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Preparation of liquid rubber utilized in construction environment

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ABSTRACT

Sealing material liquid rubber utilized in construction environment was prepared using diphenyl methane diisocyanate (MDI), polyether 330, polyether 220, butyl acetate, additives and fillers and so on. The influences of the temperature of prepolymerization reaction, the content of -NCO after prepolymerization reaction, the ratio of mixed polyether, and the amount of catalyst and fillers on product properties were investigated. The optimal preparation technology was determined. The results show that, when the temperature of prepolymerization reaction is 90°C, polyether 330 / polyether 220 is 85 / 15 (w %), the content of -NCO (w %) is 4.1%, the amount of dibutyltin dibutyl (w %) is 0.3 %, and the amount of packing (w %) is 4%, the liquid rubber prepared has better properties. It exhibits good waterproof performance when utilized in construction environment.

1. Introduction

In recent years, with the continuous development of China's modernizations construction, various kinds of civil construction, high-rise buildings have mushroomed in China, sealing material in building environment increasingly shows its importance and superiority. From the scope of use, sealing material can be used in outdoor, such as roof, external wall, highway joints and the joints of large floor-to-ceiling windows and so. It can also be used in indoor, such as toilet, bathroom, door and window joints. When this type of material is packed into the conjunctive part of the building structure, the building can be watertight and air-tightness to achieve the purpose of waterproofing and preventing heat loss.

The common sealing materials in the building environment usually have two different forms. One form is rubber finished product with a certain shape, like rubber waterstop etc. The other one is an amorphous product like liquid rubber [1]. The rubber waterstop is made by mixing and sulfurating rubber and water-absorbent resin. When the waterstop contact with water, water-absorbent resin can absorb water and be expanded, and can solve the secondary leakage problem in a short period of time. Because that the water-absorbent resin disperse in rubber in the form of powder particles, and there is almost no binding force between them. So every time it absorbs water and is expanded will result in precipitation of water-absorbent resin. After meeting with water for several times it will lose the waterproof function [2].

Based on this, in this work, liquid rubber without solvent utilized in construction environment was prepared using diphenyl methane diisocyanate (MDI), polyether 330, polyether 220, butyl acetate, additives and fillers.

It can solidify when it be poured into expansion joints, structure joints injection at room temperature and form elastic colloid waterstop. chain will swell, It can effectively plug water and be expanded again and again relying on the molecular chain, doesn't generate precipitation and has long period of validity.

1. Experimental

2.2. 1 experimental reagents

Polyether 330, Polyether 220, industrial-grade, Jiangsu haian oil chemical plant; Diphenylmethane diisocyanate (MDI), industrial-grade, Jiangsu pesticide plant; Diethyltoluene diamine, 3, 3'-dichloro-4, 4'-diphenyl methane (MOCA), industrial-grade, Suzhou advanced chemical plant; Dibutyltin dilaurate, analytical purity, Tianjin city Aqi medical pharmaceutical sales co., LTD. Light calcium carbonate, carbon black, industrial-grade, Tianjin jinqiushi chemical co., LTD. Titanium dioxide, butyl acetate, chemical purity, Tianjin guangfu chemical co., LTD.

2.2 Main experimental equipments

Three-roll grinding machine, Qinhuangdao funing chemical machinery plant; Electronic tensile testing machine, Jiangsu tianyuan test equipment co. LTD.

2.3 Preparation of liquid rubber

A component: A certain amount of polyether 330 and polyether 220 was put into three bottles to vacuum dehydration. Then MDI was added to react at a certain temperature for a certain time, and get the polyurethane prepolymer, that is A component.

B component: Mixed polyether and butyl acetate were put into three-mouth flask, Then MOCA and diethyl toluene diamine were added and heated under stirring until completely dissolved. Light calcium carbonate, carbon black, titanium dioxide, defoaming agent, fillers and additives were added respectively under stirring, and grinded uniformly on three-roll grinding machine, that is B component.

Component A and component B were mixed at the ratio of 1.5/1. Catalyst dibutyltin dilaurate was added in and stirred uniformly. Then it was poured into 25 mm × 25 mm × 2 mm square specimens at room temperature and placed for 15 d at room temperature. Then the properties determination of the specimens were conducted.

2.4 Properties determination

Shore A hardness was determined by using rubber pocket hardness testing method according to GB/t531-1999.

The tensile strength and elongation at break were determined by using the method in the determination of the tensile stress and strain properties of

vulcanized rubber or thermoplastic rubber according to GB/t528-2009. The stretching speed was 2mm/min.

The volume expansion rate was determined by using the method in the determination of the liquid resistance of vulcanized rubber according to GB/t1690-1992.

The equation for volume expansion rate is :

$$\Delta V(\%) = [(W_3 - W_4) - (W_1 - W_2)] / (W_1 - W_2) \times 100$$

Where W_1 is the mass of the specimen in air before immersion, g. W_2 is the mass of the specimen in deionized water before immersion, g. W_3 is the mass of the specimen in air after immersion, g. W_4 is the mass of the specimen in deionized water after immersion, g. Specimen size: 25 mm×25 mm×2 mm, Specimen was immersed in distilled water to constant weight.

3. Results and discussion

3.1 Effect of prepolymerization temperature

The effect of prepolymerization temperature on reaction rate is significant. With the reaction temperature rises, the reaction rate increases and the side reaction is more easy to occur. The reaction of isocyanate self-polymerization is more easy to occur, makes the system viscosity increases, even form gel. The content of -NCO of prepolymer was determined after reacting for 2h at different reaction temperatures. The theoretical content of the free -NCO after the reaction of polyether and MDI was set as 4.5%. The effect of different reaction temperatures is shown in Figure 1.

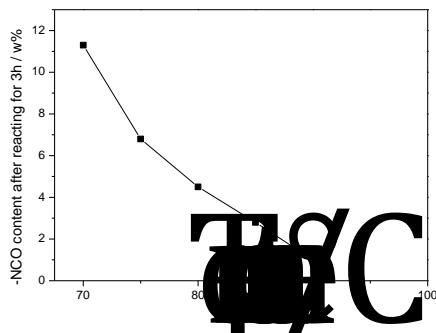


Figure 1. The effect of prepolymerization temperature

As is shown in Figure 1, when the temperature is below 90 °C, within a certain period of time, the content of -NCO of prepolymer is less than the theoretical set value, which is because the reaction rate is slow at low temperature, and when the temperature exceeds 95 °C, the reaction rate is too fast that gel is formed. Thus the prepolymerization reaction temperature is determined at 90 °C.

3.2 Effect of the content of -NCO group in prepolymer on the properties of polyurethane rubber

In prepolymer, -NCO group is the crosslinking group of the subsequent curing reaction. The content of -NCO in prepolymer has some effects on the crosslinking structure of polyurethane rubber, and the effects of different contents of -NCO on the properties of polyurethane rubber are shown in Figure 2.

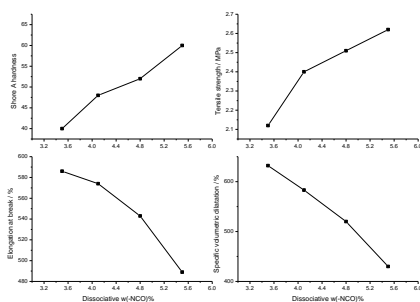


Figure 2. Effect of the content of -NCO group in prepolymer on the properties of polyurethane rubber

As is shown in Figure 2, with the increase of -NCO content in the prepolymer of A component, the hardness of polyurethane rubber and the tensile strength increase, the elongation rate and the volume expansion ratio decrease. This is because that with the increase of -NCO content, the amount of carbamic acid esters group formed increases, the hard segment content increases accordingly, which is beneficial to the microphase separation and the enhancement of tensile strength. On the other hand, due to the increase of -NCO content, crosslinking network density increases restricting the embedding of water molecules, polyether segment of crimp state in polyurethane rubber has less chance to react with water to form hydrogen bond and make it difficult to stretch the chain of crimp state. Water absorption expansion ratio of polyurethane rubber decreases [3]. Considering the tensile strength and the volume expansion rate, the content of -NCO in prepolymer was determined at 4.1 %.

3.3 Effect of polyether ratio on liquid rubber properties

Due to the difference between molecular structures of different polyethers, the ratio of different polyethers has bigger effect on the mechanical properties of polyurethane rubber, the effect of the ratio of polyethers on the properties of the polyurethane liquid rubber is shown in Figure 3.

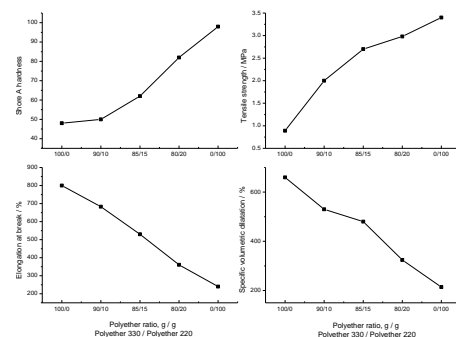


Figure 3. Effect of polyether ratio on liquid rubber properties

As is shown in Figure 3, when the polyether 330 / polyether 220 is 100/0, the elongation ratio of polyurethane rubber and the volume expansion ratio are larger, the hardness is smaller and the tensile strength is lower. When the polyether 330 / polyether 220 is 0/100, the tensile strength and hardness are higher, but the elongation rate at break and the volume expansion rate are lower. When a small amount of polyether 220 is added to the polyether 330, the tensile strength is obviously improved, the hardness is increased, the volume expansion rate and the elongation of the elongation are decreased. This is because polyether 330 is 3 functional polyols, the content of soft segment is high, and it is hydrophilic polyether, which can give polyurethane rubber better flexibility. Polyether 220 is hydrophobic 2 functionality of polyether polyols, its hard segment content is high, integrating it into the polymerization system can make the micro phase separation of the hard and soft segment be improved, and hard segment evenly dispersed in the flexible chain segment playing a role of elastic junction at room temperature [4], so as to improve the mechanical properties of the polyurethane rubber. Polyurethane liquid rubber of water swelling which is used in waterproof construction, requires a certain flexibility, better volume expansion rate and larger tensile strength. So the ratio of polyether 330: polyether 220 was determined at 85:15, then the tensile strength and volume expansion rate can satisfy engineering demand.

4.4 Effect of catalyst dosage on the properties of liquid rubber

A small amount of catalyst can be used to accelerate the reaction rate and shorten the curing time of the gel when the water-expansion polyurethane liquid rubber is prepared. -N=C=O isocyanate group has highly unsaturated, in which carbon atoms has electrophilicity, nitrogen and oxygen atoms has nucleophilicity, so both the acid and alkaline substances can be used as a catalyst. Acid catalyst is beneficial to form chain structure, alkaline catalyst is beneficial to form shape structure. Tertiary amine, organic tin and other organic metal compounds can act as a catalyst [4]. So in this work, two lauric acid tin was selected as chain extension reaction catalyst. The effects of different catalyst dosage on the properties of polyurethane rubber are shown in Figure 4, Figure 5.

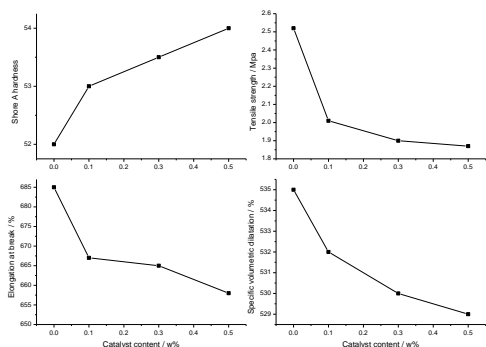


Figure 4. Effect of catalyst dosage on liquid rubber properties

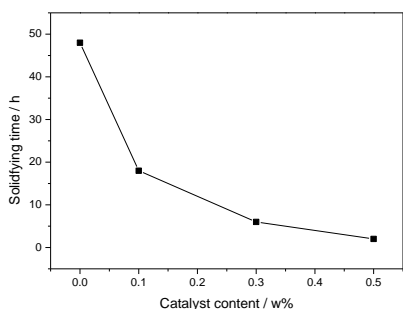


Figure 5. Relationship between catalyst dosage and curing time

As is shown in Figure 4, Figure 5, the addition of catalyst can accelerate the reaction rate, gel solidifying time is significantly shortened, the tensile strength of the polyurethane rubber decreases, and the elongation at break and the volume expansion rate changed a little. The reason may be that the gel reaction time is shortened, phase separation of hard segment and soft segment does not have enough time, so the tensile strength of the polyurethane rubber decreases. In the use process of polyurethane liquid rubber, blending on-sit calls for solidification within a certain time. If the gelling time is too long, it may cause the loss of liquid rubber, if the gelling time is too short, viscosity will increase, the grouting operation will not have enough time. So the dry time should be controlled at about 6 h. Therefore, the catalyst dosage is determined at 0.3%.

3.5 Effects of mixed fillers on the properties of polyurethane rubber

In the gelling process of prepolymers and chain extender, polyurethane surface and inside have cracks, pores and grain boundary surface. Polyurethane rubber often began to fracture in these weaknesses under the action of stress. In the beginning stage of fracture, at the crack extension direction, crack may bifurcate or change direction in case of meeting fillers. The energy accumulated because of the action of stress will spread out, delaying the fracture of the polyurethane rubber, which is beneficial to the improvement of the strength [5]. The fillers used in this work is a mixture of light calcium carbonate, carbon black and titanium dioxide with a ratio of 15:5:1. the effects of fillers quantity (w%, and the same) on the properties of polyurethane rubber is shown in Figure 6.

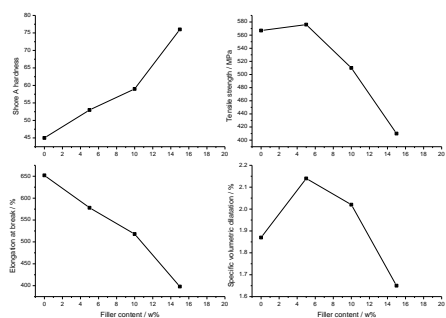


Figure 6. Effects of mixed fillers dosage on the properties of polyurethane rubber

As is shown in Figure 6 , adding suitable amount of fillers in the polyurethane crosslinking system can improve its tensile properties and volume expansion rate. It also can reduce unit production costs at the same time. But if the content is more than 4%, it will make the mechanical properties of liquid rubber decrease a lot, its tensile properties and volume expansion rate decrease, and viscosity increase at the same time, which increasing the construction difficulty [6]. So in this work, the amount of fillers is determined at 4%.

5. Application

Verified by application, the liquid rubber prepared according to the process above has the function of repeatedly expansion when contact with water. It has good mechanical properties, and high volume expansion ratio. After the liquid rubber is poured into water-stop, even if it is broken by external force, it will expand when contact with water, which makes the torn part automatically pressure, has the function of "healing". The plugging waterproof effect is good.

6. Conclusions

Sealing material liquid rubber utilized in construction environment was prepared using diphenyl methane diisocyanate (MDI), polyether 330, polyether 220, butyl acetate, additives and packing. The effects of the temperature of prepolymerization reaction, the content of -NCO after prepolymerization reaction , the ratio of mixed polyether, and the amount of catalyst and fillers on product properties were investigated. The optimal preparation technology was determined: When the temperature of prepolymerization reaction is 90°C, polyether 330 / polyether 220 is 85 /15 (w %), the content of - NCO (w%) is 4. 1%, the amount of dibutyltin dibutyl (w %) is 0. 3 %, and the amount of packing (w %) is 4%, the liquid rubber prepared has better properties. The volume expansion rate is over 520%. It exhibits good waterproof performance when utilized in construction environment.

Acknowledgments

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