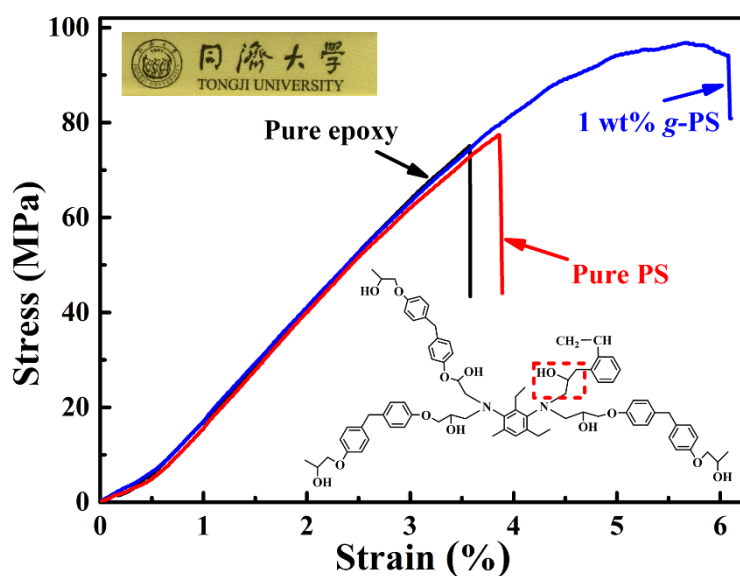


Low Loading of Grafted Thermoplastic Polystyrene Strengthened and Toughened Transparent Epoxy Composites

Hongbo Gu,^{1,*} Chao Ma,¹

¹Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, P. R. China.



The transparent epoxy composites strengthened and toughened by thermoplastic polystyrene which is grafted with epichlorohydrin (*g*-PS) have been prepared at a low loading level.

ABSTRACT

The transparent epoxy composites strengthened and toughened by thermoplastic polystyrene which is grafted with epichlorohydrin (*g*-PS) have been prepared at a low loading level. The polymer backbone of PS was manipulated by the epoxide and hydroxyl groups confirmed by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The contact angle and differential scanning calorimetry (DSC) tests indicated that the grafting process could decrease the surface tension and increase the compatibility between PS and epoxy resins. The effects of *g*-PS loading and grafting process on both the viscosity of liquid epoxy resin suspensions, as well as the physicochemical properties of cured epoxy composites have been systematically investigated. The cured *g*-PS/epoxy composites demonstrated an enhanced tensile strength (maximum of 97.4 MPa) than either cured pure epoxy (77.6 MPa) or PS/epoxy composites (79.1 MPa). The modulus of toughness for *g*-PS/epoxy composites is up to 355.9 MJ m⁻³, which is respectively 176.6 and 141.1% higher than that of cured pure epoxy and PS/epoxy composites. The uniform *g*-PS distribution in the cured *g*-PS/epoxy composites was observed by scanning electron microscope (SEM). The glass transition temperature (T_g) of cured *g*-PS/epoxy composites was shifted to a higher temperature (rising by 16.3 °C) in the dynamic mechanical analysis (DMA) compared with that of cured pure epoxy (111.7 °C). The obtained strong interfacial interaction between *g*-PS and epoxy matrix was responsible for the enhanced mechanical and thermal mechanical properties. This work provides a new sight for the investigation of interaction and

compatibility between thermoplastic and thermoset materials.

Tensile Mechanical Properties of PS/Epoxy Composites

The tensile strength and Young's modulus of cured pure epoxy and PS/epoxy composites were investigated by a unidirectional tensile test. The representative strain-stress curves of cured composites with different *g*-PS loadings are shown in Figure 1(A) and the related tensile properties are summarized in Table 1. The tension variation curve with error bars of cured epoxy composites filled with different loadings of *g*-PS is visually expressed in Figure 1(B). The tensile strength (the maximum stress in the stress-strain curve, MPa) of the cured *g*-PS/epoxy composites shows the favorable effects of grafting on the reinforcement of cured epoxy. The tensile strength increases as *g*-PS loading increases to 1.5 wt%, and reduces as the loading reaches 2.5 wt%. The largest average tensile strength of cured epoxy composites is 97.4 MPa with a *g*-PS loading of 1.5 wt%, which is remarkably increased and 25.5% higher than that of cured pure epoxy (77.6 MPa). For the cured epoxy composites with a *g*-PS loading of 0.5, 1.0, 2.0 and 2.5 wt%, the tensile strength is observed to be 22.8 (95.3 MPa), 24.9 (96.9 MPa), 24.5 (96.6 MPa), and 9.5% (85.0 MPa) higher than that of cured pure epoxy, respectively. The Young's modulus (the slope of the stress-strain curve in the low strain range) of cured epoxy composites with *g*-PS has no obvious differences from that of cured pure epoxy, while the Young's modulus of cured composites with 0.5 wt% loading of pure PS is 6.6% (2.25 GPa) lower than that of cured pure epoxy (2.41 GPa). The elongation-at-break for all of the cured epoxy and PS/epoxy composites is also listed in Table 1. It's observed that the elongation-at-break for all of the *g*-PS/epoxy

composites is much higher than that of cured pure epoxy and PS/epoxy composites. The elongation-at-break for *g*-PS/epoxy composites is increased with *g*-PS loading up to 1.0 wt% and then declined as further increasing *g*-PS loadings, exhibiting an obvious toughening effect after grafting functional groups on the PS polymer backbone. Normally, the modulus of toughness (U_t), which is used for describing an ability of materials to absorb energy and deform plastically without fracturing, is correlated to the area under the stress-strain curve.³⁵ The calculated U_t for the epoxy composites reinforced with *g*-PS loadings of 0.5, 1.0, 1.5, 2.0, and 2.5 wt% is 224.2, 355.9, 285.0, 273.7, and 268.7 MJ m⁻³ (or MPa), which is correspondingly 74.2, 176.6, 121.5, 112.7, and 108.9% larger than that of cured pure epoxy (128.7 MJ m⁻³). The U_t for the 0.5 wt% loading of PS/epoxy composites is 147.6 MJ m⁻³, which is much lower than that of *g*-PS/epoxy composites. The increased compatibility and chemical interaction between *g*-PS and epoxy matrix confirmed by contact angle and DSC tests are responsible for the increase of tensile strength and modulus of toughness.

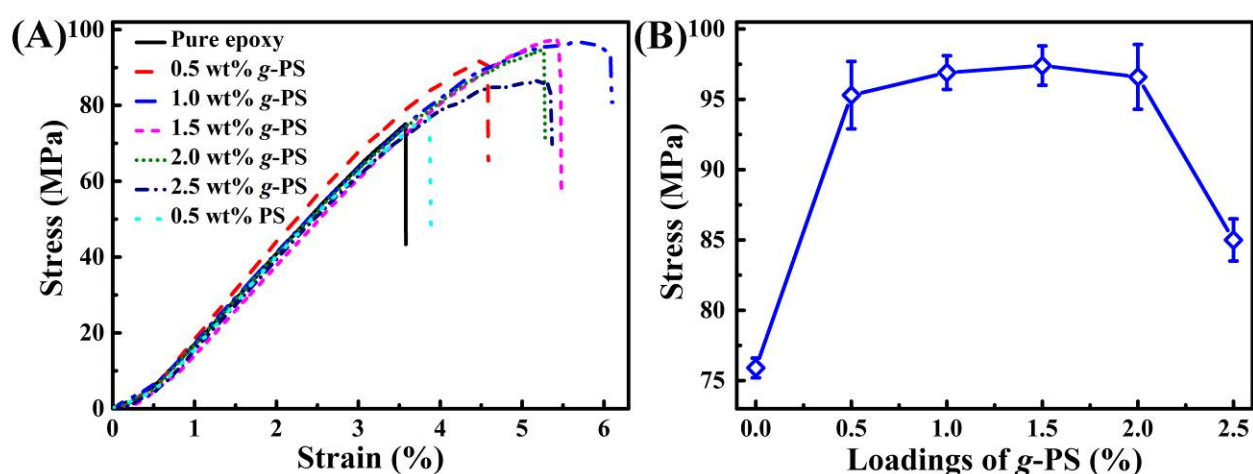


Figure 1. (A) Stress-strain curves of cured epoxy composites filled with different loadings of *g*-PS and pure PS; (B) tensile strength with error bars of cured epoxy composites filled with different loadings of *g*-PS.

Table 1. Tensile mechanical properties of cured pure epoxy and epoxy composites.

| Sample | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break (%) |
|--------------------|------------------------|-----------------------|-------------------------|
| Pure Epoxy | 77.6±0.7 | 2.43±0.1 | 3.6±0.1 |
| Epoxy/0.5 wt% g-PS | 95.3±2.4 | 2.42±0.2 | 6.0±1.4 |
| Epoxy/1.0 wt% g-PS | 96.9±1.2 | 2.43±0.1 | 6.5±0.4 |
| Epoxy/1.5 wt% g-PS | 97.4±1.4 | 2.41±0.1 | 5.6±0.4 |
| Epoxy/2.0 wt% g-PS | 96.6±2.3 | 2.36±0.1 | 5.7±0.4 |
| Epoxy/2.5 wt% g-PS | 85.0±1.5 | 2.37±0.1 | 5.3±0.1 |
| Epoxy/0.5 wt% PS | 79.1±4.1 | 2.25±0.1 | 3.8±0.4 |

Conclusion

The epichlorohydrin grafted PS (*g*-PS)/epoxy has been prepared at different powder loadings. The functional groups on the *g*-PS polymer backbone is hydroxyl and epoxide groups confirmed by FTIR, TGA, and XPS analysis. The decreased surface tension and the exothermic peak in the DSC test indicate that the *g*-PS could significantly improve the compatibility between *g*-PS and epoxy resin and chemically reacted with epoxy. The viscosity of *g*-PS/epoxy suspensions is increased with increasing *g*-PS loadings and decreased with increasing shear rates. After grafting with functional groups, the viscosity for the *g*-PS/epoxy resin suspension is much lower than that of pure PS/epoxy suspensions due to a good dispersion quality of *g*-PS within epoxy matrix. The *g*-PS/epoxy composites also exhibit a good transparency compared with pure PS/epoxy composites. The enhanced mechanical properties rising by 25.5% have been obtained in the cured *g*-PS/epoxy composites compared with cured pure epoxy. The significantly increased modulus of toughness for the cured *g*-PS/epoxy composites is much higher (rising by 176.6%) than that of cured pure epoxy (128.7 MJ m⁻³). The rough fracture surface and less holes in the epoxy composites filled with *g*-PS indicate the efficient load transfer and uniform *g*-PS distribution. The DMA results show that after grafting with functional groups, the T_g of *g*-PS/epoxy composites has moved to a higher temperature of 16.2 °C compared with that of cured pure epoxy (111.7 °C).

References

1. K. Wang, L. Chen, J. Wu, M. L. Toh, C. He and A. F. Yee, *Macromolecules*, 2005, **38**, 788-800.
2. N. Even, L. Adler-Abramovich, L. Buzhansky, H. Dodiuk and E. Gazit, *Small*, 2011, **7**, 1007-1011.
3. H. Jin, C. L. Mangun, D. S. Stradley, J. S. Moore, N. R. Sottos and S. R. White, *Polymer*, 2012, **53**, 581-587.
4. V. A. Agubra and H. V. Mahesh, *J. Polym. Sci., Part B: Polym. Phys.*, 2014, **52**, 1024-1029.
5. W. Tian, L. Liu, F. Meng, Y. Liu, Y. Li and F. Wang, *Corros. Sci.*, 2014, **86**, 81-92.
6. X.-L. Wang, Y.-Y. Yang, H.-J. Chen, Y. Wu and D.-S. Ma, *Tetrahedron*, 2014, **70**, 4571-4579.
7. C. Bao, Y. Guo, L. Song, Y. Kan, X. Qian and Y. Hu, *J. Mater. Chem.*, 2011, **21**, 13290-13298.
8. T.-I. Yang, C.-W. Peng, Y. L. Lin, C.-J. Weng, G. Edgington, A. Mylonakis, T.-C. Huang, C.-H. Hsu, J.-M. Yeh and Y. Wei, *J. Mater. Chem.*, 2012, **22**, 15845-15852.
9. P. Jyotishkumar, J. Koetz, B. Tiersch, V. Strehmel, C. Özdilek, P. Moldenaers, R. Hässler and S. Thomas, *J. Phys. Chem. B*, 2009, **113**, 5418-5430.
10. D. Zhang, A. B. Karki, D. Rutman, D. P. Young, A. Wang, D. Cocke, T. H. Ho and Z. Guo, *Polymer*, 2009, **50**, 4189-4198.
11. Z. Guo, S. Park, S. Wei, T. Pereira, M. Moldovan, A. B. Karki, D. P. Young and H. T. Hahn, *Nanotechnology*, 2007, **18**, 335704.
12. D. Zhang, R. Chung, A. B. Karki, F. Li, D. P. Young and Z. Guo, *J. Phys. Chem. C*, 2009, **114**, 212-219.
13. G. Li, Z. Huang, C. Xin, P. Li, X. Jia, B. Wang, Y. He, S. Ryu and X. Yang, *Mater. Chem. Phys.*, 2009, **118**, 398-404.
14. S. Grishchuk, O. Gryshchuk, M. Weber and J. Karger-Kocsis, *J. Appl. Polym. Sci.*, 2012, **123**, 1193-1200.
15. L. Sobrinho, V. Calado and F. Bastian, *Polym. Compos.*, 2012, **33**, 295-305.
16. B. Francis, V. L. Rao, S. Jose, B. K. Catherine, R. Ramaswamy, J. Jose and S. Thomas, *J. Mater. Sci.*, 2006, **41**, 5467-5479.
17. S. K. Shukla and D. Srivastava, *J. Mater. Sci.*, 2007, **42**, 3215-3222.
18. L. H. Sinh, B. T. Son, N. N. Trung, D.-G. Lim, S. Shin and J.-Y. Bae, *React. Funct. Polym.*, 2012, **72**, 542-548.
19. P. K. Roy, N. Iqbal, D. Kumar and C. Rajagopal, *J. Cleaner Prod.*, 2014, **21**, 1-9.
20. A. Zabaniotou and E. Kassidi, *J. Cleaner Prod.*, 2003, **11**, 549-559.
21. M. Tawfik and A. Huyghebaert, *Food Addit. Contam.*, 1998, **15**, 592-599.
22. A. Cundell, *Mar. Pollut. Bull.*, 1973, **4**, 187-188.
23. B. G. Kwon, K. Saido, K. Koizumi, H. Sato, N. Ogawa, S.-Y. Chung, T. Kusui, Y. Kodera and K. Kogure, *Environ. Pollut.*, 2014, **188**, 45-49.

24. C. Hoppe, M. Galante, P. Oyanguren, R. Williams, E. Girard-Reydet and J. Pascault, *Polym. Eng. Sci.*, 2002, **42**, 2361-2368.
25. T. Sun, Z. Wu, Q. Zhuo, X. Liu, Z. Wang and H. Fan, *Composites Part A*, 2014, **66**, 58-64.
26. A. C. Baudouin, J. Devaux and C. Bailly, *Polymer*, 2010, **51**, 1341-1354.
27. H. Gu, S. B. Rapole, Y. Huang, D. Cao, Z. Luo, S. Wei and Z. Guo, *J. Mater. Chem. A*, 2013, **1**, 2011-2021.
28. H. Gu, H. Lou, J. Tian, S. Liu and Y. Tang, *J. Mater. Chem. A*, 2016, **4**, 10174-10185.
29. J. Schultz and M. Nardin, *Handbook of adhesive technology*, 1994, 19-33.
30. K. L. Mittal and A. Pizzi, *Adhesion promotion techniques : technological applications*, Marcel Dekker, 1999.
31. J. Jang, J. Bae and K. Lee, *Polymer*, 2005, **46**, 3677-3684.
32. H. Gu, S. Tadakamalla, X. Zhang, Y.-D. Huang, Y. Jiang, H. A. Colorado, Z. Luo, S. Wei and Z. Guo, *J. Mater. Chem. C*, 2013, **1**, 729-743.
33. P. Pötschke, T. D. Fornes and D. R. Paul, *Polymer*, 2002, **43**, 3247-3255.
34. J. Zhu, S. Wei, J. Ryu, L. Sun, Z. Luo and Z. Guo, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2100-2107.
35. L. Chen, C. Zhang, Z. Du, H. Li and W. Zou, *Mater. Lett.*, 2013, **110**, 208-211.
36. M. H. Pahl and D. Hesekamp, *Rheology*, 1993, **3**, 97-104.
37. J. Zhu, S. Wei, M. J. Alexander, T. D. Dang, T. C. Ho and Z. Guo, *Adv. Funct. Mater.*, 2010, **20**, 3076-3084.
38. Y. Li, H. Zhu, H. Gu, H. Dai, Z. Fang, N. J. Weadock, Z. Guo and L. Hu, *J. Mater. Chem. A*, 2013, **1**, 15278-15283.
39. H. Gu, J. Guo, H. Wei, S. Guo, J. Liu, Y. Huang, M. A. Khan, X. Wang, D. P. Young and S. Wei, *Adv. Mater.*, 2015, **27**, 6277-6282.
40. J. Gu, C. Liang, X. Zhao, B. Gan, H. Qiu, Y. Guo, X. Yang, Q. Zhang and D.-Y. Wang, *Compos. Sci. Technol.*, 2017, **139**, 83-89.
41. Q.-P. Feng, X.-J. Shen, J.-P. Yang, S.-Y. Fu, Y.-W. Mai and K. Friedrich, *Polymer*, 2011, **52**, 6037-6045.
42. H.-B. Hsueh and C.-Y. Chen, *Polymer*, 2003, **44**, 5275-5283.