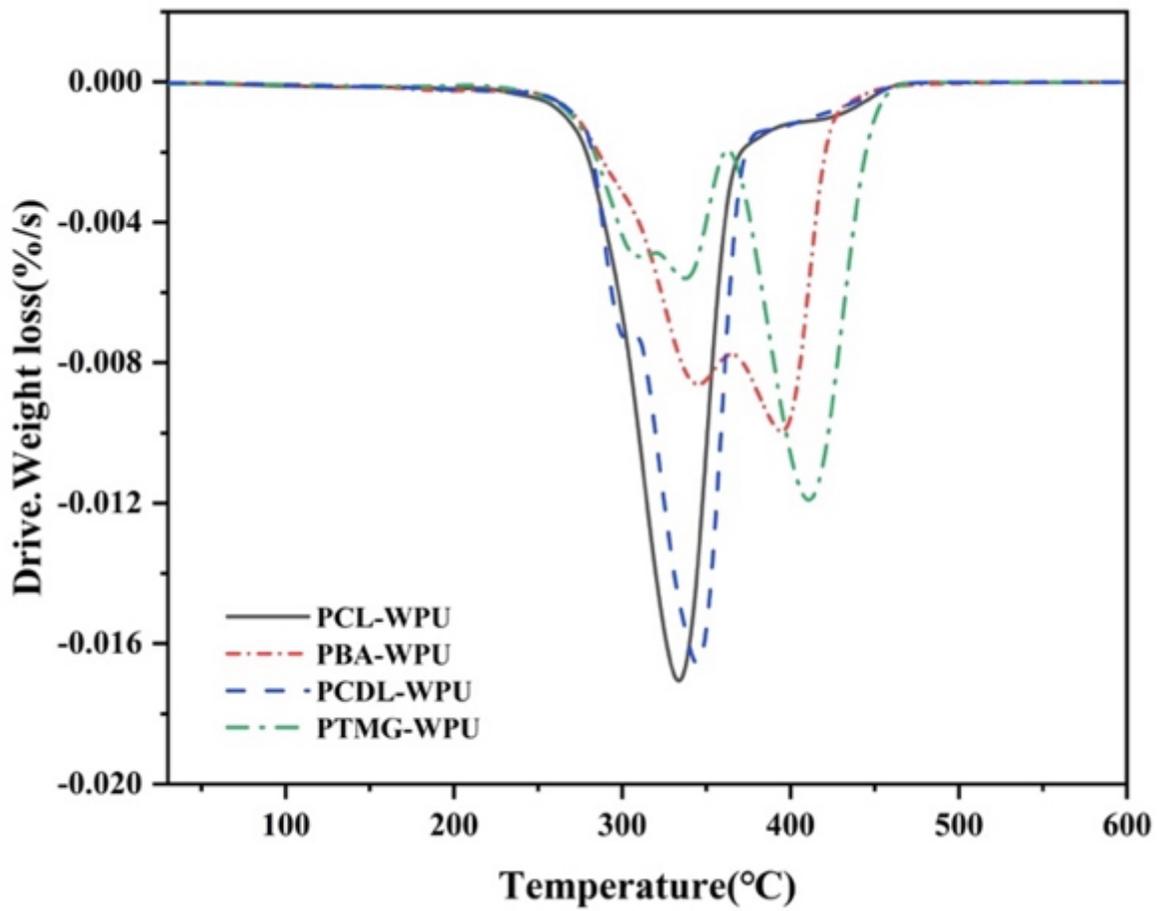


Figure 7

DTG of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

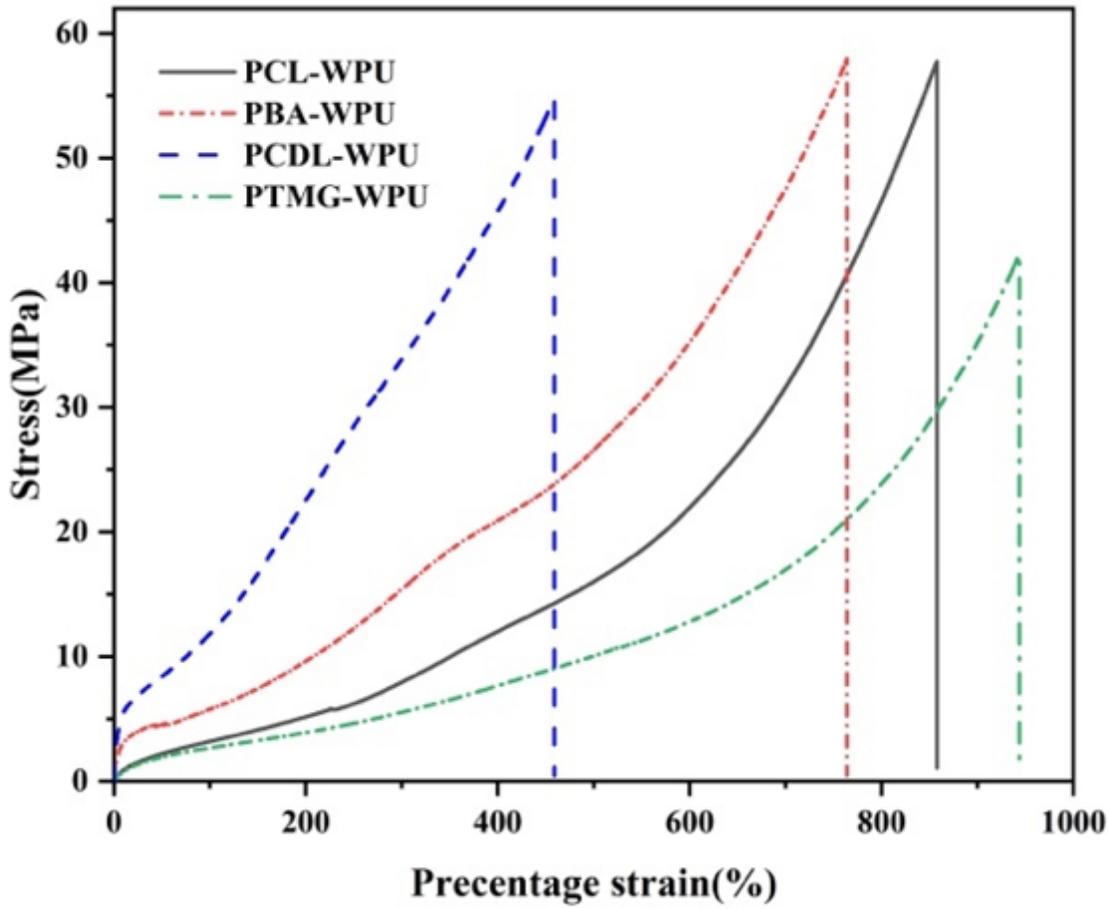


Figure 8

Stress-strain behaviors of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films

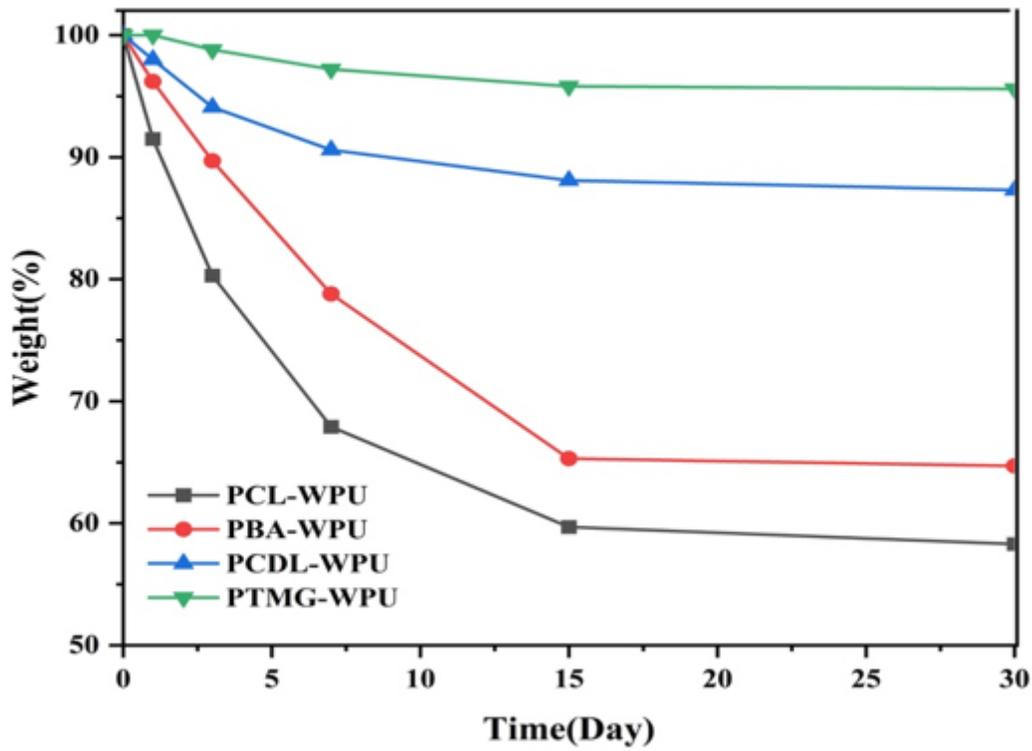


Figure 9

Weight loss of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films with impregnation time in 0.6% lipase PBS buffer solution

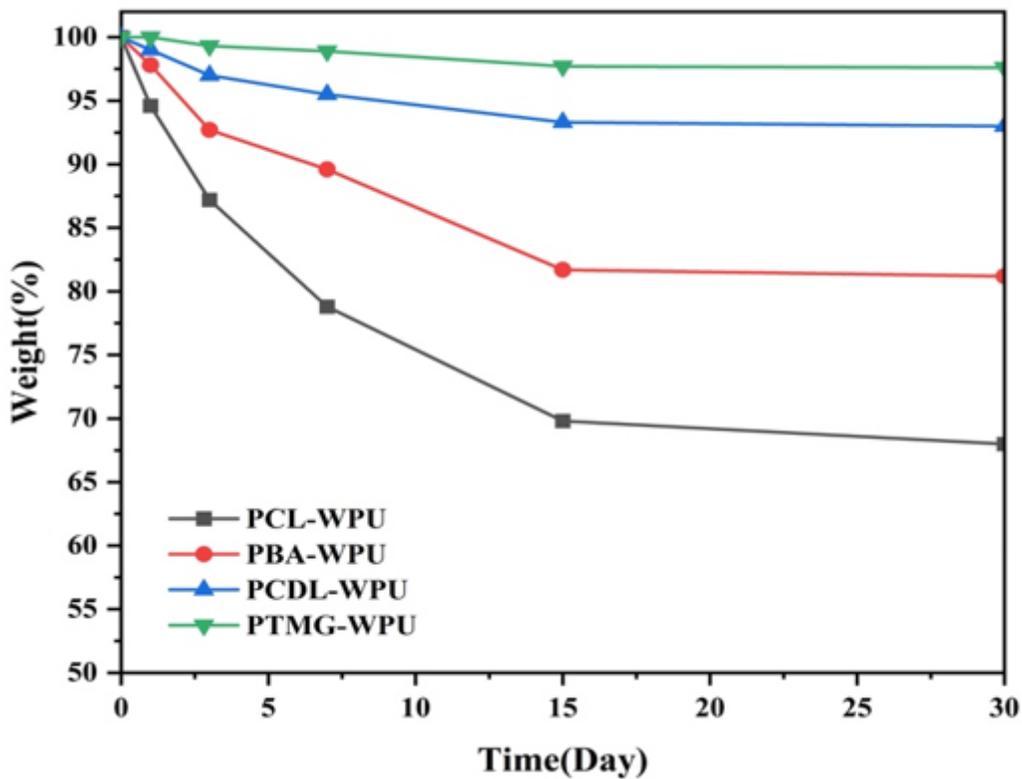


Figure 10

Weight loss of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films with impregnation time in soil

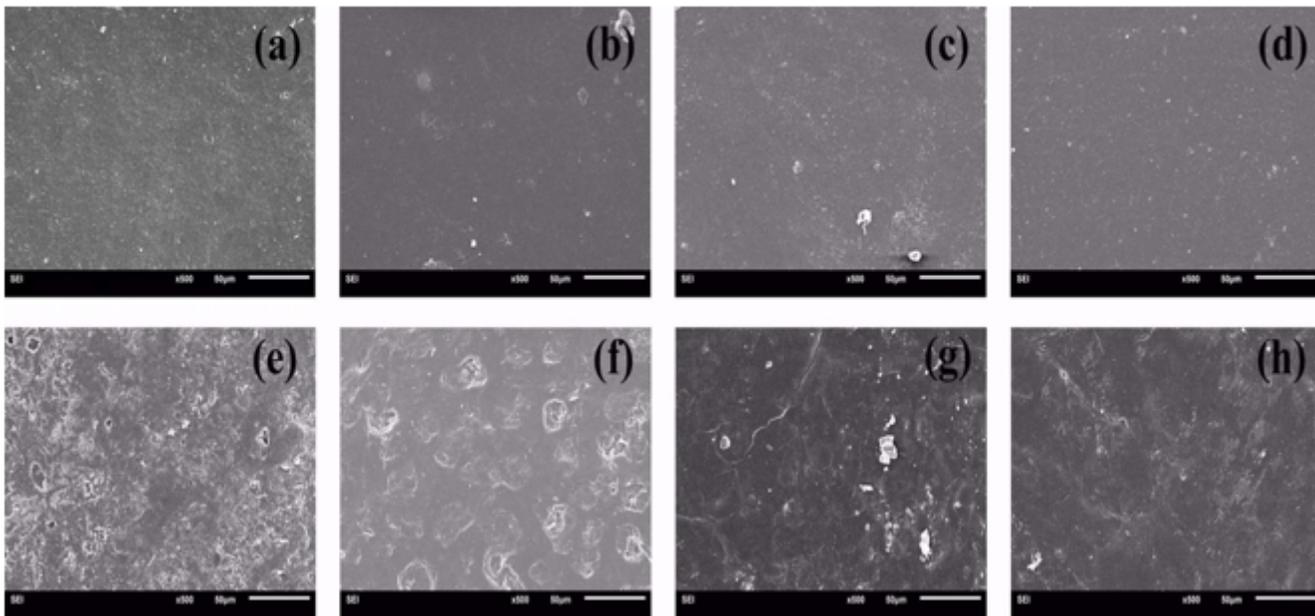


Figure 11

Surface electron microscope images of degradation of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films in 0.6% lipase PBS buffer solution, (a) surface morphology of PCL-WPU after 3 days of degradation, (b) surface morphology of PBA-WPU after 3 days of degradation, (c) surface morphology of PCDL-WPU after 3 days of degradation, (d) surface morphology of PTMG-WPU after 3 days of degradation, (e) surface morphology of PCL-WPU after 7 days of degradation, (f) surface morphology of PBA-WPU after 7 days of degradation, (g) surface morphology of PCDL-WPU after 7 days of degradation, (h) surface morphology of PTMG-WPU after 7 days of degradation

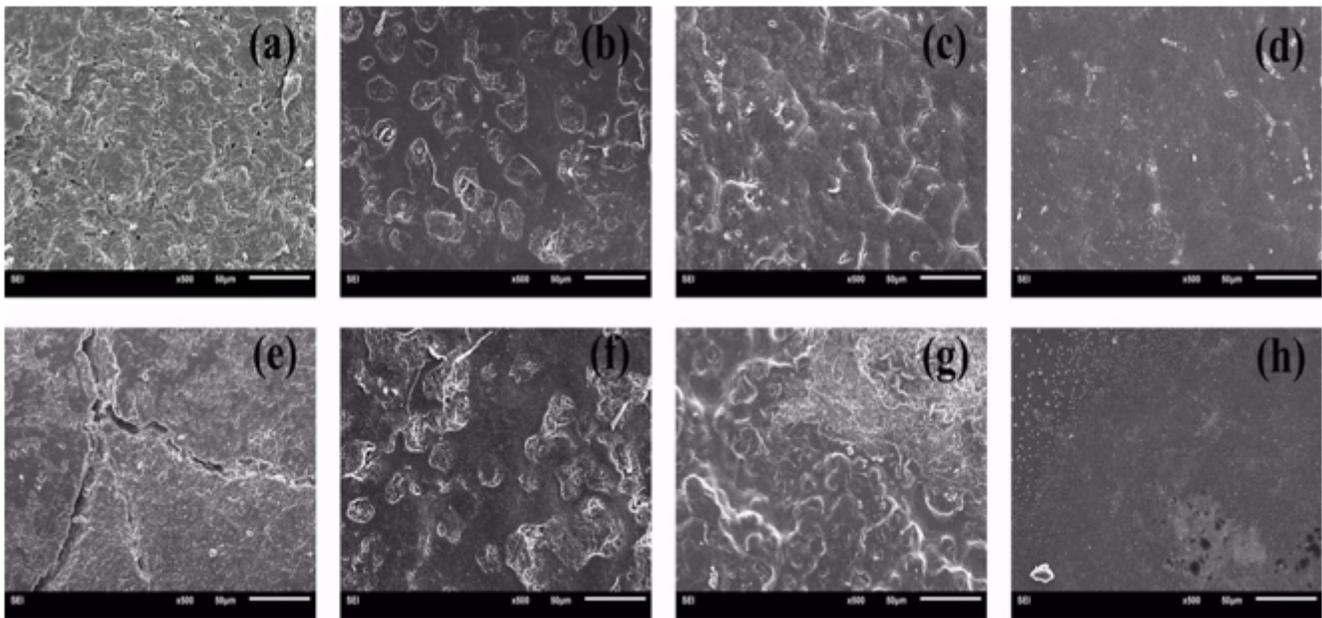


Figure 12

Surface electron microscope images of degradation of PCL-WPU, PBA-WPU, PCDL-WPU and PTMG-WPU films in 0.6% lipase PBS buffer solution and soil, (a) surface morphology of PCL-WPU lipase degradation after 15 days, (b) surface morphology of PBA-WPU lipase degradation after 15 days, (c) surface morphology of PCDL-WPU lipase degradation after 15 days, (d) surface morphology of PTMG-WPU lipase degradation after 15 days, (e) surface morphology of PCL-WPU soil degradation after 15 days, (f) surface morphology of PBA-WPU soil degradation after 15 days, (g) surface morphology of PCDL-WPU soil degradation after 15 days, (h) surface morphology of PTMG-WPU soil degradation after 15 days

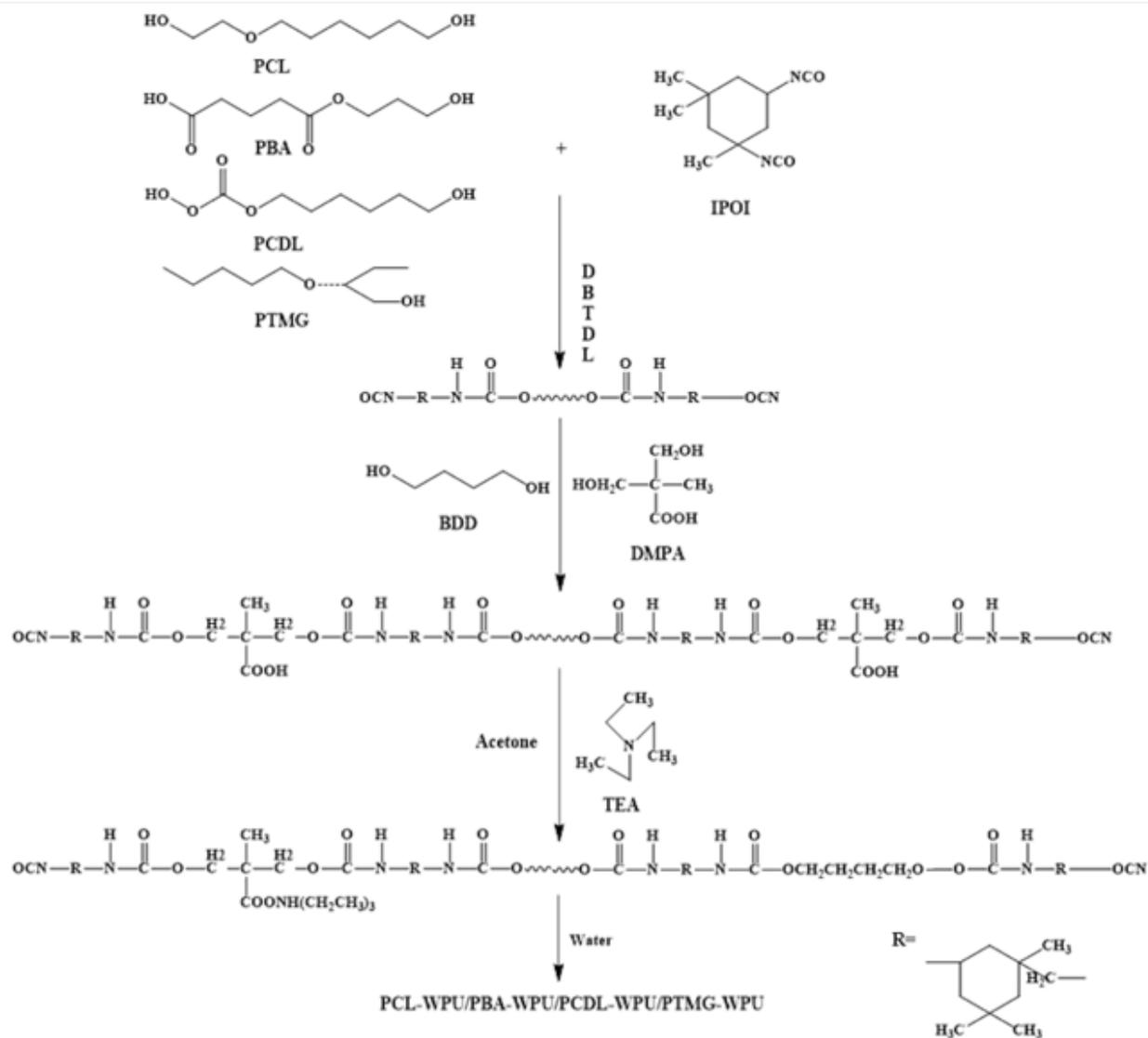


Figure 13

Scheme 1 Synthesis of PCL-WPU, PBA-WPU, PCDL-WPU, PTMG-WPU