Effects of Maleinized Polybutadiene on the Elongation and Impact Peel Strength of Epoxy Resins

Albin Davies · Archana Nedumchirayil Manoharan · Youngson Choe[†]

School of Chemical Engineering, Pusan National University, Busan 46241, Republic of Korea

Abstract: The effect of maleinized polybutadiene (MPB) on the mechanical properties of epoxy resins including adhesion strength, elongation and impact peel resistance was investigated in this study, in which MPB is an anhydride-functionalized polybutadiene prepolymer. Different molecular weights (3.1K and 5.6K) of MPB were added to diglycidyl ether bisphenol-A (DEGBA), an epoxy resin, to increase its impact peel strength and elongation. At various loading percent (5, 10, 15, 20 and 25 wt%) of MPB in the epoxy resin, significant improvements of mechanical properties were observed. According to the comparative analysis results, the modified epoxy system with 15 wt% (3.1K) MPB exhibited the highest lap shear strength, about 40% higher than that of neat epoxy. The tensile strength and elongation steadily and simultaneously increased as the loading percent of MPB increased. The impact peel strengths at low (-40°C) and room (23°C) temperatures were substantially improved by MPB incorporation into epoxy resins. Reactive and flexible MPB prepolymer seems to construct strong nano-structured networks with rigid epoxy backbones without sacrificing the tensile and adhesion strengths while increasing impact resistance/toughness and elongation properties. For higher impact peel while maintaining adhesion and tensile strengths, approximately 10−15 wt% MPB loading in epoxy resin was suggested. Consequently, incorporation of functionalized MPB prepolymer into epoxy system is an easy and efficient way for improving some crucial mechanical properties of epoxy resins.

Keywords: *High performance adhesion, Modified epoxy resin, Maleinized polybutadiene (MPB), Lap shear strength, Impact peel strength, Elongation*

[†] Corresponding author: Youngson Choe (choe@pusan.ac.kr)

1. Introduction

Epoxy resins are ubiquitous in industries owing to its wide applications. They possess special characteristics, such as high tensile strength, superior adhesion, low residual stress, and exceptional mechanical and dielectric properties [1]. The functionality of epoxy groups is determined by the amount of epoxy and other chemical groups present which are involved in forming a cross-linked three-dimensional network [2,3].

However, epoxy resins have a lengthy curing process, weak toughness, low impact strength, and intrinsic brittleness of the cured resin [4-7]. Recently, many researchers have attempted to improve the adhesive strength, elongation, toughness, and impact peel strength of epoxy resins [8-12]. The force required to separate two bonded materials under motion and vibration environment can be referred to as the shear strength, peel strength and impact peel strength. Impact peel strength may identify the resistance of the adhesive to delamination or peeling forces as well as impact strength. Impact peel strength is crucial in various applications and industries, where strong and lasting connections are required[13]. This measurement is critical for the longevity and dependability of products in manufacturing, automotive, aerospace, and packaging sectors, where an understanding of behavior of adhesives under peeling pressures is key [14-20]. Elongation is often expressed as a percentage of the raw material length and high elongation epoxy resins may bend and consume more energy before breaking, which increases their durability. Notably, toughness is not exclusively influenced by elongation [21,22]. The type of the epoxy composition and any additives employed, among other things, also influence toughness [23]. Based on the intended purpose of epoxy resin, balancing these features is critical. A trade-off between these opposing attributes, obtained by modifying epoxy compositions using additives or reinforcements like fibers, increases both strength and toughness [24,25]. Epoxy resins are employed in various applications where a balance of toughness and strength is necessary [26]. Unlike conventional epoxy resins, which can be more brittle, these toughened epoxy resins are designed to better endure impact, stress, and environmental variables for use in various parts in automotive and others[27-29]. By adding additives or changing the chemical composition of a resin, the toughness of epoxy resins is often improved while maintaining their impact peel strength [30]. Core-shell polymers, inorganic nanoparticles, carbon black, rubber shavings, and other additives have been successfully used to increase the toughness of epoxy resins. The addition of proper quantity of core shell polymers can increase the impact strength of epoxy resins, and the adhesion performance of epoxy can be improved by adding inorganic polymers [31-36]. Elastomers and other polymers that improve the capacity of resin to absorb energy and resist cracking or breaking under stress can also be added to epoxy resins. Depending on the intended qualities and the industry in which they are employed, the precise formulation and use of toughened epoxy resins may significantly vary [27].

Maleinized polybutadiene (MPB) is ideal for modifying the mechanical properties of epoxy resins owing to its outstanding hydrophobicity, superior compatibility, and extraordinary strengthening properties [32,33]. Owing to its superior chemical and mechanical properties, MPB has a wide range of applications in the coating, automotive, and electronics sectors [34,35]. CSR (Core Shell Rubber) nanoparticles considerably increase the toughness of epoxy resins, and thus, strengthen the brittle epoxy resins without lowering their glass transition temperature (T_g) [36]. However, CSR nanoparticles provide lower elongation properties.

This study was primarily aimed at investigating the effects of MPB as a modifier on the mechanical properties
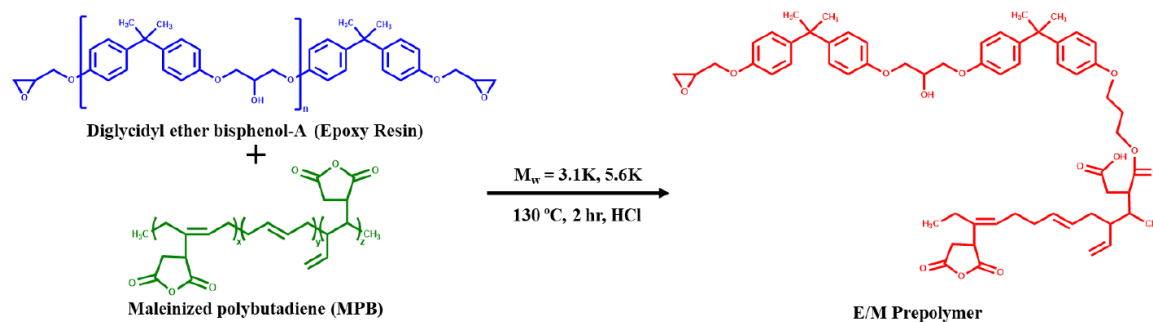
Scheme 1. Synthetic routes of MPB-modified epoxy resin (epoxy/MPB).

of an epoxy/MPB (E/M) blends. To investigate the performance following epoxy modification, MPB additives with two molecular weights (3.1K and 5.6K) and varying quantities were utilized. The effect of MPB on the elongation and impact peel resistance of the modified epoxy resins was analyzed in terms of lap shear, tensile, and impact peel strengths. The mechanical properties of epoxy resin can be affected by variations in the molecular weight and loading percent of MPB in epoxy resins.
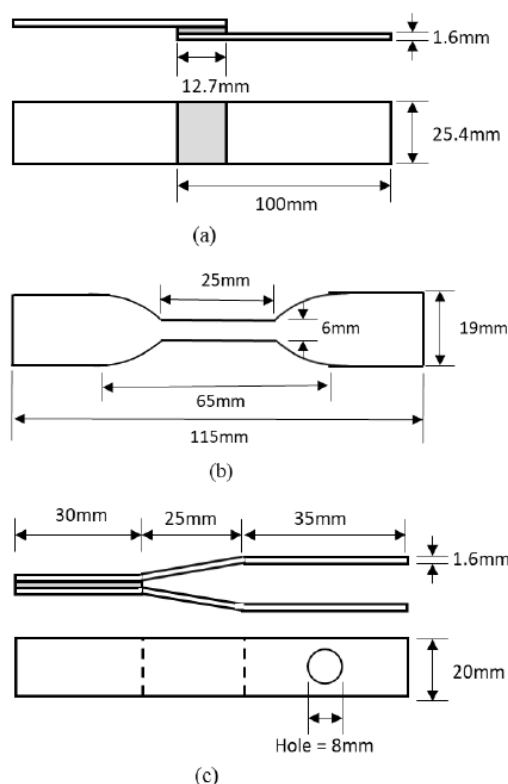
2. Experiment

2.1. Materials

As a liquid epoxy resin based on diglycidyl ether bisphenol-A (DGEBA), YD 128 (Kukdo Chemical Co., Ltd.) was used and has an epoxide equivalent weight (EEE) of 185 g/eq. Anhydride equivalent weight (AEW) 490 MPB (Ricon 131MA20) was purchased from Kangshin Industrial Co., Ltd. Dicyandiamide (DICY) (purity level of above 99%) from Merck was used as a curing agent. A catalyst called 1-cyanoethyl-2-4-methylimidazole (2E4MZ-CNS) was used to expedite the polymerization process. Analytical-grade hydrochloric acid (HCl) was purchased from Sigma-Aldrich.

2.2. Preparation of epoxy/MPB (E/M) blends

To increase MPB dispersion, two molecular weights of MPB (3.1 K and 5.6 K) were mixed with an epoxy resin (28.74 g) in the presence of 2 ml of HCl at 130°C for 2 h using a high-shear mixer at 3000 rpm. DICY (9.30 g) was added to the mixture, which was then agitated for 3 min at 2000 rpm under air pressure until a homogenous mixture was obtained. The E/M blend was transferred to a Teflon mold and cured at 160°C for 3 h. The created E/M blend mixed with various molecular weights of MPB were divided into two groups based on their molecular weight and weight percentage: E/M (3.1K) with 5, 10, 15, 20 and 25 wt% MBP were the first five sets; and E/M (5.6K) with 5, 10, 15, 20, and 25 wt% MBP were the elements of the second set. Scheme 1 depicts the synthetic routes of MPB-modified epoxy resin.

2.3. Characterization

The lap shear and impact peel strengths of the specimens were determined using ASTM D 1002 and ISO 11343, as shown in the Fig. 1. Tensile properties of neat epoxy and E/M blends were measured at room temperature according


Figure 1. Specimen setup for (a) lap shear strength, (b) tensile strength, and (c) wedge impact peel strength test.

to ASTM D638 using a universal tensile tester (INSTRON 68TM-30). The specimens used in the experiment were injection-molded dumbbells; the length and width of the measuring section were 25 and 6 mm, respectively; the thickness of the specimen was 4 mm, and the crosshead speed was 5 mm/min.

3. Results and Discussion

MPB-modified epoxy resins (E/M blends) with curing agent were prepared and a lap shear test was performed to determine the effect of epoxy resins with MPB incorporation on the bonding strength. The lap shear strength-displacement curves for the neat epoxy resin and MPB-modified epoxy resins with different molecular weights are shown in Fig. 2. The lap shear strength of the neat epoxy resin is approximately 24 MPa, which is lower than that of the blended samples. The micro cracks on the inside of the epoxy matrix may explain the weak lap shear strength of the neat epoxy resin [37]. These cracks may minimize toughness and compressive strength, possibly resulting in mechanical instabilities.
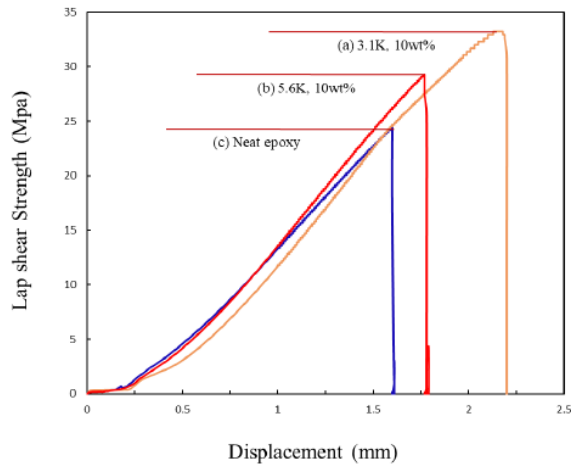
Figure 2. Lap shear strength–displacement curves for both E/M (3.1K) and E/M (5.6K) containing epoxy/MPB blends.

Polybutadiene segment in MPB-modified epoxy backbones efficiently blocks the crack propagation in the current epoxy blend matrix leading to improvement of mechanical performances. Among the E/M (3.1 K) samples, E/M (3.1K, 15 wt%) exhibited an outstanding lap shear strength of 34 MPa, which is about 40% higher than that of the neat epoxy resin, as shown in Fig. 3 and compared between E/M 3.1K and 5.6K. This increased lap shear strength indicated that the use of MPB significantly reduces the tendency of the epoxy matrix to break or prevents microcracks from spreading throughout the epoxy matrix. The addition of high molecular weight MPB (5.6K) prepolymer significantly enhanced the fracture toughness of the epoxy resin with the lap shear strength of 32 MPa (10 wt%), which was about 30% higher than that of the neat epoxy resin.
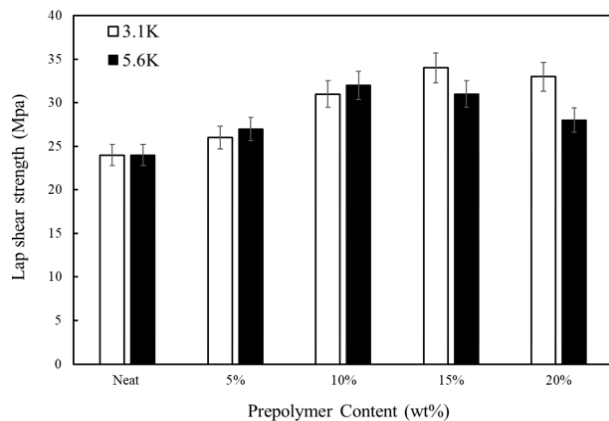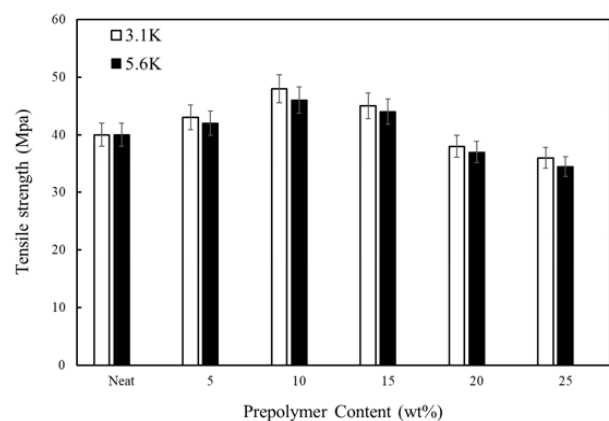
Additionally, it is recognized that the increased toughness may improve the resistance to impact and tensile strength [38]. The lap shear strength of E/M (5.6K, 15 wt%) was 31 MPa, whereas that of E/M (5.6K, 20 wt%) showed a slight decrease to 28 MPa. E/M (3.1K) exhibited higher lap shear strength compared to E/M (5.6K) at 15 and 20 wt%. E/M (3.1K, 15 wt%) exhibited the maximum lap shear strength of 34 MPa, whereas the corresponding value for E/M (5.6K, 10 wt%) was 32 MPa. These results indicate that short-chain MPBs are better additives for improving the mechanical properties of epoxy resins, whereas long-chain MPBs provides more segment flexibilities in epoxy matrix, possibly leading to reducing the resistance to shearing forces. The blends of E/M can be assumed to exhibit optimized lap shear strengths within the range of 10~15 wt%.

A decrease in the lap shear strength value is indicated by a further increase in MPB content since too higher segment flexibilities could reduce the resistance to shearing forces in the matrix. The tensile strength of neat epoxy resin and E/M blends increased until the MPB content increased to 10 wt% regardless of the molecular weight, as shown in Fig. 4. The tensile strength of the neat epoxy resin was 40 MPa. The tensile strength of cured E/M blends of both molecular weights (3.1K and 5.6K) increased thereafter. The tensile strength of epoxy incorporated with 5.6K MPB was slightly less than that of 3.1K MPB. It is known that the tensile strength, a basic mechanical property, is the highest pulling or stretching stress that a material can bear before failing or breaking [39].

E/M (3.1K, 10 wt%) was found to be the most effective with the highest tensile strength (48 MPa), which was

Figure 3. Comparison of lap shear strength between E/M (3.1 K) and E/M (5.6K) epoxy blends with different MPB wt%.

Figure 4. Tensile strength of E/M (3.1K and 5.6K) blends with different MPB weight percentages.

about 20% higher than that of neat epoxy. From the results shown in Fig. 4, it can be concluded that the addition of a particular amount of MPB into the rigid epoxy resin changes the internal residual stress and eventually enhances the strength. Moreover, many hydrogen bonds present in MPB improve the tensile strength of the cured epoxy matrix. However, the addition of high amount of MPBs may cause the epoxy matrix to be more flexible and decrease the macro-scale stiffness of the epoxy matrix, leading to a weak tensile strength. The shear strength of E/M (3.1K and 5.6K) significantly decreased with increase in the MPB from 10 to 15 wt%. In the previous study, it is discussed that the phase separation or agglomeration may result in reduced surface free energy and poor interfacial bonding in the thermoplastic/epoxy blend system such as MPB/epoxy blends in the present study [36,40]. Epoxy loaded with 25 wt% (5.6K) MPB demonstrated the lowest tensile strength (34.5 MPa) since more flexible domains or agglomeration among flexible domains could easily break under tensile forces. To achieve the desired material characteristics in composites such as epoxy-MPB systems, the proper amount of MPB in the epoxy matrix should be crucial. Therefore, for a relatively low MPB content in the epoxy (5~10 wt% of both 3.1K and 5.6K), the tensile strength increases owing to appropriate toughness effect of MPB and higher than 10 wt%, the tensile strength begins to decrease owing to the gradual reduction of cohesive bonding strength in MPB-rich epoxy networks. Regardless of the molecular weight, the graph indicates that the ideal weight percentage of MPB with improved tensile strength is 10~15 wt%.

Along with the tensile properties, the incorporation of
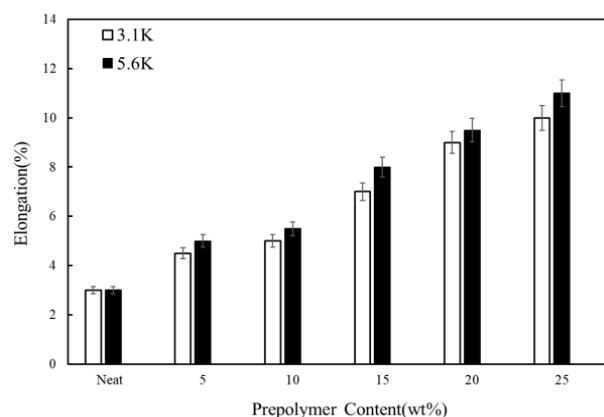
flexible MBP into epoxy resin can lead to high elongation properties of E/M blends. In a tensile test, to determine elongation, a material sample is stretched until it breaks [24]. The elongation properties increase steadily with increasing MPB content. The highest elongation of 11% was exhibited by epoxy incorporated with 25 wt% (5.6K) MPB. Given that MPB is flexible and rubbery, the ductility of the blend can be considered to have improved. It can be used as a toughening agent in epoxy to increase the absorption of energy by the material before breaking and its resistance to deformation. The higher addition of MPB has a detrimental effect on other properties, although the elongation increases gradually.

A wedge impact peel test, as shown in Fig. 6, was performed to evaluate the impact resistance of E/M blends. It involves applying a controlled force to a specimen using a specially designed wedge, which induces a peeling or delamination force at the interface of the bonded materials. It is sensitive to resin characteristics and interlaminar bond strength. Thus, the wedge peel test was selected as a mechanical quality indicator of high performance adhesives [41]. The addition of MPB in epoxy/MPB (E/M) blends improves the adhesive strength and fracture energy of the blends. [36]. This may be caused by the functional groups of MPB such as maleic anhydride moieties that can form covalent bonds with the epoxy resin. These interactions create a stronger and more stable interface between the MPB and epoxy molecules. In Fig. 6, the impact peel energy and impact load versus time of E/M at minimum temperature (-40°C) and room temperature (23°C) were plotted. The impact peel strength of material was obtained from the area under the double-sided arrow. The E/M (5.6K, 10 wt%) at -40°C exhibited higher load value than at 23°C. However, E/M (3.1 K, 10 wt%) exhibited lower load at -40°C than at 23°C. The first case exhibited an about 25% increase, whereas the second case shows an about 50%

Figure 5. Elongation of E/M (3.1K and 5.6K) blends with different weight percentage.
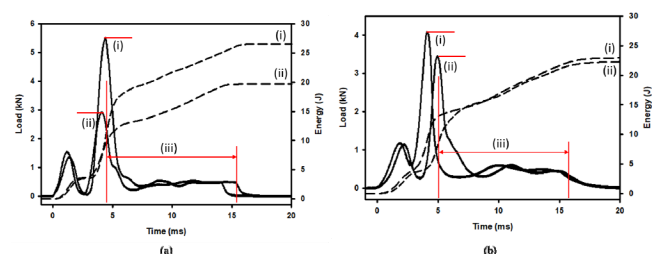
Figure 6. Impact load and impact energy vs. time curves of (a) E/M at -40°C (b) E//M at 23°C ((i) 5.6K, 10 wt%, (ii) 3.1K, 10 wt%, (iii) fracture energy).
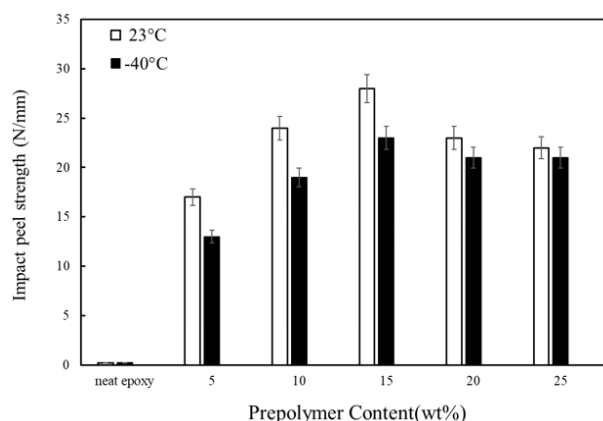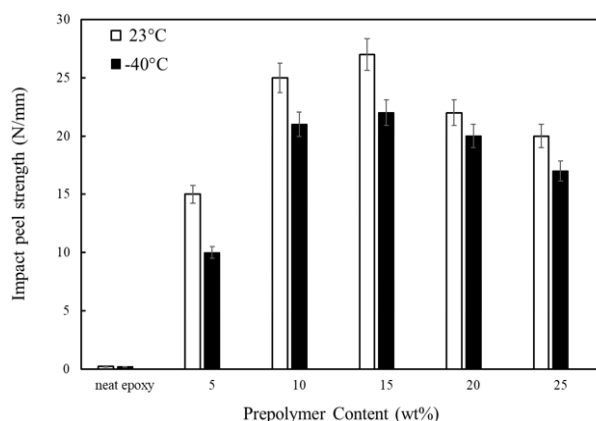
Figure 7. Comparison of impact-peel strength of E/M (5.6K) at 23 and -40°C.

Figure 8. Comparison of impact-peel strength of E/M (3.1K) at 23 and -40°C.

decline. This indicates that long-chain MPBs are more effective on resistance to impact load at lower temperature ranges. The increased performance of E/M (5.6K, 10 wt%) indicates that the cohesive interaction inside the epoxy matrix was significantly reduced after the addition of flexible segments from E/M blends in a sufficient amount into epoxy matrix. In addition, the presence of these flexible segments form E/M blends improved the energy absorption of the epoxy resin by preventing the formation of new microcracks. At both temperatures, the fracture energies of both specimens increased up to a point and then gradually decreased.

Influence of molecular weight on impact peel strength at two temperatures, 23 and -40°C, is shown in Fig. 7 and 8. As shown in Fig. 7, the specimen at 23°C exhibited higher impact peel strength than the specimen at -40°C. Impact peel strength increased up to 15 wt% MPB and then decreased. The impact peel strength of E/M (3.1K) at 23 and -40°C with 15 wt% MPB was about 25% and 20% higher than that of neat epoxy, respectively. As shown in Fig. 7, the highest peak of impact peal strength was at 15 wt% for E/M (5.6K) at both low and room temperatures.

The minimum impact peel strength of E/M (5.6K) at both temperatures was in the 5 wt% range. Among the specimens, the 15 wt% E/M (5.6K) specimen exhibited a 3% higher impact peel strength than E/M (3.1K) at 15 wt%. That is, E/M (5.6K) at 15 wt% formed exceptionally efficient resin networks with high impact peel energy and strength. In both cases, neat epoxy exhibited essentially no influence on impact peel strength. The impact test results indicate that preparing epoxy resins with 15 wt% of E/M prepolymers allows for high impact peel strengths or impact peel resistances under room and lower temperature settings.

4. Conclusion

The study was primarily aimed at evaluating and examining the enhanced adhesive qualities of modified epoxy resins containing MPB. The epoxy system with 15 wt% (3.1K) MPB exhibited the highest lap shear strength (about 40% higher than that of neat epoxy). This confirmed that there should be strong interactions between the MPB and epoxy resins at the presence of curing agent. According to the tensile strength results, the addition of 10 wt% (3.1K) MPB considerably increased the tensile strength to 48 MPa (about 20% higher than that of neat epoxy). E/M (5.6K and 3.1K) blend with 15 wt% MPB is considered as exceptionally efficient epoxy system with high impact peel energy and strength. The elongation characteristics increased gradually as the MPB loading level increased. All measured mechanical properties clearly indicate an efficient improvement with an addition of MPB but only up to certain loading amount of MPB in the epoxy resin. The amount of MPB required for improving the elongation of epoxy while maintaining its impact peel strength was determined. Approximately 10~15 wt% was identified as the ideal range of MPB that improved elongation while maintaining its adhesion characteristics (3.1K and 5.6K MPB prepolymers). Thus, MPB incorporation into epoxy resin is an efficient way to construct high performance epoxy networks for a variety of future adhesive applications owing to its remarkable properties.

Acknowledgement

References

1. J.C. Capricho, B. Fox, and N. Hameed, *Polym. Rev.*, **60**, 1 (2020).
2. Q. Xiang and F. Xiao, *Const. Building Mater.*, **235**, 117529 (2020).
3. S. Li, Q. Wu, H. Zhu, Q. Lin, and C. Wang, *Polymers*, **9**, 684 (2017).
4. C. Lou and X. Liu, *Compos. B Eng.*, **136**, 20 (2018).
5. Z. Sun, L. Xu, Z. Chen, Y. Wang, R. Tusiime, C. Cheng, S. Zhou, Y. Liu, M. Yu, and H. Zhang, *Polymers (Basel)*, **11**, 461 (2019).
6. G. Fernández Zapico, N. Ohtake, H. Akasaka, and J. M. Munoz-Guijosa, *Sci. Rep.*, **9**, 17343 (2019).
7. U. Farooq, J. Teuwen, and C. Dransfeld, *Polymers*, **12**, 1908 (2020).
8. S.M. Nejad, R. Srivastava, F.M. Bellussi, H.C. Thielemann, P. Asinari, and M. Fasano, *Int. J. Ther. Sci.*, **159**, 106588 (2021).
9. S. Wu, S. Peng, and C.H. Wang, *Polymers*, **10**, 542 (2018).
10. L. Li, M. Wang, X. Wu, W. Yi, and Q. Xiao, *Sci. Rep.*, **11** 9917 (2021).
11. S. Li, Q. Lin, and C. Cui, *J. Mater. Res.*, **31**, 1393 (2016).
12. M.P.A. Muthalif and Y. Choe, *Adv. Polym. Technol.*, **2022**, 2309235 (2022).
13. Z.K. Chen, G. Yang, J.P. Yang, S.Y. Fu, L. Ye, and Y.G. Huang, *Polymer (Guildf)*, **50**, 1316 (2009).
14. T. Wu, Y. Liu, N. Li, G.W. Huang, C.B. Qu, and H. M. Xiao, *Polym. Testing*, **74**, 45 (2019).
15. S. Ok and Y. Choe, *Mol. Cryst. Liq. Cryst.*, **579**, 55 (2013).
16. Y. Jo and Y. Choe, *Mol. Cryst. Liq. Crys.*, **539**, 190 (2011).
17. M. Preghenella, A. Pegoretti, and C. Migliaresi, *Polymer (Guildf)*, **46**, 12065 (2005).
18. M. Battistella, M. Cascione, B. Fiedler, M.H.G. Wichmann, M. Quaresimin, and K. Schulte, *Compos. Part A: Appl. Sci. Manuf.*, **39**, 1851 (2008).
19. D.I. Tee, M. Mariatti, A. Azizan, C.H. See, and K.F. Chong, *Compos. Sci. Technol.*, **67**, 2584 (2007).
20. H. Kang, J.H. Lee, Y. Choe, and S.G. Lee, *Nanomaterials*, **11**, 872 (2021).
21. F. Lei, C. Zhang, Z. Cai, J. Yang, H. Sun, and D. Sun, *Polymer (Guildf)*, **150**, 44 (2018).
22. W. Cai, Z. Yuan, Z. Wang, Z. Guo, L. Zhang, J. Wang, W. Liu, and T. Tang, *React. Funct. Polym.*, **164**, 104920 (2021).
23. Q. Duan, S. Wang, Q. Wang, T. Li, S. Chen, M. Miao, and D. Zhang, *ACS Appl. Mater. Interfaces*, **11**, 36278 (2019).
24. X. Ma, W. Guo, Z. Xu, S. Chen, J. Cheng, J. Zhang, M. Miao, and D. Zhang, *Compos. B: Eng.*, **192**, 108005 (2020).
25. C. Lv, J. Wang, Z. Li, K. Zhao, and J. Zheng, *Compos. B: Eng.*, **177**, 107270 (2019).
26. S. Kang, D. Kim, T. Kim, W. Lee, H.G. Kim, J.S. Chung, C.S. Lim, S.M. Chang, and B. Seo, *J. Nanosci. Nanotechnol.*, **17**, 7429 (2017).
27. Y. Liu, Y. Lin, Y. Wang, K. Wu, B. Cao, and L. Wang, *J. Appl. Polym. Sci.*, **139**, 32 (2022).
28. B.J. Rohde, K.M. Le, R. Krishnamoorti, and M.L. Robertson, *Macromolecules*, **49**, 8960 (2016).
29. J. Yang, H. Wang, X. Liu, S. Fu, and P. Song, *Compos. Sci. Technol.*, **212**, 108884 (2021).
30. E.D. Bain, D.B. Knorr, A.D. Richardson, K.A. Masser, J. Yu, and J.L. Lenhart, *J. Mater. Sci.*, **51**, 2347 (2016).
31. X. Dong, Z. Wu, Y. Wang, T. Li, X. Zhang, H. Yuan, B. Xia, P. Ma, M. Chen, and W. Dong, *Polym. Test.*, **93**, 106926 (2021).
32. H. Yang, X. Cao, Y. Ma, J. An, Y. Ke, X. Liu, and F. Wang, *Polym. Eng. Sci.*, **52**, 481 (2012).
33. S.S. Choi and D.H. Han, *J. Anal. Appl. Pyrolysis*, **78**, 58 (2007).
34. G. Fernández Zapico, N. Ohtake, H. Akasaka, and J. M. Munoz-Guijosa, *Sci. Rep.*, **9**, 17343 (2019).
35. S. Kumar, S. Krishnan, S.K. Samal, S. Mohanty, and S.K. Nayak, *Ind. Eng. Chem. Res.*, **57**, 2711 (2018).
36. M.P.A. Muthalif and Y. Choe, *Appl. Surf. Sci.*, **508**, 145297 (2022).
37. A.D.M. Charles and A.N. Rider, *Polymers*, **10**, 888 (2018).
38. H. Liu, and J. Zhang, *J. Polym. Sci. Part B: Polym. Phys.*, **49**, 1051 (2011).
39. S.F. Resan, S.M. Chassib, S.K. Zemam, and M.J. Madhi, *Case Stud. Const. Mater.*, **12**, e00347 (2020).
40. H.P.S. Abdul Khalil, H.M. Fizree, A.H. Bhat, M. Jawaid, and C.K. Abdullah, *Compos. B. Eng.*, **53**, 324 (2013).
41. C.M. Stokes-Griffin, A. Kollmannsberger, P. Compston, and K. Drechsler, *Compos. Part A: Appl. Sci. Manuf.*, **121**, 84 (2019).