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UV curable hyperbranched polyester polyurethane acrylate for hydraulic machinery coating

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Abstract

The content of river cement and sand in our country is relatively high, and the surface of hydraulic machinery in hydropower stations is often subject to fatigue damage and erosion. This topic is mainly used to solve the problem of abrasion and corrosion of hydraulic machinery coatings. UV curable polyester polyurethane acrylate (PUA) can be quickly solidified into film and directly coated on the surface of hydraulic machinery with excellent anti-wear, adhesion properties and low cost. In this work, a hyperbranched polyester synthesized by the stepwise reaction of trimethylolpropane (TMP) and dimethylolpropionic acid (DMPA) was as a ‘nucleus’, and the polyurethane prepolymer was obtained by grafting IPDI and PTMG. The UV-curing hyperbranched polyester polyurethane acrylate (PUA-1) was prepared by capping with HEA. Another UV-curing hyperbranched polyester polyurethane acrylate (PUA-2) was prepared as comparison by using TDI and PTMG as the main raw materials. Fourier Transform Infrared Spectrometer, ¹H-nuclear magnetic resonance spectroscopy, Gel Permeation Chromatography, thermogravimetric analysis and dynamic thermomechanical analysis were used to characterize its structure and properties. The wear rate of the two hyperbranched polyesters measured by the underwater steel ball method is below 3%, The swelling rate of PUA-1 is between 250%–300%, and the swelling rate of PUA-2 is around 260%, indicating that PUA-2 has better solvent resistance than PUA-1, and the internal structure of the film is more dense. TG analysis showed that the thermal stability of the two materials was good.

1. Introduction

The sediment content in the rivers of our country is relatively high. Approximately 40% of hydropower stations have sediment erosion problems, which have a great impact on the service life and working efficiency of hydraulic machinery such as water pumps and turbines. The annual shutdown and maintenance cause huge economic losses. Therefore, improving the abrasion resistance of hydraulic turbines has always been an important research direction in the field of hydraulic machinery.

Ultraviolet (UV) curing polyurethane acrylate (PUA) coatings have been widely studied and used because they solve the problems of large hydraulic machinery and difficult construction. The film can be directly cured by UV irradiation, exhibiting good abrasion resistance and bonding performance. Hu [1] used hydroxyl-
terminated hyperbranched polymer and TDI, PEG, hydroxy silicone oil, dimethylolpropionic acid, etc as raw materials to prepare silicon-modified hyperbranched PUA. The adhesion of the photocurable film after coating was one Grade, hardness 4H, good water resistance and wear resistance. Through the method of molecular design, Feng [2] introduced the triblock polyether ester PLEL soft segment into the polyurethane acrylate segment, obtaining a cross-linked PUA material by UV curing. Li [3] used polyurethane composite resin mortar technology to protect the flow parts of the turbine from abrasion. Not only its anti-wear performance was significantly improved, but it also overcomes the shortcomings of epoxy carborundum coating’s poor anti-cavitation performance in water turbine applications. But the bonding strength and wear resistance are not enough for hydraulic mechanical surface.

PUA coating combines the advantages of both polyurethane and acrylate. When subjected to external stress, the hydrogen bond breaks due to molecular absorption energy, thus avoiding the breakage of urethane bond and even the degradation of polymer. It also has the advantages of good weather resistance, ultraviolet light degradation and yellowing resistance of acrylate. Therefore, the application of UV curable PUA in the field of hydraulic machinery is expected to make significant technological progress.

UV hyperbranched PUA are three-dimensional network structure polymers with a large amount of active characteristic end-groups. Compared with its linear counterpart, they possess greater advantages than the linear counterpart in terms of performance.

A high crosslink density after film formation of hyperbranched PUA makes hardness increase, solvent resistance enhance as well as curing fast; the hyperbranched PUA branches are mostly long alkyl chains, reducing the shrinkage of the film during UV curing and increasing the adhesion of the coating; nano-scale gaps which can accommodate inorganic fillers to improve their properties exist between hyperbranched PUA branching groups; hyperbranched PUA has spherically symmetric three-dimensional structure as well as no entanglement occurring within molecular and between molecules, it offers lower viscosity and higher solubility to improve the fluidity of resins and reduce solvent usage, thereby reducing the emission of harmful gases, and more in line with environmental requirements.

They possess great advantage and broad application prospects in the fields of coatings, functional film materials, biomedical materials and so on [3]. Polytetrahydrofuran (PTMG2000) as the soft chain end of block polyurethane can make the PUA material have good mechanical properties and lower glass transition temperature. Usually, UV-cured films prepared with this type of hyperbranched PUA exhibit excellent hardness, chemical resistance and scratch resistance.

In this paper, trimethylolpropane (TMP) was used as the ‘nucleus’ as shown in figure 1, and dimethylolpropionic acid (DMPA) was used as the raw material. The hyperbranched polyester was synthesized by stepwise polymerization. The hyperbranched PUA was prepared from the polyurethane prepolymer of the group, and its molecular structure, mechanical properties, molecular weight and thermal stability were investigated [4].
2. Experimental section

2.1. Materials
PTMG2000 was treated by rotary steaming before using, and dimethyl carbonate (DMC) was used to remove water before using 4 Å molecular sieve. Trimethylolpropane (TMP), 2,2-dimethylolpropionic acid (DMPA), P-toluenesulfonic acid (p-TSA), Isophorone disocyanate (IPDI), Toluene disocyanate (TDI), Polytetrahydrofuran (PTMG2000), Hydroxyethyl acrylate (HEA), Dibutyltin dilaurate (DBTDL), Tripropylene glycol diacrylate (TPGDA), Benzoin dimethyl ether was purchased at Shanghai Macklin Biochemical Technology Co., Ltd. In contrast, Dimethyl sulfoxide (DMSO) was purchased at National Pharmaceutical Reagent Co., Ltd.

2.2. Synthesis of hyperbranched polyester
The reaction needs to be carried out in a device with good airtight conditions and protected with nitrogen. We can see from the figure 4 that 0.17 g TMP and 0.50 g DMPA (molar ratio 1:3) were first added into three bottles with DMSO as solvent and p-TSA (about 1 wt%) as catalyst. The catalyst was added to the solvent, then the solvent was dropwised into the reaction system. Reaction temperature must be reduced before adding the catalyst.

Maintain the stability of the reaction temperature at 140°C to prevent hyperbranched polyester from violent polymerization to gel, reflux reaction was heated for 5 h. A suitable amount of p-TSA and 1.01g of DMPA were added again by step-by-step polymerization method. The viscosity of the reaction was observed at all times to control the speed of the hyperbranched reaction. After reaction for 5 h, hyperbranched polyurethane prepolymer was obtained. And 1.74 g of HEA was added as end-capping agent to prepare hyperbranched PUA-1. Appropriate amount of active diluent TPGDA and photoinitiator benzoin dimethyl ether (about 5%wt of the reaction component) was added to the system, stirred evenly, poured into the PTFE mould. The uniform and transparent film can be cured quickly in about 10 min under UV light irradiation. In addition to the second step of reacting TDI with PTMG2000 (molar ratio 1:2), the other reaction steps are the same as above, and PUA-2 can be obtained. Synthetic routes of PUA-1 and PUA-2 are showed in figure 3. The overall flow chart of the experiment is shown in figure 4.

2.3. Synthesis of PUA-1 and PUA-2
Bulk polymerization was carried out by adding 6.67 g of IPDI and 30 g of PTMG2000 (molar ratio of 2:1) to obtain a polyurethane prepolymer containing –NCO groups. The hyperbranched polyurethane prepolymer was prepared by reaction of hyperbranched polyester with polyurethane prepolymer under 70°C for 4 h, during which a moderate amount of DMC with low-boiling point was added as solvent, then hyperbranched polyurethane prepolymer was obtained. And 1.74 g of HEA was added as end-capping agent to prepare hyperbranched PUA-1. Appropriate amount of active diluent TPGDA and photoinitiator benzoin dimethyl ether (about 5%wt of the reaction component) was added to the system, stirred evenly, poured into the PTFE mould. The uniform and transparent film can be cured quickly in about 10 min under UV light irradiation. In addition to the second step of reacting TDI with PTMG2000 (molar ratio 1:2), the other reaction steps are the same as above, and PUA-2 can be obtained. Synthetic routes of PUA-1 and PUA-2 are showed in figure 3. The overall flow chart of the experiment is shown in figure 4.

2.4. Testing Process
2.4.1. Structure characterization
2.4.1.1. ATR-FT-IR
PUA liquid without additives such as active diluent and initiator was coated on KBr salt tablets. ATR-FT-IR was carried out at 25°C by SHIMADZU FT-IR-8700 infrared spectrometer with resolution of 4 cm⁻¹ and wave number range of 4000–500 cm⁻¹.
2.4.1.2. $^1$H-NMR

A sample of more than 5 mg was taken and dissolved in deuterated chloroform, and subjected to 1H-NMR measurement via the Acance III-400 MH type nuclear magnetic resonance spectrometer (NMR).

Figure 3. Synthetic routes of (a) PUA-1 and (b) PUA-2.
2.4.1.3. GPC
The PUA liquid was treated with a rotary evaporator to remove the solvent. A gel of about 5 mg was obtained and
dissolved by chromatographic grade six fluoroisopropyl alcohol to prepare the sample to be tested. By using the
Waters Corp Waters 1515 Isocratic HPLC Pump instrument, the sample containing three FLUOROACETIC
acid, six fluoroisopropanol as solvent and the mobile phase testing system, was adopted. The molecular weight
and its distribution of the sample can be calculated.

2.4.2. Tensile performance
According to GB/T 528–2009, the PUA cured film is cut into a type 3 dumbbell-shaped sample by a cutter and a
tableting machine, the experimental length is 10.0 ± 0.5 mm, and the spline thickness is 2.0 ± 0.2 mm (the
thickness is measured by an electronic vernier caliper, Take the middle and the average of both ends). The spline
was placed on the fixture of universal tension machine to make the specimen symmetrical and the testing speed
was 200 mm min⁻¹.

2.4.3. Shear strength
According to GB/T 7128–2008, the tensile shear strength of PUA was measured. The rigid material was made of
smooth plexiglass plate or metal aluminum plate. The length of the bonding surface was 12.5 ± 0.5 mm, and the
end of the bonding surface was 50 ± 1 mm from the bonding surface. The number of samples tested in each
group is not less than five, and the average value of the breaking load (N) is taken during data processing. The
shear strength of samples is the same as Formula (1):

\[
\text{Tensile shear strength (MPa)} = \frac{\text{Failure load (N)}}{\text{Shear area (mm}^2\text{)}}
\]  

2.4.4. Curing time
A proper amount of PUA liquid was poured into the polytetrafluoroethylene mold and cured by LED UV light
curing system. The time of light reaction was recorded. Each formula was tested for 10 groups and taken the
average value.

2.4.5. Hardness of cured film
According to GB/T 2411–2008, the indentation hardness (Shore hardness) was determined by using a hardness
tester. The sample was made into a smooth film with a thickness of more than 4 mm. The average value was
taken after five measurements on the surface of the same sample were maken. Each measurement point was
more than 9 mm from the edge of the sample, and the interval between any two measurement points was not less
than 6 mm.
2.4.6. Dynamic mechanical performance
PUA curing film was cut into 4 dumbbell-shaped standard specimens with thickness of 0.5–1.0 mm. The dynamic mechanical properties of PUA were measured under N₂ protection by using Q 800 dynamic mechanical property analyzer of TA instrument in USA. The test conditions were: DMA multi-frequency strain mode, tension-film fixture, strain set to 0.2%, test frequency was 1 Hz, heating rate was 5 °C min⁻¹, temperature range was −75 °C–5 °C.

2.4.7. Thermogravimetric analysis
Using STA 449C thermogravimetric analyzer of NETZSCH company in Germany, the sample quality is about 8 mg, protected by N₂, the heating rate is 10 °C min⁻¹, and the temperature range is 30 °C–600 °C.

2.4.8. Anti-abrasion performance
With reference to the experimental method in standard SL 352–2006 and literature, after the anti-abrasion concrete base was treated with primer, the PUA film of 1000 mm × 1000 mm × 2 mm was bonded and injected into the die testing machine. Clean water, the steel ball combination simulating wear media was 30 mm for 3, 25.4 mm for 17, 19.1 mm for 33, 12.5 mm for 62, the projected area of the steel ball covered 50% of the surface of the base. The speed of the stirring paddle was adjusted to 3000 r min⁻¹ (at this time, the near-bottom flow velocity of the sample surface was about 3.2 m s⁻¹), the erosion time was 8 h, and the film surface was carefully observed every 2 h during the period. Finally, the wear and erosion resistance of the film were calculated, the relative abrasion resistance of the material was assessed.

2.4.9. Water absorption and swelling ratio
The cured film after drying was cut into 30 mm × 30 mm × 2 mm square sample and weighed as W₀. The sample was immersed in 100 °C boiling water for 10 h, and the sample was taken out every 2 h. After drying the surface with absorbent paper, the weight was measured once and recorded as W₁. Five groups of data were recorded. The calculation of water absorption of samples is the same as Formula (2):
Table 1. The molecular weight and distribution of PUA-1 and PUA-2.

| Decomposition temperature (°C) | M_d (g/mol) | M_w (g/mol) | PDI  |
|--------------------------------|-------------|-------------|------|
| PUA-1                          | 24.9 × 10^3 | 56.3 × 10^3 | 2.5  |
| PUA-2                          | 25.3 × 10^3 | 39.9 × 10^3 | 1.6  |

\[
\text{water absorption (\%) = } \frac{W_f - W_0}{W_0} \times 100\% \quad (2)
\]

Firstly, the cured film of 30 mm × 30 mm × 2 mm was dried and weighed as \( W_0 \). The sample was immersed in 500 ml acetone and weighed as \( W_f \) every 2 h until it was measured to 10 h. The swelling rate of cured film is calculated by the same formula as Formula (3):

\[
\text{swelling ratio (\%) = } \frac{W_f}{W_0} \times 100\% \quad (3)
\]

3. Results and conclusions

3.1. Structure characterization

The FTIR diagram of the polyhydroxy hyperbranched polyester is showed in figure 5(a). The broad absorption peak at about 3410 cm\(^{-1}\) for the association peak of strong hydroxyl group (–OH) appears, indicating that there are a large number of hydroxyl groups in the product, while the stretching vibration peak for ester carbonyl group (–C=O) at 1713 cm\(^{-1}\) can be found. The strong peak at 1030 cm\(^{-1}\) is the ester group (–CH\(_2\)–O–CO–), which indicates the formation of hyperbranched polyester containing hydroxyl group. Figure 5(b) is the FT-IR diagram of PUA. The peak near 3320 cm\(^{-1}\) is the stretching vibration peak of N–H and the bending vibration peak of N-H at 1532 cm\(^{-1}\) [6, 7]. The characteristic peaks in the range of 2275–2240 cm\(^{-1}\) indicate that the system contains residual –NCO groups; the in-plane and out-of-plane bending vibration absorption peaks of the –C–H group on HEA are at 1409 cm\(^{-1}\) and 810 cm\(^{-1}\), respectively [8]. In addition, the absorption peaks of hydroxyl groups near 3400 cm\(^{-1}\) did not appear, indicating that hyperbranched polyester and acrylate have completely reacted. The above results show that PUA has been synthesized.

Figure 5(c) is a \(^1\)H-NMR diagram of the hyperbranched polyester, and \( \delta = 0.60 \) to 1.11 is an absorption peak of a methyl group. The strong absorption peak at \( \delta = 2.40 \) is a peak of a hydroxyl group (–OH), demonstrating the presence of a large amount of hydroxyl groups in the molecular structure; \( \delta = 3.31 \) to 3.57 is a peak of a methylene group (–CH\(_2\)–OH) bonded to a hydroxyl group. \( \delta = 4.00 \) to 4.62 is a peak of a methylene group (–CH\(_2\)–O–CO–) bonded to an ester group [9, 10]. Combined with the nuclear magnetic resonance spectrum of PUA-1 and PUA-2 given in figure 5(d), the peaks at 7.29 ppm correspond to the chloroform; The peaks at 5.8 to 6.5 are three sets of characteristic peaks, which proves the presence of acrylate groups in the molecular structure [11, 12]; The peaks appearing at 3.2 to 3.8 ppm correspond to a hydrogen atom belonging to a methylene group bonded to an ether group or a hydroxyl group [13]; The peaks at 2.65 and 1.65 ppm are due to hydrogen on the methylene group attached to the amide group and methylene (–CH\(_3\)–), The peaks at 0.85 to 1.27 ppm represent methyl (–CH\(_3\)) of three different chemical environments, which are branched unit (D), linear unit (L), tree-shaped unit (T). The branching degree (DB) of PUA-3 and PUA-4 are 0.63 and 0.84 according to the calculation of peak area and branching formula, indicating that the hyperbranched PUA has been synthesized containing expected structures.

The previous \(^1\)H-NMR has demonstrated that both PUA-1 and PUA-2 have hyperbranched structure from a qualitative point of view. GPC, on the other hand, gives a quantitative view to obtain the relative molecular weight and molecular weight distribution of the two materials. As can be seen from the data in table 1, the Mn of PUA-1 and PUA-2 were 24.9 × 10^3 g mol\(^{-1}\) and 25.3 × 10^3 g mol\(^{-1}\), respectively, and the Mw was 56.3 × 10^3 g mol\(^{-1}\) and 39.9 × 10^3 g mol\(^{-1}\), the PDI index of both are 2.5 and 1.6, indicating that PUA-1 has more by-products.

It is speculated that the different structure of hyperbranched polyurethane generated in the reaction stage is due to the heterogeneous molecular weight of PTMG in the raw materials. In addition, the cross-linking reaction caused by the break of the double bond in acrylate during the photocuring stage will lead to the increase of side reactions and increase of PDI [14].

The characterization and analysis results of FT-IR, \(^1\)H-NMR and GPC show that hyperbranched polyester PUA has been successfully synthesized.
3.2. Mechanical properties

Mechanical properties are one of the important test indicators for practical hydraulic mechanical coatings. The stress-strain curves of PUA-1 and PUA-2 are shown in figure 6. Both materials exhibit good mechanical properties. Yet it is not just that the reaction between the polyhydroxy hyperbranched polyester and the polyurethane prepolymer containing the –NCO group increases the degree of crosslinking of the polymer, in addition, the double bond in the acrylate is broken under UV irradiation to generate a new crosslinking point to further increase the crosslinking density.

From the data in table 2, PUA −1 has a tensile strength of 28.6 Mpa while an elongation at break of 340%, a tensile strength of PUA-2 is 37 Mpa while an elongation at break of 610%, both of which are higher than PUA-1, demonstrating that PUA-2 has higher strength and better toughness than PUA-1.

| Sample | PUA-1 | PUA-2 |
|--------|-------|-------|
| Tensile modulus of elasticity (MPa) | 14.5 ± 1.8 | 7.5 ± 1.2 |
| Tensile strength (MPa) | 28.6 ± 3.2 | 37.0 ± 1.7 |
| Tensile strength (%) | 340 ± 11 | 610 ± 18 |
| Hardness (Hs) | 83 ± 2.5 | 82 ± 4.2 |

Figure 6. Stress-strain curves of PUA-1 and PUA-2 film.

Figure 7. Shear strength, curing time and Anti-abrasion performance of PUA-1 and PUA-2.

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3.3. Shear strength, curing time and anti-abrasion performance

Totally speaking, the shear strength of PUA-1 and PUA-2 is strong. The two materials in direct contact are both long-chain macromolecular structures. According to the adsorption theory, the molecular chain penetrates and diffuses into the substrate gully area \[15\], intertwining each other, increasing the effective contact area and forming a strong bonding interface.

Curing time is one of the important indicators to be considered for practical PUA systems. In the process of preparing a 1 mm PUA film, the liquid was poured into a Teflon mold. Under the irradiation of a 50-W LED ultraviolet lamp, PUA-1 was cured to form a film within 3–10 min and PUA-2 was within 5–13 min. Both of them can be cured quickly and the resulting film is smooth, transparent, dense and uniform.

The curing time of PUA-1 is slightly shorter than that of PUA-2. This is due to the PUA-1 film made by IPDI is colorless, transparent and has good light transmission while the film made by TDI is yellowish, so PUA-2 is less transparent than PUA-1, leading to the longer curing time.

The underwater steel ball method is used to simulate the damage of the bedrock in the sand-containing water flow, that is, the friction and impact damage of the coarse particles moving in the water flow by jumping, rolling or stratification on the surface of the sample. It can be seen from figure 7 that the wear rate of these four hyperbranched polyesters are all below 4%; from the figure 8, we can see that the samples have strong anti-abrasion performance. The two samples on the left are PUA-1, while the other two on the right are PUA-2. The concrete base without PUA coating protection is severely worn, a large number of concrete particles fall off, and there are deep pits of different sizes on the surface; while the PUA film has no other abnormalities except slight peeling combined with the observation results before and after the experiment, which indicates the wear resistance of PUA film in the experiment is good and has potential to be used for repair Hydraulic mechanical device or hydraulic concrete base and wall that have been eroded by high-speed flow with sand for a long time.

3.4. Dynamic mechanical properties

As a common method to measure the relationship between the mechanical properties of viscoelastic materials and time, temperature or frequency, Dynamic thermomechanical measurements were used to determine...
viscoelastic properties of UV cured PUA, Tg, etc. The temperature dependence of storage modulus and tan(δ) peak of UV cured PUA is shown in figure 9. The glass transition temperature (Tg) of PUA-1 and PUA-2 is showed from the peak of the tan(δ), which are $-54.9 \degree C$ and $-59.9 \degree C$, respectively. The network homogeneity of UV cured samples is expressed by the width of the tan(δ) peak while the height of tan(δ) peak reflects the mobility of the chain segments within the glass transition temperature region. On the one hand, the tan(δ) peak of PUA-3 moves toward the high temperature and the broad wide and low tan(δ) peaks were observed for PUA-3 indicating that the broad distribution of chain lengths and low mobility of segments. Tan(δ) peak of PUA-4 moves towards high temperature continuously, becoming higher and narrower, which indicates that chain relaxation transition is difficult, and more energy is needed. The change of peak narrowing indicate that molecular structure is compact, the degree of crosslinking increases, and the dispersion decreases.

### 3.5. Thermal stability

Thermal stability of polymers refers to their ability to maintain chemical structure or composition stability at high temperatures. The TGA and DTG curves in figure 10 show that the thermal decomposition behavior of PUA-1 and PUA-2 is similar, and the decomposition rate is slower at the beginning stage, then comes the rapid degradation process. Degradation is mainly divided into two stages: about 20% weight loss between 270 °C–350 °C, mainly cleavage of urethane bond and a small amount of urea group; weight loss between 350 °C–460 °C

![Figure 10. TGA and DTG curves of PUA-1 and PUA-2.](image)

| Decomposition temperature (°C) | PUA-1 | PUA-2 |
|-------------------------------|-------|-------|
| $T_{10}$                       | 311   | 303   |
| $T_{50}$                       | 400   | 394   |
| $T_{\text{max}}$               | 409   | 400   |
| $T_{\text{end}}$               | 477   | 464   |

Table 3. Decomposition temperature of PUA-1 and PUA-2.

![Figure 11. Swelling of PUA films in water (a) or acetone (b).](image)
is about 70%, mainly ester bond, ether bond and the breakage of the carbon chain [16]. The loss of about 5% before 270 °C is presumed to be caused by the volatilization of small molecules such as photoinitiators and reactive diluents that are not involved in the reaction. Combining the data of figure 9 and table 3, we can see that both of them show good thermal stability. The initial decomposition temperature (IDT), maximum decomposition temperature (Tmax) and end point temperature (Tend) of PUA-2 are all lower than those of PUA-1, indicating that PUA-1 has better thermal stability than PUA-2.

3.6. Water and solvent resistance

The main working environment of the coating for hydraulic machinery is under water, so the water resistance of PUA materials is very high. There are two main aspects to the effect of water on PUA membranes. On the one hand, water enters the molecule, and the urethane bond in the molecule acts to generate hydrogen bonds, which weakens the interaction between the molecules; on the other hand, the PUA resin may decompose in water.

The PUA-1 and PUA-2 films with a thickness of 1 mm were immersed in boiling water at 100 °C. It can be found from the observations in figure 11 that the water absorption of both materials within 10 h is less than 5%. In the same way, soaking in acetone for 10 h, the swelling rate of the two PUAs was below 280%, which afforded the two PUAs with good water and solvent resistance performance.

This is mainly ascribed to the hyperbranched structure of the two materials, the physical entanglement of molecular chains and the breakage of double bonds in UV curing process further increase the degree of crosslinking, which makes the force between the molecular chain segments larger, making it difficult to carry out relative slip between the chain segments [17]. Therefore, water molecules are hard to enter into the inner part of the materials, resulting in low water absorption. At the same time, they resist the interaction of organic solvents on the polymer chains, swelling to a certain extent in water or solvent is balanced by the entropy elasticity of the molecular chain, resulting in swelling balance. Solvent resistance of the membranes can be improved by swelling and dissolution of the membranes [18, 19].

4. Conclusions

In this paper, hyperbranched PUA was synthesized by the designability of PUA molecular structure. The protective coatings of PUA for hydraulic machinery were successfully prepared by UV curing. The coatings were tested and characterized respectively. In this study, hyperbranched polyester was prepared by using TMP and DMPA as raw materials and DMSO as solvent, which was used as linear polyurethane prepolymerization system containing-NCO group on 'core' grafting to obtain hyperbranched PUA.

Two types of PUA has been synthesized successfully and characterized adequately by FTIR, HNMR and GPC. FT-IR demonstrates the synthesis of polyhydroxyl hyperbranched polyesters. The hyperbranched structure of PUAs can be verified qualitatively by nuclear magnetic resonance spectroscopy combined with gel permeation chromatography. The tensile strength and elongation at break of PUA-2 were higher than PUA-1, showing better mechanical properties; the IDT, Tmax and Tend of PUA-2 were lower than PUA-1; In addition, DMA results showed that Tg of PUA-1 was higher and PUA-2 was more crosslinked. The mechanical properties of PUA-1 and PUA-2 were tested. It can be found easily that the tensile strength of PUA-1 is 28.6 MPa, the elongation at break is 340%, the tensile strength of PUA-2 is 34.0 MPa, and the elongation at break is 610%, which is higher than PUA-1, indicating that PUA-2 has higher strength and better toughness than PUA-1. TGA and DTG curves show that the thermal decomposition behavior of the two materials is similar, which can be divided into two stages. The initial decomposition temperature (IDT), maximum decomposition temperature (Tmax) and end point temperature (Tend) of PUA-2 are lower than PUA-1, which indicates PUA-1 has better thermal stability than PUA-2 via the thermal stability test of two materials. PUA-2 exhibits stronger shear strength and anti-abrasion performance, therefore it is more suitable for the use of hydraulic machinery.

In this paper, the application of UV curing PUA in the field of hydraulic machinery is preliminarily explored. Compared with polyurethane or polyurea materials, the prepared hyperbranched PUA can not only accelerates the UV curing process and makes the construction process more simple and convenient, but also has better mechanical properties, and achieves the corresponding design requirements in terms of wear resistance, solvent resistance and so on. It is expected that it will have a good application prospect in the field of hydraulic machinery. The future research direction can consider further improving the bonding performance of PUA, so that it can be directly and firmly bonded to metal or concrete surface without the aid of bottom glue treatment. Futural research directions can consider further improving the bonding performance of PUA, so that it can be directly and firmly bonded to metal or concrete surfaces without the use of primer treatment. In the follow-up work, a series of problems encountered in the actual construction process will be further explored and studied.
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