



## Study on a Single-Component Solvent-Free Polyurethane Adhesive Prepared with Latent Curing Agent

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A novel single-component solvent-free polyurethane adhesive is prepared by using an environmental latent curing agent. As the reaction between free isocyanate groups and H<sub>2</sub>O replaced by latent curing agent and H<sub>2</sub>O, the release of CO<sub>2</sub> during intermediate steps is avoided. Constantly, there is no foam in film. The performance of adhesive is improved due to the bifunctional structure of latent curing agent.

**Key Words:** Single-component solvent-free, Polyurethane adhesive, Latent curing agent.

### INTRODUCTION

In recent years, single-component solvent-free polyurethane adhesive has been applied in various areas like automotive, aerospace, packaging and electronics, due to its good adhesion, excellent mechanical properties, chemical and weather resistance<sup>1,2</sup>. Single-component solvent-free polyurethane adhesive can cure at temperature without any plus energy and the polymers is achieved by the reaction between free isocyanate groups (-NCO) in prepolymers and H<sub>2</sub>O in the air or active hydrogen atoms on substrate surface. But the release of CO<sub>2</sub> during intermediate steps forms foam in the film. Therefore performance of adhesive is weakened<sup>3</sup>. As a novel type of curing agent, latent curing agent is studied to solve this problem. It can coexist with polyurethane adhesive (PU) system without any moisture. While in moisture condition, -NCO group don't react with H<sub>2</sub>O but with -NH<sub>2</sub> or -OH group which is generated in the process of latent curing agent reacting with H<sub>2</sub>O. During the whole process there is no CO<sub>2</sub> release, so the film achieved is of intact morphology and has better performance<sup>4,5</sup>.

In this paper, firstly a prepolymer terminated with -NCO group is prepared by using polyether polyol (PPG), modified 4,4'-diphenyl methane diisocyanate (MDI) and multimethylene multiphenyl multiisocyanate (PAPI) as key raw materials. Then an environmental latent curing agent with bifunctional structure is mixed with the prepolymer to perform the latent curable polyurethane adhesive (LPU). In order to achieve best adhesion properties, we choose 1,4-butanediol (1,4-BDO) as chain extender and dilaurate dibutyltin (DBTDL) as catalyst.

### EXPERIMENTAL

**Preparation of prepolymers:** Polyether polyol is dried at 150 °C for 2 h before being mixed with modified MDI/PAPI mixture in a 500 mL 4-necked glass flask. The flask is equipped with a stirrer, a thermometer, a nitrogen inlet and a condenser. When H<sub>2</sub>O % of polyether polyol is less than 0.08 %, the mixture starts to be heated slowly up to 67 °C and is kept at 65-68 °C for about 3.5-4 h under nitrogen atmosphere. Then the prepolymer is attained after being cooled below 50 °C, with viscosity at about 2000 mPa.s.

**Preparation of polyurethane adhesive:** The chain extender (1,4-BDO) and catalyst are added into prepolymers with stirring. The reaction is continued under nitrogen with stirring for about 1 h until NCO % attained the theoretical value. Then various dosage of latent curing agent is added into the system. A novel polyurethane adhesive dispersion is achieved after keeping stirring for another 0.5 h. It should be kept in a closed container after being cooled below 30 °C.

**-NCO content analysis:** The NCO content is measured by dissolving polyurethane adhesive in acetone-dibutylamine solution and titration with *N,N*-dibutylamine. Consumption of *N,N*-dibutylamine is tested by standard HCl solution (1 mol/L) and compared with the initial value.

**Viscosity analysis:** The viscosity of the polymers are measured at room temperature in a rotational viscometer (Model NDJ-1), with the spindles R-4 at 50 r/m.

**Tensile strength and elongation at break analysis:** Dried dumbbell shaped specimens with length at 40 mm and thickness at 1.0 mm are prepared before testing. The test is performed by using a tensile testing mashine at a crosshead speed of 40 mm/min (ASTM D2095-96).

**Shear strength analysis:** Shear strength is measured by using single lap joint specimen (Metal/polymers adhesive joints). The metal samples is of  $100 \times 25 \times 2$  and joint area  $12.5 \times 25$ . It is tested in a universal test machine at a loading speed at 5-7 mm/min (ASTM D3164).

**Differential scanning calorimetry analysis:** Differential scanning calorimetry analysis is carried out with a differential scanning calorimetry analyzer under nitrogen atmosphere with heating speed at  $10 \text{ }^\circ\text{C/m}$  from  $-100 \text{ }^\circ\text{C}$  to  $100 \text{ }^\circ\text{C}$ . Each sample contains about 2 g polymers.

## RESULTS AND DISCUSSION

A novel single-component solvent-free polyurethane adhesive containing latent curing agent is prepared *via* conventional polymer method. Fig. 1 shows the test results by differential scanning calorimetry analysis. One glass transition is concluded in the figure and the glass transition temperature ( $T_g$ ) value of polyurethane adhesive films is  $-26.9 \text{ }^\circ\text{C}$ , which is lower than that of conventional single-component solvent-free polyurethane adhesive. Therefore it can exhibit better flexibility and higher initial cohesion strength. This is probably due to the coaction of mass ratio of soft and hard segments, crosslinking density and the hydrogen bonding content.

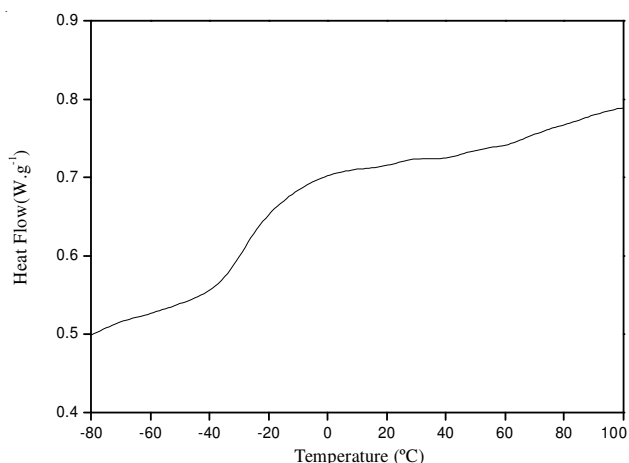


Fig. 1. Differential scanning calorimetry thermograms of the polyurethane adhesive

Fig. 2 shows the variation of viscosity as a function of the molar ratio of NCO/OH in prepolymers. There is a decrease of viscosity as the increase of NCO/OH molar ratio. Because the viscosity of polymers depends on the average molecular weights. Existence of excess -NCO contributes to prepolymers with low molecular weight. Therefore the higher the excess -NCO content, the lower the molecular weight of prepolymers and the lower the viscosity of polymers.

Fig. 3 shows the variation of shear strength as a function of molar ratio of NCO/OH. In general, shear strength depends on both molecular weights and crosslinking density of polymers. Increasing in ratio of -NCO contributes to more free isocyanate group, polymers with low molecular weights but high crosslinking intensity are achieved. The combination of these two opposite actions can exactly explain the behavior of shear strength in Fig. 3. It is suggested that the moderate molar ratio of NCO/OH is 4:1.

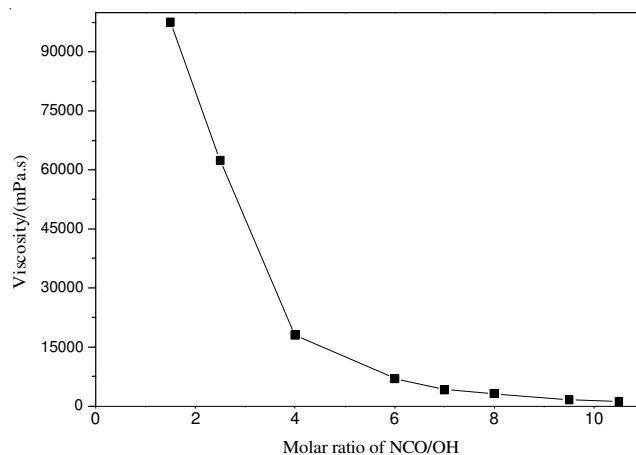


Fig. 2. Viscosity of polyurethane adhesive as a function of molar ratio of NCO/OH

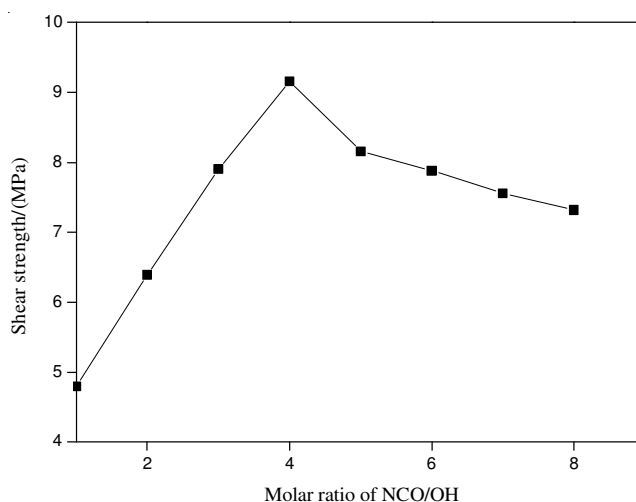


Fig. 3. Shear strength of polyurethane adhesive as a function of molar ratio of NCO/OH

On condition molar ratio of NCO/OH is 4:1, a series of adhesive is prepared with various dosage of free isocyanate. Variation of adhesion properties is showed in Fig. 4. It is found as the free -NCO content increases the shear strength exhibit a initial increase. This is probably due to hydrogen bond and van der Waals force generated from the reaction between isocyanate and hydrogen on substrate surface. So adhesion properties of polymers is enhanced. When the content is higher than 3.5 % resulted a strength decrease. Because polymers with low molecular weight are achieved as increase of -NCO content. Consequently, the intermolecular interactions between chains become less important, which gives a low shear strength value. At the same time, the viscosity of polymers keep an increasing trend. The higher the -NCO content, the higher the viscosity of polymers. In order to achieve moderate viscosity and shear strength, the -NCO content should be controlled at about 3.5 %.

The adhesion properties of polyurethane adhesive as a function of molecular weights of polyether polyol are showed in Table-1. As molecular weights of polyether polyol increases, tensile strength decreases and elongation at break increases. Both of the two trends can be explained considering the -NCO content. When preparing polymers with the same molecular weights, the higher the molecular weights of polyether polyol,

the lower the -NCO content needed. Constantly, the intermolecular interaction between chains become weaker. At the same time, lower crosslinking intensity in compound is attained and shear strength is in reduction too. In this paper, molecular weights of polyether polyol = 1000 is the best choice.

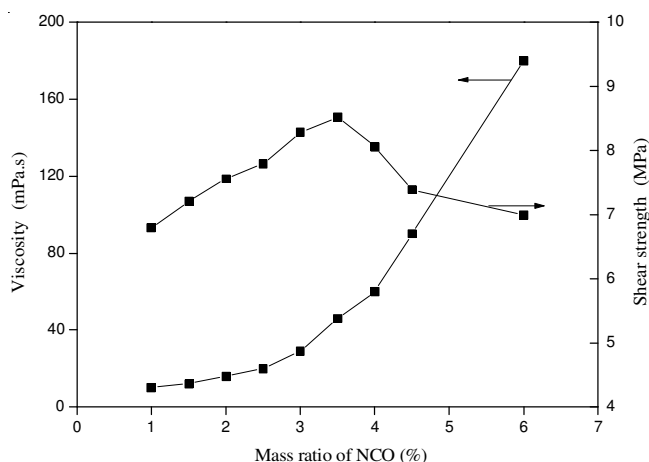


Fig. 4. Viscosity and shear strength variation of polyurethane adhesive as a function of mass ratio of NCO

TABLE-1  
EFFECT OF POLYETHER POLYOL WITH DIFFERENT  
MOLECULAR WEIGHTS ON MECHANICAL  
PROPERTIES OF POLYURETHANE ADHESIVES

PPG( $M_n$ )	Shear strength (MPa)	Elongation At break (%)	Tensile strength (MPa)
PPG204 ( $M_n = 400$ )	8.25	170	19.36
PPG210 ( $M_n = 1000$ )	7.68	230	17.05
PPG220 ( $M_n = 2000$ )	6.76	280	13.58

Based on above research, when molar ratio of NCO/OH is 4:1, mass ratio of -NCO is 3.5 % and molecular weights of polyether polyol is 1000, the polyurethane adhesive is prepared. Because latent curing agent can react with  $H_2O$  prior to reaction between -NCO and  $H_2O$ , the intermediate step to release  $CO_2$  is avoided. Fig. 5 showed that the addition of latent curing agent contributes to reduction in foam diameter of films, indicating that the release of  $CO_2$  is limited. There will be no foaming phenomenon in films when content of latent curing agent is up to 3 %. Furthermore, the variation of shear strength is showed in Fig. 5 and it indicates an initial increase with dosage increase of latent curing agent. The latent curing agent is a bifunctional substance, which can provide polymers with more urethane bonding or urea bonding as curing. Therefore intermolecular interactions are enhanced. But the existence of excess latent curing agent makes function group wrapped by macromolecular. That is the reason that shear strength results in reduction when the dosage is more than 3 %.

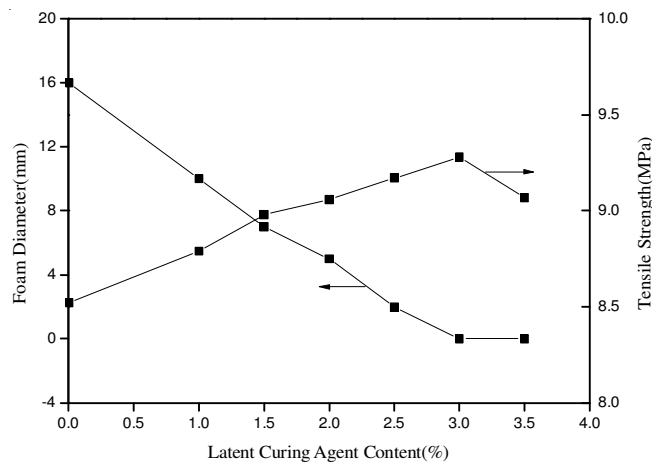


Fig. 5. Effect of latent curing agent content on foam diameter of films

## Conclusion

A novel single-component solvent-free polyurethane adhesive containing latent curing agent is prepared. There is a reduction in  $T_g$  tested by DSC analysis and the exact value of  $T_g$  is  $-26.9\text{ }^\circ\text{C}$ . The higher the molar ratio of NCO/OH, the higher the viscosity of polymers. While shear strength of polymers shows a initial increase and results in a reduction. As molecular weight increase of polyether diol, the tensile strength and shear strength are in reduction, but the elongation at break increases. Addition of latent curing agent can be a limitation of  $CO_2$  release and when content of latent curing agent is up to 3 %, the film achieved exhibits no foam phenomenon. With more reactive function provided, tensile strength of polymers are increased. But the reaction is weakened when latent curing agent content is up to 3 %, hence a decrease results.

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## REFERENCES

- S.-C. Wang, P.-C. Chen, J.-T. Yeh and K.-N. Chen, *React. Funct. Polym.*, **67**, 299 (2007).
- A.L.D. da Silva, J.M. Martin-Martinez and J.C.M. Bordado, *Int. J. Adhes. Adhes.*, **26**, 355 (2005).
- Y.-L. Liu, *Polyurethane Industry*, **14**, 3 (1999).
- L.-L. Bian, D. Zhao, H.-D. Wu, Y.-J. Shi and Z.-Y. Luo, *Polyurethane Industry*, **25**, 2 (2005).
- G. Malucelli, A. Priola, F. Ferrero A. Quaglia, M. Frigione and C. Carfagna, *Int. J. Adhes. Adhes.*, **25**, 87 (2005).