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Property Study of Polyurethane Template Materials for Molding Concrete

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Abstract. In this paper, polyether diol (CASPOL1861 (V)), liquefied diphenylmethane diisocyanate (103C) and small molecular diol (CASPOL1905) were used as the main reaction materials to synthesize polyurethane template materials for the molding concrete. According to the requirements of polyurethane template materials on high strength, high elongation at break, moderate hardness, low water absorption rate and high alkali resistance, the effect of the types of the soft segments and the types of isocyanate on the mechanical properties, alkali hydrolysis resistance, water absorption, thermal properties and aging properties of the prepared polyurethane template materials were studied by characterizing the properties of polyurethane template materials by mechanical tests, TG, DSC, and other methods.

1. Introduction

Molding concrete is an environment-friendly material popular and widely promoted in the main developed countries in recent years. It enables the plain concrete surface to achieve the paving effects similar to that of natural marble, granite, brick and tile by means of the innovative design with texture and irregular lines, and to have the characteristics with beautiful and natural look, being firm, robust and durable.

The key technology for the production of the molding concrete is molding template. The part of the template in direct contact with concrete during the concrete production decides the shape, size and appearance of concrete. The existing template materials mainly include silica gel material and polyurethane material. Silica gel material is characterized by convenient forming, moderate price and high alkali resistance, and has been widely used. But due to low strength, it is easy to be torn off, so it is generally used as the template material for one-time use or occasional use.

Polyurethane material is characterized by high strength and good tear resistance, so polyurethane material can be used in the template for repeated use. But polyurethane material generally has poor alkali resistance, it will result in the shrinkage after being used for times. Particularly for the precast concrete, the temperature is relatively high because the steam curing is used in order to reduce the production cycle, and concrete has large alkalinity, so the general template materials cannot meet the use requirements. Thus a polyurethane template material with high tensile strength, excellent alkaline hydrolysis resistant properties and good ageing resistance is in urgent need in the market.

To achieve the polyurethane template material with moderate hardness, high strength, high elongation at break, low water absorption and excellent alkaline hydrolysis resistant properties, polyether diol (CASPOL1861 (V)) and liquefied diphenylmethane diisocyanate (103C) with relatively small molecular polarity have been used in this experiment as the main reaction raw materials for the



synthesis of the preformed polymer, and small molecular diol (CASPOL1905) is used as the chain extender, to synthesize a series of polyurethane template materials, so as to study the influence of isocyanate and soft segment category on the properties of the synthesized polyurethane template material, and select the optimal formula suitable as polyurethane template material.

2. Experimental raw materials

Table 1 lists some of the raw materials used in the experiment.

Table 1. Raw materials.

| Raw material | Name of raw material | Category | Source of raw material |
|-----------------|----------------------------------|-------------------|---------------------------|
| 103C | Liquefied MDI | Polyisocyanate | BASF |
| HMDI | Dicyclohexylmethane diisocyanate | Polyisocyanate | Yantai Wanhua Chemicals |
| HDI | Hexamethylene diisocyanate | Polyisocyanate | Mitsui Chemicals |
| PTMG1000 | Polytetrahydrofuran polyether | Polyether polyol | DuPont USA |
| CO | Castor oil | Bio-based polyol | Xingji Chemical Co., Ltd. |
| CASPOL1861 (V) | Polyether diol | Polyolefin polyol | Beijing Chengzhi Xinyuan |
| CASPOL1861 (VI) | Polyether diol | Polyolefin polyol | Beijing Chengzhi Xinyuan |
| CASPOL1905 | Small molecular diol | Chain extender | Beijing Chengzhi Xinyuan |

3. Experiment methods

3.1. Tensile test

Tensile test shall be carried out by referring to the national standard GB/T 528-2009, and type 2 cutting knife is used to cut several dumbbell-shaped test specimens with the size of 75mm×4mm, and the sample thickness shall be controlled at 2mm. The sample shall be clamped on the universal testing machine, for the tensile test, to measure the tensile strength and elongation at break.

3.2. Shore hardness test

Shore hardness test is carried out with LX-A rubber durometer by referring to the national standard GB/T 531-2009, and choosing multiple points in different positions on the sample to be tested, for the measurement of the hardness, taking the mean value as the final hardness.

3.3. DSC test

DSC test is carried out with NETZSCH-DSC204 F1 differential scanning calorimeter. A small amount of the sample is taken from polyurethane template material, and placed into the instrument for the test and analysis. The test conditions: atmosphere is nitrogen, the test temperature is -70°C-150°C, the temperature rise rate is set as 10°C/min, and the flow rate is 30ml/min.

3.4. Thermal weight loss test

Thermal weight loss test is carried out with NETZSCH-TG 209C thermal weight loss analytical tester. A small amount of the sample is taken from polyurethane template material, and placed into the instrument for the thermal analysis. The atmosphere is nitrogen, the test temperature range is 20°C-700°C, the temperature rise rate is set as 10°C/min, and the flow rate is 30ml/min.

3.5. Alkaline hydrolysis resistant property test

To make the test results of alkaline hydrolysis resistance closer to the actual production, we have defined a test method of alkaline hydrolysis resistant properties. Referring to the national standard GB/T 528-2009, the samples with the thickness of about 2mm are made, and four dumbbell-shaped test specimens with the size of 75mm×4mm are cut with type 2 cutting knife. Take two specimens for the determination of the tensile strength with the universal testing machine, and take the mean value as F0; then take two specimens and place them into the beaker, pour 10% potassium hydroxide solution into the beaker, seal the beaker with the preservative film, and place it into the 80°C baking oven for one day. Take it out and cool it down to the room temperature, for the determination of tensile strength, and taken the mean value as F1. The alkaline hydrolysis resistant properties of the material are considered with the strength loss rate W. Strength loss rate may be calculated with the following formula.

$$W = (F_0 - F_1) / F_0 \times 100\% \quad (1)$$

4. Experiment results

4.1. Influence of soft segment category on polyurethane template material

4.1.1. Preparation of polyurethane template materials of different soft segments

In this experiment, isocyanate radical index R value is set as 1.05, and while keeping that other experiment conditions remain unchanged, the soft segment category is changed, for comparison of the mechanical and physical properties, alkaline hydrolysis resistance and water absorption of the prepared samples, so as to select the polyol raw material most suitable for the preparation of polyurethane template material, with the detailed formula for the experiment as shown in Table 2.

Table 2. Composition formula for polyurethane template materials of different soft segment categories

| No. | A1 | A2 | A3 | A4 |
|-----------------------|----------|-------|----------------|-----------------|
| Soft segment category | PTMG1000 | CO | CASPOL1861 (V) | CASPOL1861 (VI) |
| Polyol use/g | 50g | 50g | 50g | 50g |
| 103C/g | 14.7 | 21.39 | 6.66 | 9.52 |
| Organic bismuth/g | 0.12 | 0.12 | 0.12 | 0.12 |

4.1.2. Influence of soft segment category on mechanical properties of polyurethane template material

From the test analysis, the detailed experiment data is shown in Table 3.

Table 3. Influence of soft segment category on mechanical properties of polyurethane template material

| No. | A1 | A2 | A3 | A4 |
|-----------------------|---------|-------|-------------------|--------------------|
| Category | PTMG-PU | CO-PU | CASPOL1861 (V)-PU | CASPOL1861 (VI)-PU |
| Hardness/Shore A | 34 | 70 | 48 | 50 |
| Tensile strength/MPa | 1.97 | 11.9 | 2.35 | 3.00 |
| Elongation at break/% | 775 | 585 | 250 | 300 |

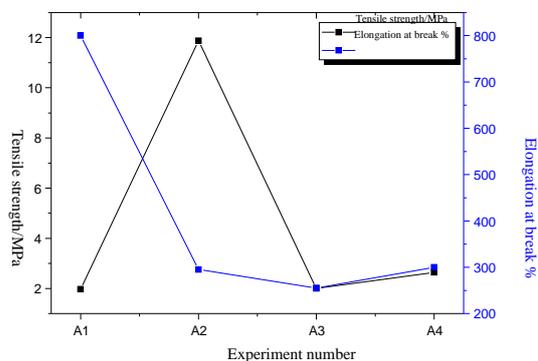


Figure1. Influence of soft segment category on mechanical properties of template material

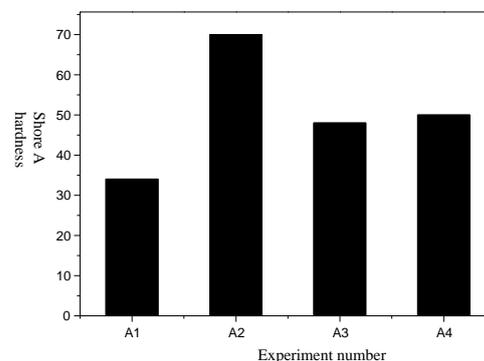


Figure2. Influence of soft segment category on the hardness of template material

From Figure1 and Figure2, it can be seen that, castor oil has the highest tensile strength as the polyurethane template material of soft segment, followed by the polyurethane template material with polyether diol as the soft segment, and the one with the weakest tensile strength is PTMG1000 group. Castor oil is polyhydroxyl compound, and for the polyurethane template material with castor oil as the soft segment, it does not have the linear structure but the body structure, and during the tension, its molecular weight is not easily slipped, so the polyurethane material made with castor oil has excellent mechanical properties, but low elongation at break. For PTMG1000, it has the relative molecular mass smaller than that of CASPOL1861 (V). A bigger the molecular mass causes a poorer compatibility between hard segment and soft segment, thus being beneficial for microphase separation. In addition, CASPOL1861 (V) is nonpolar molecule and it is unbeneficial for the formation of hydrogen bond between hard segment and soft segment, thus higher microphase separation degree is beneficial for crystallization of hard segment phase. So the tensile strength of polyurethane template material prepared with CASPOL1861 (V) is higher than that of PTMG1000 polyurethane template material, while the elongation at break is lower than that of PTMG1000 polyurethane template material. Tensile strength and hardness of A3 is higher than that of A3, and the raw material for both groups is polyether diol CASPOL1861. But polyether diol for group A4 has higher hydroxyl value, and relatively speaking, it has lower molecular weight, the hard segment formed by the reaction with isocyanate is relatively concentrated, and the hydrogen bond density is high. So it has better mechanical properties and hardness.

4.1.3. Influence of soft segment category on alkaline hydrolysis resistant properties of polyurethane template material

From Figure3, it can be seen that, among the polyurethane template materials prepared from different soft segment categories, the template material prepared with PTMG1000 has the poorest alkaline hydrolysis resistant properties, the polyurethane template material prepared with polyether diol CASPOL1861 has the best alkaline hydrolysis resistant properties, and the polyurethane template material prepared with castor oil has the alkaline hydrolysis resistant properties slightly stronger than that of PTMG1000. Since the polyurethane molecular chain is not easily damaged by the alkaline medium due to strong interaction among the molecular chains in hard segment, soft segment becomes the part with the poorest alkaline hydrolysis resistant properties^[1-3]. Polyether diol CASPOL1861 has good flexibility and is nonpolar molecule with low electron cloud density, and it is not easily attacked by the electronegative OH^- . In addition, there is no atom with strong electronegativity in polyether diol soft segment to form hydrogen bond, and hydrogen bond only exists in hard segment phase, beneficial for the formation of the microphase separation structure, so that polyether diol has good hydrolysis resistance as the polymer of soft segment.

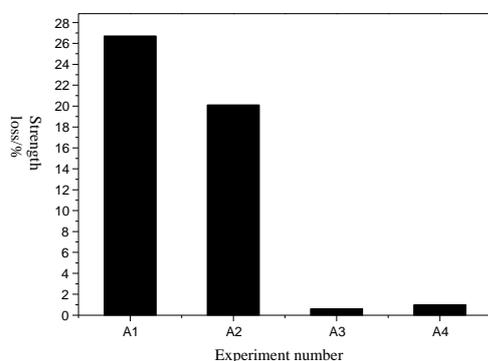


Figure3. Influence of soft segment category on alkaline hydrolysis resistant properties of template material

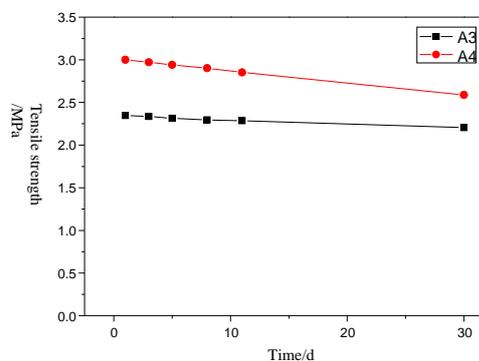


Figure4. Influence of soft segment category on the tensile strength of template material

After the alkaline resistance test, the formula A4 has larger loss of strength, and for more accurate comparison of alkaline hydrolysis resistant properties, we carried out a long-time tracking test of alkaline hydrolysis resistant properties. From Figure4, it may be seen that, by comparison with formula A4, the formula A3 has lower strength loss rate, and has better alkaline hydrolysis resistant properties mainly because lower hydroxyl value of polyether diol CASPOL1861 in A3 group. Relatively speaking, it has high relative molecular weight, good flexibility, resulting in poorer compatibility between the soft and hard segments, and the increase of the phase separation of soft segment and hard segment, thus promoting the crystallization of hard segment. For common polyurethane, soft segment is the part with the poorest alkaline hydrolysis resistant properties, and for polyether diol, its soft segment is nonpolar, and not easily attacked by the electronegative OH^- , so hard segment has become the part with the poorest alkaline hydrolysis resistant properties. A3 group has higher crystallization degree of hard segment than that of A4 group, so A3 group has stronger alkaline hydrolysis resistant properties than A4 group.

4.1.4. Influence of the soft segment category on water resistant properties of polyurethane template material

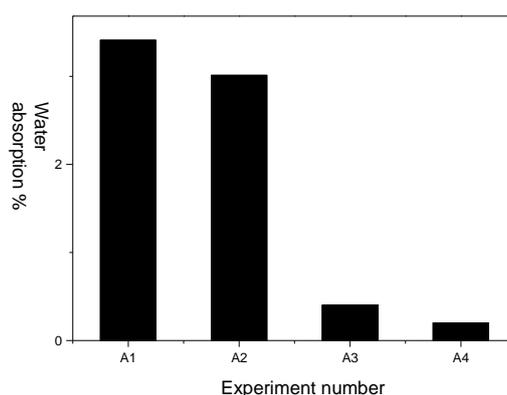


Figure5. Influence of soft segment category on the water absorption of template material

From Figure5, it can be seen that, PTMG-PU has the highest water absorption, which is followed by CO-PU, and then CASPOL1861-PU. PTMG1000 molecule contains a large number of ether bonds, hydrophilic group of ether bond, and its flexible molecular chain is not in curly state, and water molecule is convenient for penetration, so it has the highest water absorption. The molecule of

polyether diol CASPOL1861 is nonpolar and very difficult to work with water molecule to form the hydrogen bond, and in polyether diol soft segment, there is no electronegative atom to form the hydrogen bond, and hydrogen bond only exists in the hard segment phase, which is beneficial for the formation of microphase separation structure. The hard phase is dispersed in the soft phase, playing the role of physical crosslinking, and the increase of the interaction among the molecular chains also makes water molecules more difficult for penetration. So the polyurethane template material with polyether diol CASPOL1861 as the soft segment has the lowest water absorption. Polyether diol CASPOL1861 used in A4 formula has smaller molecular weight than that of A3 group, the hard segment formed by the reaction with isocyanate is relatively concentrated, and the hydrogen bond density is high. The interaction among the molecular chains is relatively strong and the water molecules are difficult for penetration, so A4 group has the lowest water absorption.

4.2. Influence of isocyanate category on alkaline hydrolysis resistant properties of polyurethane template material

4.2.1. Preparation of different categories of isocyanate polyurethane template materials

In this experiment, isocyanate radical index R value is set as 1.05, and while keeping that other experiment conditions remain unchanged, the isocyanate category is changed, for comparison of the mechanical and physical properties, alkaline resistance and water absorption of the prepared samples, so as to select the isocyanate raw material most suitable for the preparation of polyurethane template material, with the detailed formula for the experiment as shown in Table4.

Table4. Synthesizing formula of polyurethane template materials for different types of isocyanate

| No. | B1 | B2 | B3 |
|---------------------|-------|-------|-------|
| Isocyanate category | 103C | HDI | HMDI |
| Isocyanate use/g | 21.39 | 12.85 | 20.05 |
| CO/g | 50 | 50 | 50 |
| Organic bismuth/g | 0.12 | 0.12 | 0.12 |

4.2.2. Influence of isocyanate category on the thermal properties of polyurethane template material

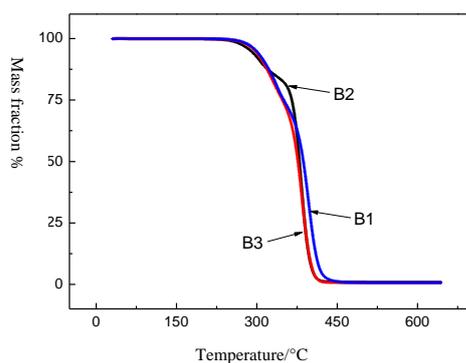


Figure6. Thermal weight loss curve of polyurethane template material for different isocyanate categories

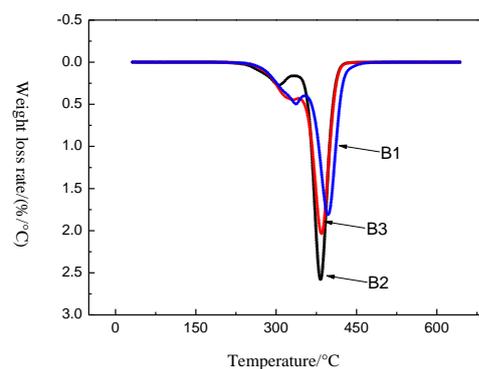


Figure7. Thermal weight loss rate curve for different isocyanate polyurethane template materials

From the above Figure6 and 7, it can be seen that, the experiment number B1 to B3 have basically the same thermal weight loss curve. Below 200°C, thermal weight loss is almost 0, and the curves have two thermal weight loss procedures. At about 230°C, carbamate group starts fracturing, as the first-

step decomposition, and the second-step decomposition happens near 300°C, when polyols are decomposed into olefins, amines and carbon dioxide. But in the comparison of initial decomposition temperature with the temperature at the highest thermal weight loss rate, it may be found that initial decomposition temperature is $B2 < B3 < B1$ and maximum weight loss rate is $B2 > B3 > B1$.

So, we can believe that, 103C polyurethane has the best heat resistance, because 103C molecules have benzene rings and high molecular symmetry, which is quite beneficial for crystallization. There is strong interaction between hard segments and high microphase separation degree, beneficial for the improvement of material heat resistance. Then HMDI has good molecular regularity, and polyurethane prepared with HMDI has the crystallization level slightly weaker than that of 103C group. So its tolerance is weaker than that of 103 groups and higher than HDI group with the poorest molecular regularity.

4.2.3. Influence of isocyanate category on the thermal properties of polyurethane template material

From Figure 8, Figure 9 and Figure 10, it can be seen that, the polyurethane template material prepared with 103C, HDI and HMDI largely varies in mechanical properties, with the tensile strength and hardness of $103C\text{-PU} > \text{HMDI-PU} > \text{HDI-PU}$, and elongation at break of $\text{HDI-PU} > 103C\text{-PU} > \text{HMDI-PU}$. HDI is a long-chain aliphatic compound, where C-C bond is easy for rotation without the retarding effect of large steric hindrance group, and the formed hard segment will be very easily deformed and dissolved into the soft segment phase, reducing the microphase separation degree, thus having low tensile strength and hardness, while high elongation at break. 103C and HMDI have regular molecular structure, both containing rigid group. Polyurethane template material prepared with 103C and HMDI has high crystallization degree, large hydrogen bond density, good mechanical properties and large hardness. But a large amount of hydrogen bonds and large steric hindrance groups have had the retarding effect on the slide of molecular chains. So 103C-PU and HMDI-PU have low elongation at break. But 103C molecular structure contains benzene rings, and the prepared polyurethane material has large cohesive energy and more physical crosslinking points and crosslinking density, so 103C-PU has bigger tensile strength and hardness than that of HMDI-PU.

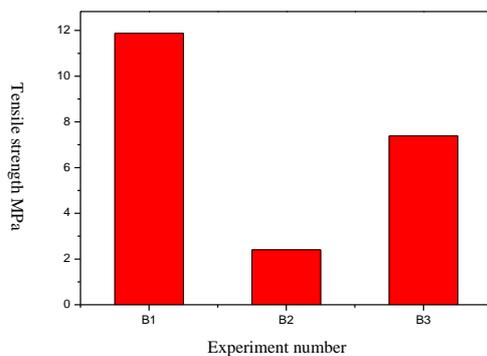


Figure 8. Influence of isocyanate category on the tensile strength of template material

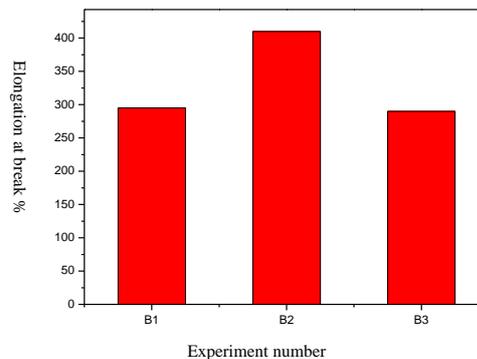


Figure 9. Influence of isocyanate category on the elongation at break for template material

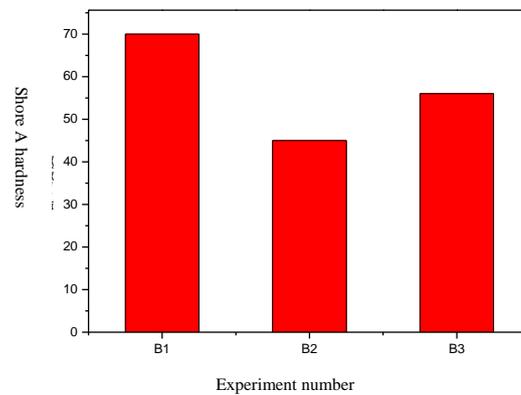


Figure 10. Influence of isocyanate category on the hardness of template material

4.2.4. Influence of isocyanate category on alkaline hydrolysis resistant properties of polyurethane template

From Figure 11, it can be seen that, polyurethane template material prepared with HDI has the best alkaline hydrolysis resistant properties, which is followed by polyurethane template material taking 103C as the hard segment, and the polyurethane template material with HMDI group has the poorest alkaline hydrolysis resistant properties. HDI is a long-chain aliphatic compound, where C-C bond is easy for rotation without the retarding effect of large steric hindrance group, and the formed hard segment will be very easily deformed and dissolved into the soft segment phase. The hydrogen bond is more easily formed between hard segment and soft segment, playing a very good protective role in the soft segment, the part with the poorest alkaline resistance in polyurethane is also soft segment. HMDI-PU and 103C-PU have high microphase separation degree, the hydrogen bond type is mainly of hard segment-hard segment, and hydrogen bond does not have strong protective effect on the soft segment. Therefore, polyurethane template material prepared with HDI has the highest alkaline hydrolysis resistant properties.

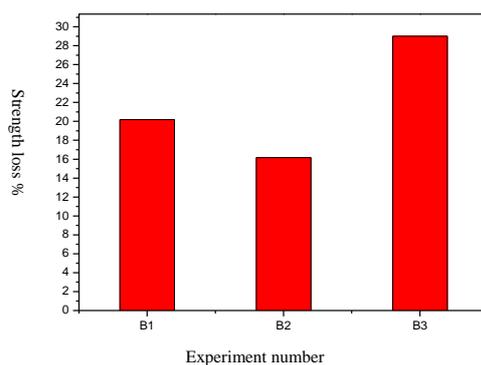


Figure 11. Influence of isocyanate category on alkaline hydrolysis resistant properties of template material

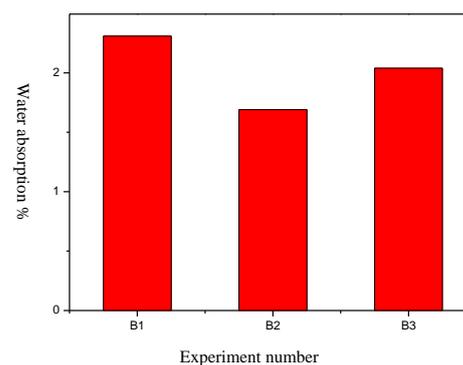


Figure 12. Influence of isocyanate category on the water resistant properties of template material

4.2.5. Influence of isocyanate category on the water resistant properties of polyurethane template

From Figure 12, it can be seen that, 103C-PU has the highest water absorption, which is followed by HMDI-PU, and then HDI-PU. Because in the experiment for this group, the castor oil use is fixed and R value is fixed, the content of hard segment is 103C-PU>HMDI-PU>HDI-PU. Because castor oil has

long fatty group and has good water resistant properties, the higher hard segment content means less castor oil content. In addition, with the increase of the polar carbamate in molecular chain, the water resistance of the polymer becomes worse. The water resistance level is 103C-PU<HMDI-PU<HDI-PU.

5. Conclusion

The mechanical and physical properties, alkali resistance and water absorption of the samples were studied experimentally. The following conclusions were drawn:

1) The tensile strength of CASPOL1861 (V) group is lower than that of castor oil group, higher than that of PTMG1000 group; the hardness of CASPOL1861 (V) group is lower than that of CO group, but higher than that of PTMG1000 group, with moderate hardness.

2) The alkaline hydrolysis resistant properties of CASPOL1861 (V) group are far higher than that of CO group and PTMG1000 group, and the strength loss in the alkaline hydrolysis resistance test is less than 1%. Polyether diol CASPOL1861 with lower hydroxyl value has better alkaline hydrolysis resistant properties, and CASPOL1861 (V) group with low hydroxyl value has better alkaline hydrolysis resistant properties than that of CASPOL1861 (VI) group with high hydroxyl value.

3) The polyurethane template material prepared in 103C group has the highest decomposition starting temperature and lowest thermal weight loss rate, as well as the best heat resistance. 103C group has the highest tensile strength and hardness, which is followed by HMDI group, and TDI group has the lower tensile strength. In addition, elongation at break in 103C group is stronger than that of HMDI group, and weaker than that of TDI group. The alkaline hydrolysis resistance test results have shown that, HDI group has the best alkaline hydrolysis resistant properties, 103C group has the alkaline hydrolysis resistant properties slightly weaker than that of TDI group.

4) After comprehensive consideration of tensile strength, elongation at break, hardness, alkaline hydrolysis resistant properties, and water absorption, CASPOL1861 (V) is determined as the best raw material for the soft segment of polyurethane template material, and 103C is the best hard segment raw material for polyurethane template material.

In addition to soft segment and isocyanate, chain extender and R value will have influence on the properties of polyurethane template material, and the project team will continue the study in subsequent experiments, to improve the properties of polyurethane template material.

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