Preparation and characterization of aqueous polyurethane oil/polyacrylate latex interpenetrating polymer network

M M Zhou, L L Ma, J Du, F Cao and J J Xiao

School of Materials Science and Engineering, Hebei University of Science and Technology, 050018 Shijiazhuang, P.R. China

E-mail: jijunxiao@aliyun.com

Abstract. A series of aqueous polyurethane oil (network I) /polyacrylate (network II) latex interpenetrating polymer networks (LIPNs) were synthesized via the technology of latex interpenetrating polymer network combined seed emulsion polymerization process. Fourier transform infrared (FTIR) spectroscopy, laser particle size distributing analyzer and universal tension machine were utilized to characterize the bulk structures and mechanical properties of LIPNs. For used as damping material, the damping performance of LIPNs were analyzed by dynamic mechanical analysis (DMA). It was found that the damping temperature region of LIPN was wider than those of aqueous polyurethane oil, the temperature region with greater tanδ changed with the TPGDA content and hard-/soft-segment mass weight ratio (mMMA/mBA) and the glass transition temperature (Tg) of the network I and network II in LIPN occurred within shift each other, even overlap with increasing mMMA/mBA value. The results show that LIPNs synthesized through the combined process have greater tanδ and wider damping temperature region, which is suitable for the use of damping coatings.

1. Introduction
In recent years, the research of technologies reducing vibration noise and materials has been paid more attention because of the serious noise pollution problem. The polymer damping coating is a kind of functional materials, which can reduce the vibration and noise of various mechanical vibrations [1, 2]. The polymer has higher damping values in the glass transition temperature (Tg) range. Generally, the glass transition temperature region of a single polymer is only 20°C-30°C, while the change of environmental temperature region is bigger than the Tg region of polymers. In order to meet the requirements of different environments, people have need to synthesis polymers with Tg more than 60°C. The technology of interpenetrating polymer networks (IPNs) could solve noise pollution problem [3-5]. The IPNs are a novel type of polymer blend composed of cross-linked polymer, combining the advantages of each component forming networks [6, 7]. In order to reduce the cost and the danger of organic solvent volatilization, the rapid development of waterborne damping coatings have been obtained, especially in the Latex interpenetrating polymer network (LIPN). LIPN is a unique type of polymer blend prepared by seed emulsion polymerization [8]. LIPN exhibits excellent properties superior to those of each component, being attributed to their morphological structure [9]. In this study, LIPN was composed of waterborne polyurethane oil referred to as network I and the

1 Address for correspondence: J J Xiao, School of Materials Science and Engineering, Hebei University of Science and Technology, 050018 Shijiazhuang, P.R. China. E-mail: jijunxiao@aliyun.com.
polymer derived from methyl methacrylate and butyl acrylate as network II.

2. Experimental

2.1. Materials
The raw materials used were polyurethane oil (PUO, made by ourselves), methyl methacrylate (MMA, Shanghai Huayi Company), n-butyl acrylate (BA, Beijing Eastern Petrochemical Company), tripropylene glycol diacylate (TPGDA, Ji’nan Venus Chemical Industry), potassium persulfate (Tianjin Yongda Chemical Reagent Company Limited), potassium bicarbonate (Tianjin Yongda Chemical Reagent Company Limited).

2.2. Synthesis of latex interpenetrating polymer network (LIPN) of aqueous polyurethane oil/polyacrylate
Polyurethane oil was put into a 500 mL four-flask with a mechanical stirrer, a thermometer and a reflux condenser, and stirred gradually heated to 70°C. Then the solution of potassium persulfate and sodium bicarbonate and the mixture of MMA, BA and TPGDA were added to the system by dropping under nitrogen for 2 h, and heated to 80°C. Subsequently the system was maintained for 1 h at approximately 80°C. After cooling to room temperature, the LIPN was obtained.

2.3. Measurements
FTIR spectra were collected on a Nicolet 6700/FTIR-Raman modules spectrometer. The particle size of LIPN was measured by dynamic light scattering analyzer (MALVERN NANO-S90). Dynamic mechanical analysis (DMA) were performed on a Q800 dynamic mechanical analyzer with film tensile-mode in a temperature range from -60°C~80°C at a frequency of 2 Hz and a heating rate of 5°C/min. The tensile tests were performed in a universal testing machine (CMT7104) with a stretching rate of 500 mm/min.

3. Results and discussion

3.1. FTIR analysis
The FTIR spectra of polyurethane oil (Network I) and LIPN (solid content of 30%, hard-/soft-segment mass weight ratio ($m_{MMA}:m_{BA}$)=1:1, the amount of crosslinking agent of 0.2% relative to monomer ) are shown in figures 1 and 2, respectively.

In figure 1, a strong stretching band located at 3336 cm$^{-1}$ corresponding to characteristic absorption peak of the N-H group, a stretching vibration band centered around 1719.4 cm$^{-1}$ corresponding to one of the C=O group, and a strong stretching band located at 1241 cm$^{-1}$ due to one of the C-O-C group are observed, indicating the existence of NHCOOR in network I. The results suggest that the network I was polyurethanes. It can also be observed that there was no absorption bands at 811 cm$^{-1}$ (H-C=C) in figure 2, indicating that the network II have formed via radical polymerization of monomers. These results suggest that LIPN was successfully prepared.

![Figure 1. FTIR spectrum of polyurethane oil (network I).](image1)

![Figure 2. FTIR spectrum of LIPN.](image2)
3.2. Influence of various factors on latex particle size for LIPN

3.2.1. Effect of mMMA/mBA value on particle size of the LIPN. Figure 3 shows the influence of \( m_{\text{MMA}}/m_{\text{BA}} \) on the of average particle size of LIPN. The results shown that average particle size of LIPN decreases with the increasing \( m_{\text{MMA}}/m_{\text{BA}} \) value, indicating the greater the soft monomer BA, the softer the particles and more easy to coagulate to form larger particles.

3.2.2. Effect of the TPGDA content on particle size of the LIPN. As seen from figure 4, the average particle size of latex particle for LIPN initially increases with the increasing TPGDA content. As the TPGDA content is more than 0.4%, that of LIPN decreases. Because a small amount of crosslinking agent is equivalent of monomer which can not develop the role of crosslinking agent. While the amount of the crosslinking agent exceeds 0.4%, the crosslinking agent plays the role of crosslinking, and the maromolecular chains were cross-linked together to obtained smaller particles.

![Figure 3](image1.png)  ![Figure 4](image2.png)

**Figure 3.** Effect of \( m_{\text{MMA}}/m_{\text{BA}} \) on LIPNs particle size.

**Figure 4.** Effect of TPGDA content on LIPNs particle size.

3.3. Dynamic mechanical analysis (DMA)

3.3.1. DMA curve of LIPN compared as network I. The loss factor (\( \tan \delta \)) represents the damping properties of polymers. In general, the greater \( \tan \delta \), the better damping properties of polymer. As shown figure 5, there were two peaks of \( \tan \delta \). In figure 5(a), one of peaks was corresponding to \( T_g \) (-49.54°C) of soft segment for aqueous polyurethane oil, the other was \( T_g \) (64.25°C) of hard segment. While in figure 5(b), one was corresponding to \( T_g \) (-23.35°C) of network II, the other was \( T_g \) (57.49°C) of aqueous polyurethane oil in LIPN. It can be seen from figure 5, the damping temperature region of LIPN was wider than those of aqueous polyurethane oil.

![Figure 5](image3.png)

**Figure 5.** DMA curves of aqueous polyurethane oil and LIPN.
3.3.2. Effect of mMMA/mBA value on glass transition temperature ($T_g$) for LIPNs. The loss factor (tan$\delta$) of LIPNs are shown in figure 6. According to FOX equation, the $T_g$ of network II corresponding to the $m_{MMA}/m_{BA}$ of 1:5, 1:2, 1:1, 1:0.5 were -39.7°C, -20.8°C, 1.4°C, 28.4°C respectively. It can be seen from Figure 6, The $T_g$ of network I in LIPN was observed at approximately 54°C, and shifted to lower temperature compared with the $T_g$ (65°C) of pure network I. The $T_g$ of network II corresponding to the $m_{MMA}/m_{BA}$ of 1:5, 1:2, 1:1, 1:0.5 were -25°C, 8°C, 27°C, 56°C, respectively, shifted to higher temperature with increasing $m_{MMA}/m_{BA}$ value and greater than corresponding calculated value. The $T_g$ of the network I and network II in LIPN occurred within shift each other, even overlap with increasing $m_{MMA}/m_{BA}$ value. This result may be attributed to the physical entanglement between the network I and network II.

3.3.3. Effect of TPGDA content on $T_g$ of LIPNs. Figure 7 shows the influence of crosslinking agent TPGDA content on tan$\delta$ and $T_g$ of LIPNs. As can be seen, with increasing TPGDA content, the two peaks of LIPNs move within each other, the valley became smaller and gradually tend to be flat, or even overlap, Those results may be attributed to higher physical entanglement and interpenetrating of network I and network II at interface, resulting in lower phase separation and greater forced compatibility.

![Figure 6](image6.png) Effect of MMA/BA on $T_g$ of LIPNs.

![Figure 7](image7.png) Effect of TPGDA content on $T_g$ of LIPNs.

![Figure 8](image8.png) Effect of TPGDA content on the tensile strength of LIPNs.

![Figure 9](image9.png) Effect of $m_{MMA}/m_{BA}$ on the tensile strength of LIPNs.

3.4. Influence of various factors on the tensile properties for LIPN films

3.4.1. Effect of TPGDA content on the tensile strength for LIPN films. The influence of TPGDA
content of LIPNs on tensile strength was shown in figure 8. It can be seen that the tensile strength of LIPN films increased with increasing TPGDA content. The results shown the interpenetrating degree of two networks in latex particle was widened, and improve the tensile strength of LIPN film.

3.4.2. Effect of \( m_{\text{MMA}}/m_{\text{BA}} \) on the tensile strength for LIPN films. The effect of \( m_{\text{MMA}}/m_{\text{BA}} \) on tensile strength for LIPN films was investigated. It can be found from figure 9 that the tensile strength of the LIPN films increase with the increasing \( m_{\text{MMA}}/m_{\text{BA}} \) value. Because MMA as hard segment could increase the strength of the LIPN film; While BA as soft segments could reduce the strength of the LIPN film.

4. Conclusions
A series of aqueous polyurethane oil/polyacrylate interpenetrating polymer networks (LIPNs) have been successfully synthesized via the technology of latex interpenetrating polymer network combined seed emulsion polymerization process. It shows good damping performances while the mass weight ratio of hard-/soft-segment (\( m_{\text{MMA}}/m_{\text{BA}} \)) was 1.2. The peak of damping temperature for LIPNs shifted gradually towards within each other, the \( T_g \) corresponding to maximal loss factor (\( \tan\delta_{\text{max}} \)) increased and the damping temperature range narrowed with increasing \( m_{\text{MMA}}/m_{\text{BA}} \) and TPGDA content. It indicated that the \( T_g \) and temperature range of damping materials would be satisfied by changing the TPGDA content and \( m_{\text{MMA}}/m_{\text{BA}} \). This result implied that this type of LIPNs in our experiments is potential application in aqueous damping material with wider temperature region.

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