Novel *Eucommia ulmoides* Gum-based Damping Materials for Multicomponent Latex Interpenetrating Polymer Networks

Xiang Li, Jichuan Zhang, Zhaohong Xue*, Ruifang Yan, and Shibi Fang

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

Received December 31, 2005; accepted August 7, 2006

This work describes a series of novel *Eucommia ulmoides* gum (EUG)-based damping materials with excellent damping properties by using the interpenetrating polymer network (IPN) method for the first time; this is an innovative application of EUG. The novel core-shell structure of an EUG-based multicomponent latex interpenetrating polymer network (LIPN) can be controlled by selecting a suitable initiator system, emulsification method, and polymeric sequence and by regulating the miscibility among the components. The damping properties and morphology of multicomponent LIPNs were investigated by dynamic mechanical analysis (DMA) and transmission electron microscope (TEM) in order to reveal the relationship between structure and performance. The results show that some LIPNs that use EUG as the seed in the multicomponent core-shell structure have a high damping factor ($\tan\delta$) at a broader temperature range. For example, the EUG/PS/PBA LIPN (1/1/1 by weight) possesses excellent damping properties; its temperature range for $\tan\delta > 0.3$ extends to almost 130°C. EUG-based LIPNs, particularly the ternary EUG-based LIPNs are novel damping materials with good potential for development.

Key words: *Eucommia ulmoides* gum; latex interpenetrating polymer network; core-shell structure; damping property

Introduction

Conventionally, some viscoelastic polymers such as rubber-like polymers have been employed as damping materials; however, their useful damping temperature ranges usually extend to approximately 20°C–30°C around their glass transition temperature (T_g); this is not suitable for practical applications. In order to improve the damping capabilities of polymers, IPNs are promising candidates for the synthesis of novel polymer alloys with broad damping temperature ranges and excellent damping performance. IPNs generally comprise two or more cross-linked polymer networks bound by topological catenation, and therefore, each polymer network exhibits a different synergistic effect because of the forced compatibility due to mutual permanent entanglement and a dual-phase continuous microstructure¹⁾.

LIPNs, a type of prevailing IPN, are typically prepared by the sequential *in situ* polymerization of various monomers diffused in a cross-linked “seed” latex (*i.e.*, the EUG latex) to form a core-shell structure. Generally, no significant additional surfactant is added in the second step to avoid the fresh nucleation of other polymer latexes that would lead to the formation of simple latex blends.

Recently, several distinct types of LIPN damping materials have been reported, such as polyurethane, polyacrylate, and a silicone-based LIPN system^{2–4)}. Although these materials exhibit good damping properties to a certain extent due to their special characteristics, generally, their temperature ranges for a high $\tan\delta$ value (>0.3) do not exceed 100°C. Further, the $\tan\delta$ values of the damping platform cannot re-

main stable since the means used to improve compatibility, for example, using a copolymer as a compatibilizer and adjustment of solubility parameter by controlling the constitutive composition of polyurethane, usually result in a shift in the trends of T_g , and it is not possible to maintain consistent compatibility without fulfilling the requirement of excellent damping properties. Moreover, after the formation of the LIPN structure, the processability and durability of these materials are typically further deteriorated compared to that of the original polymers^{5–7)}.

In this work, it has been found that the EUG-based IPNs, particularly the ternary EUG-based LIPNs, substantially overcome the problems described above and are a novel type of damping structure with good potential for development. Additionally, this work also discovered a novel method for preparing an EUG seed latex to form a LIPN seed emulsion for polymerization to ensure the formation of a stable core-shell structure and avoid unexpected latex blends.

Materials and Methods

1. Materials

In this study, we used styrene (St) and *n*-butyl acrylate as materials for the monomers. They were distilled under reduced pressure to remove the inhibitor prior to use; EUG was dissolved in toluene and then purified by deposition in acetone⁸⁾.

2. Methods

EUG-based multicomponent LIPNs were prepared by

*Corresponding author: Tel +86-01-62562816; E-mail duzhong@iccas.ac.cn

Fig. 1. (a) DMA curves of EUG/PS IPNs in various component ratios (b) DMA curves of EUG/PBA IPNs in various component ratios

a two-stage emulsion polymerization technique. First, the EUG was dissolved into benzene with or without an initiator and added into a water-containing emulsifier in a reaction vessel and stirred. Benzene was then removed under a specific condition to obtain TPI latex. Second, monomer I and a cross-linker and initiator were added into the cooled EUG latex; the EUG latex particles were sufficiently swollen by stirring and the equilibrium distribution of the monomer in the matrix was achieved, resulting in the formation of the seed latex for the next stage. Finally, monomer II and a cross-linker and an initiator were added into the seed latex while polymerization was carried out; the resulting sample was the desired LIPN.

The damping properties and morphology of the LIPN were investigated by DMA and TEM.

Results and Discussion

1. EUG/PS and EUG/PBA IPNs

Fig. 1 shows the plots of $\tan \delta$ against the temperature of the EUG/PS (a) and EUG/PBA (b) IPNs with different component ratios of EUG and PS or PBA (ranging from 30/70 to 70/30 by weight). As shown in Fig. 1(a), the plots of all EUG/PS IPNs show two distinct peaks. The temperature difference between both peaks of all samples is different; the temperature difference between the two peaks of the 50/50 EUG/PS IPN is less than that between the two peaks of the 30/70 and the two peaks of the 70/30 EUG/PS IPNs. This implies that EUG/PS is an immiscible polymer couple even in IPNs. In addition, the 50/50 EUG/PS IPN also exhibits a undesirable damping properties due to the fact that the damping platform between the two separate peaks representing Tg of EUG and PS respectively has low $\tan \delta$ value. As shown in Fig. 1(b), only one damping peak appears in all the EUG/PBA IPN plots, and the magnitude of the peaks increases as the PBA component increases; this implies that the EUG/PBA couple is more compatible than the EUG/PS couple.

The results can be attributed to the fact that the damping properties of IPN are mainly affected by the compatibility between the networks. The compatibility between PS and EUG is poor because of the large solubility parameter difference ($\Delta\delta$) between PS ($1.81 \times 10^4 \text{ J}^{1/2} \text{ m}^{2/3}$) and EUG (1.70

$\times 10^4 \text{ J}^{1/2} \text{ m}^{2/3}$). Since the $\Delta\delta$ value of PBA ($1.74 \times 10^4 \text{ J}^{1/2} \text{ m}^{2/3}$) and EUG is smaller than that of PS and EUG, the compatibility of the EUG/PBA IPN can be improved. Further, Tg of PBA is in the vicinity of that of EUG; therefore, the damping properties of PBA and EUG can be effectively enhanced within their Tg ranges.

The results are also attributable to the effects of the differences in morphology on the damping properties of IPNs. Fig. 2 shows the TEM images of a EUG/PS and EUG/PBA LIPN at a 50/50 component ratio by weight. As shown in Fig. 2, the phase boundary of the EUG/PBA LIPN in Fig. 2(b) is blurred compared with that of the EUG/PS LIPN in Fig. 2(a) in which the cellular microstructure has been formed. Therefore, we can conclude that the compatibility of the EUG/PBA LIPN is better than that of the EUG/PS LIPN.

2. The damping properties of three-component EUG-based LIPNs

The traditional structure of LIPNs is a network of plastics having a high Tg component and rubber having a low Tg component formed by the forced compatibility method. However, generally, the desired compatibility, damping, and mechanical properties cannot be obtained simultaneously; for example, the PS and PBA couple. Accordingly, a third component such as a compatibilizer must be incorporated to improve the compatibility between the couple.

Fig. 3 shows the plots of $\tan \delta$ against temperature for the LIPNs of PS and PBA and those of EUG, PS, and PBA at different polymerization orders. As shown in Fig. 3, it is evident that the order of the damping performance can be EUG/PS/PBA > PS/PBA > EUG/PBA/PS > PBA/PS. The damping property of PS/PBA LIPNs is poorer than that of PBA/PS LIPNs because hydrophobic PS serves as an outer shell that deteriorates the interpenetrating effect. This proves that polymerization orders have a key effect on the final damping properties of LIPNs. Further, the damping properties of the EUG/PS/PBA and EUG/PBA/PS LIPNs were observed to be better than those of the PS/PBA and PBA/PS LIPNs because of the high $\tan \delta$ platform value between both the Tg peaks. Among the four LIPNs, the damping property of the EUG/PS/PBA LIPN (1/1/1 by weight) is the best because its temperature ranges for $\tan \delta > 0.3$ extends to almost 130°C.

Fig. 2. (a) EUG/PS (50/50) LIPN TEM image

(b) EUG/PBA (50/50) LIPN TEM image

Fig.3. DMA curves of two-components LIPNs of PBA and PS and three-component LIPNs with EUG as the core component in different polymerization orders

The results can be attributed to the fact that EUG is a material with plastic-rubber duality and a double bonded structure. The compatibility of EUG with PS as plastic and PBA as rubber is higher than the compatibility between PS and PBA. Further, EUG is also cross-linked with PS and PBA, and therefore, it can serve as a public interpenetrating network to improve the compatibility between PS and PBA and the damping properties of the resulting materials. Moreover, the damping curve platform of EUG/PS/PBA exhibits higher $\tan\delta$ than that of EUG/PBA/PS, that is to say, EUG/PS/PBA has the better damping properties over EUG/PBA/PS. The cause may be that EUG/PBA is more compatible than EUG/PS so that the EUG/PS core IPN first forms and then the PBA shell structure forms; thereby EUG/PS/PBA can form the entangled three-component IPN structure. However, in the case of EUG/PBA/PS, since PBA is hydrophilic, it may cover the EUG core, and therefore, PS is blocked by the PBA layer when St polymerizes; thus, PS will be unable to swell the EUG core sufficiently to form an effective entanglement within the three-component IPN resulting in lower compatibility and poorer damping properties.

The TEM images of the EUG/PS/PBA and EUG/PBA/PS LIPNs in Fig. 4 show that the morphology of EUG/PBA/PS LIPN has a distinct boundary separating each cellular structure, but the morphology of EUG/PS/PBA shows an inde-

scribable boundary and all the cells blend together. Hence, the compatibility of the EUG/PBA/PS LIPN is better than that of the EUG/PBA/PS LIPN; this is in accordance with the DMA data.

The results can be explained as follows. The PS shell cannot blend due to high T_g , hardness, and the hydrophobic of PS; this indicates that the EUG/PBA/PS LIPN is not a complete interpenetrating network when it forms a film at room temperature. However, the PBA shell can be easily blended under capillary stress induced by water evaporation under identical conditions due to low T_g , high adhesiveness, and the hydrophilic of PBA. Accordingly, EUG/PBA/PS LIPNs are useful as damping materials since they form films easily.

Conclusion

EUG cannot exhibit a good synergetic effect in the two-component EUG/PS and EUG/PBA LIPNs since it is incompatible with PS and has a low absolute $\tan\delta$ value. However, it has potential application in multicomponent LIPNs as a compatibilizer due to its plastic-rubber duality and double bonded structure.

This work first revealed the damping properties of EUG-based multicomponent LIPNs and the relationships between the morphology and damping properties of LIPNs. Excellent damping is obtained by incorporating EUG as the core component in the core-shell structure of LIPNs to enhance compatibility among the components.

The results show that LIPNs that use EUG as the seed in the multicomponent core-shell structure have a suitable structure. These LIPNs have a high damping factor ($\tan\delta$) at a broader temperature range; in particular, EUG/PS/PBA LIPN (1/1/1 by weight) possesses excellent damping properties, its temperature range with $\tan\delta > 0.3$ covers almost 130°C.

In comparison with other LIPN materials that undergo deterioration, the ternary EUG-based LIPNs have better processability and durability since EUG serves as a soft and stable core and has a wide high T_g range; therefore, the ternary EUG-based LIPNs can form films easily and undergo plasticity with other rubber materials. Accordingly, the mul-

Fig. 4.(a) EUG/PBA/PS (1/1/1) LIPN TEM image

(b) EUG/PS/PBA (1/1/1) LIPN TEM image

ticomponent EUG LIPNs not only act as a type of damping material having excellent damping properties but can also be combined with rubber or plastics to improve their viscoelastic properties.

Therefore, the use of EUG-based LIPNs as damping materials, particularly trinary EUG-based LIPNs is a novel EUG application with good potential for development.

References

- 1) Sperling, L.H.(1981) *Interpenetrating polymer networks and related materials*, Plenum Press, New York.
- 2) Schneider, M., Pith, T., Lambla, M.(1996) Preparation and morphological characterization of two- and three-component natural rubber-based latex particles. *J. Appl. Polym. Sci.*, 62, 273-290.
- 3) Nemirovski, N., Silverstein, M.S., Narkis, M.(1996) Latex interpenetrating polymer networks: From structure to properties. *Polym. Adv. Tech.*, 7, 247-256.
- 4) Buravalla, V.R., Remillat, C., Rongong, J.A., Tomlinson, G.R.(2001) Advances in damping materials and technology. *Smart Mater. Bull.* 8, 10-15.
- 5) Fay, J.J., Murphy, C.J., Thomas, D.A., Sperling, L.H.(1991) Effect of morphology, crosslink density, and miscibility on interpenetrating polymer network damping effectiveness. *Polym. Sci. Eng.*, 24, 1731-1741.
- 6) Tamai, T., Imagawa A., Qui, T.C. (1994) Semi-Interpenetrating polymer networks prepared by in situ photo-Cross-linking of miscible polymer blends. *Macromolecules*, 27, 7486-7489.
- 7) Ali, S.A.M., Hourston, D.J.(1995) Thermoplastic interpenetrating polymer networks based on a Poly (styrene- β -butadiene) copolymer and a poly(styrene-co-sodium methacrylate) ionomer. *Eur. Polym. J.*, 31, 1-8.
- 8) Yan, R.F.(1996) *Eucommia ulmoides* gum, *Polymeric Materials Encyclopedia* (Salamone, J.C., Ed.) , CRC Press, Vol.3, pp.2291-2299.