Novel thermoplastic toughening agents in epoxy matrix for vacuum infusion process manufactured composites

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Abstract

This study suggests the novel thermoplastic toughening agent, which can be applied in the monomer forms without increasing the viscosity of the epoxy resin and polymerized during the resin curing. The diazide (*p*-BAB) and dialkyne (SPB) compounds are synthesized and mixed with the epoxy resin and the carbon fiber reinforced epoxy composites are prepared using vacuum infusion process (VIP). Then, flexural and drop weight tests are performed to evaluate the improvement in the toughness of the prepared composites to investigate the potential of the novel toughening agent. When 10 phr of *p*-BAB and SPB is added, the flexural properties are improved, maintaining the modulus as well as the toughness is improved. Even with a small amount of polytriazolesulfone polymerized, due to the filtering effect of the solid SPB by the layered carbon fabrics during the VIP, the toughening and strengthening effect were observed from the novel toughening agent, which could be added in monomer forms, *p*-BAB and SPB. This suggests that the novel toughening agent has a potential to be used for the composites prepared from viscosity sensitive process, such as resin transfer molding and VIP.

Key words: epoxy resin, carbon composites, polymer matrix composites, fracture toughness, vacuum infusion process, polytriazolesulfone

1. Introduction

Carbon fiber reinforced epoxy-based composite materials are widely used in aerospace and automotive industries because of their excellent mechanical and thermal properties, dimensional stability, and chemical resistance [1-5]. However, their applications are limited by the low impact resistance and fracture toughness resulted from the highly cross-linked network structures, compared to the metallic materials [6,7]. Many researchers have suggested various additives as toughening agents to enhance the toughness of the epoxy matrix system.

Soft polymers and hard nanoparticles are widely used as toughening agents to enhance the toughness of the brittle epoxy resin. Rubber and thermoplastic polymers are the typical soft polymer type toughening agents. The polymers are initially miscible with epoxy resin but during the resin curing, the miscible polymer-epoxy mixture undergoes phase separation, resulting in the improvement of interlaminar toughness. As the fraction of the soft polymer increases, the morphology of the mixture is changed from phase separation to co-continuous, and finally phase inverted morphology. These changes in the morphology lead to the higher improvement of the toughness. However, it also decreases the other mechanical properties and chemical resistance to organic liquids [8-20].

Carbon nanotubes [21,22], nanoclays [23-25], and silica [26-28] are hard nanoparticles to improve the toughness as well as the thermal properties, elastic modulus, and the fire resistance [29] even with a small amount of the filler content.

However, the addition of these toughening agents significantly raises the viscosity of the epoxy resin-toughening agent mixture. Considering the needs of the out-of-autoclave technologies such as resin transfer molding (RTM) and vacuum infusion process (VIP), which require low viscosity resin mixture
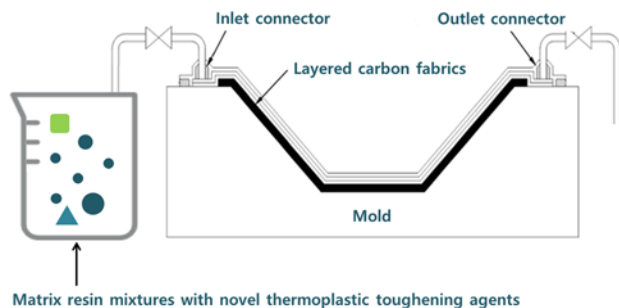
Fig. 1. Schematic diagrams of the VIP in this study to prepare the carbon fiber reinforced epoxy composites toughened with the novel toughening agent.

for injection and impregnation into the preform, this can limit the use of the toughened epoxy resin mixture in RTM or VIP. Moreover, nanoparticles in the resin mixture can be filtered during the resin injection by the fiber based preform [30].

Therefore, this study suggests the novel thermoplastic toughening agent, which can be applied in the monomer forms without increasing the viscosity of the epoxy resin and polymerized during the resin curing. The diazide and dialkyne compounds are synthesized and mixed with the epoxy resin and the carbon fiber reinforced epoxy composites are prepared using VIP (Fig. 1). During the curing process, epoxy resin is polymerized to crosslinked network polymer and the diazide and dialkyne compounds are polymerized to polytriazolesulfone through azide-alkyne click reaction without interrupting the epoxy curing reaction (Fig. 2). Then, flexural and drop weight tests are performed to evaluate the improvement in the toughness of the prepared composites to investigate the potential of the novel toughening agent.
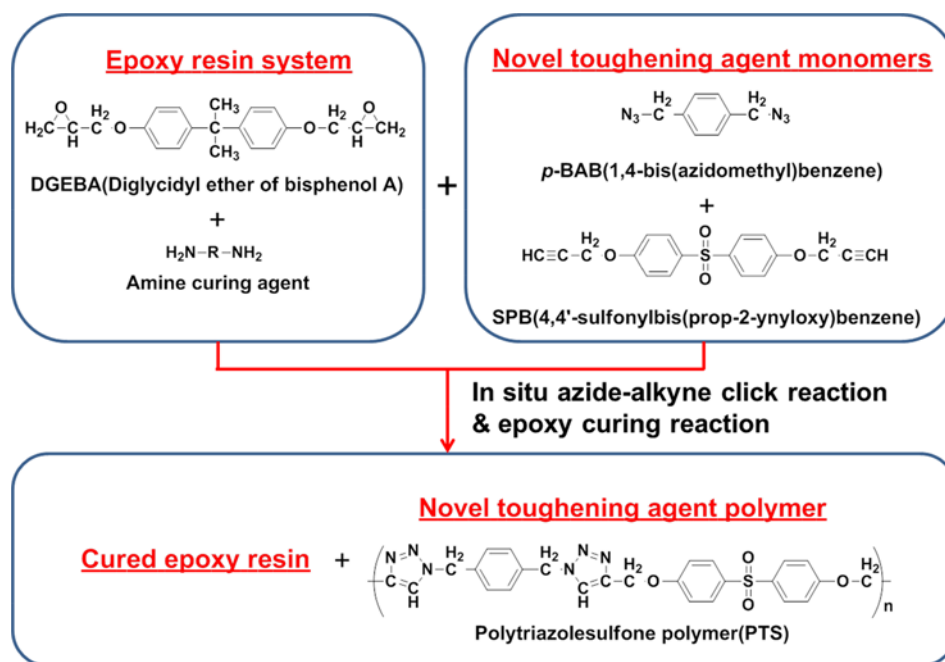
2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (KFR-120) and amine type curing agent were purchased from Kukdo chemical Co. (Korea) and used to prepare the carbon fiber-epoxy composites. The carbon fabric (3K, twill, T300) was purchased from Toray Co. (Japan) and used to prepare the composites.

2.2. Synthesis of the novel toughening agent

The reaction scheme of the diazide and dialkyne compounds are shown in Fig. 2 and after the syntheses, the chemical structures of the novel toughening agent was confirmed using ^{1}H NMR (Bruker Advance III 500).

2.2.1. Synthesis of the diazide compound

Twenty grams of α,α'-dichloro-*p*-xylene (Aldrich, 98%) was dissolved in 200 mL of acetonitrile (Duksan Chemicals Co., Korea, 95%). Then, 400 mol% of sodium azide (Aldrich, 95%) were added and stirred for 48 h at 80°C. The mixture was cooled to room temperature and then unreacted sodium azide was extracted using methylene chloride and water with extraction funnel. Finally, the solvent was removed and the 1,4-bis(azidomethyle)benzene(*p*-BAB) was obtained as a clear liquid (95% yield).

2.2.2. Synthesis of the dialkyne compound

Twenty grams of 4,4'-sulfonyldiphenol (Aldrich, 98%) was dissolved in 300 mL of tetrahydrofuran and 400 mol% of potassium carbonate (Aldrich, 95%) were added slowly. Then, nitrogen gas purging was carried out for 30 min and propargyl bromide (Aldrich, 80% in tolu-

Fig. 2. Schematic diagram of the polymerization of the novel toughening agent monomers during the epoxy resin curing reaction.

Fig. 3. The reaction scheme of the novel toughening agent monomers, (a) *p*-BAB and (b) SPB.

ene) were added and stirred for 40 h at 60°C. The mixture was cooled to room temperature and then filtered. The filtrate was evaporated to give the 4,4'-sulfonylbis(propynyloxy)benzene(SPB) as a white solid (99% yield).

2.3. Preparation of the carbon fiber-epoxy composites

The carbon fiber-epoxy composites were prepared using VIP. The carbon fabrics were cut with the size of 400 mm×400 mm and 15 plies of the cut fabric was placed on the stage. Then, the layered carbon fabrics were covered with bagging film, infusion mesh, and peel-ply.

The epoxy resin and 5 or 10 phr of the novel toughening agents, *p*-BAB and SPB, were mixed for 30 min with a mechanical stirrer. Then, 29 phr of the curing agent was added to the resin mixture and stirred for 10 min. To compare with the commercial toughening agent, 5 phr of polyethersulfone (PES, Solvay, Belgium) was also used instead of *p*-BAB and SPB. The final resin mixture was injected to the layered carbon fabrics for VIP and after the resin injection, the composite was cured at 80°C for 4 h and post-cured for 12 h. During the curing process, *p*-BAB and SPB were expected to be polymerized as the novel toughening agent, polytriazolesulfone. When preparing the composites, 5 phr was the maximum addition of the conventional toughening agent, PES, whereas 10 phr was the maximum addition of the new toughening agent, *p*-BAB and SPB. Above this level, the resin mixture could not be injected and prepared as the composites.

2.4. Characterization and evaluation of the prepared toughening agents and composites

To confirm that *p*-BAB and SPB were polymerized to polytriazolesulfone, *p*-BAB, SPB, epoxy resin and curing agent were mixed and heated to 80°C for 4 h and post-cured at 120°C for 12 h. Then, FT-IR analysis was carried out with PerkinElmer (Frontier) FT-IR/NIR spectrophotometer to investigate the synthesis of polytriazolesulfone in the resin mixture during the curing process. Flexural and drop weight tests of the prepared composites were carried out based on ASTM D790 and ASTM D3763 to investigate the toughness of the prepared composites. Thermal mechanical analysis (TMA) was carried out to measure Tg of the matrix resin in the prepared composites using TA Instrument Q400 from 30 to 200°C with heating rate of 5°C/min under 100 mN.

3. Results and Discussion

3.1. Chemical structure and reaction confirmation of the novel toughening agents

The reaction scheme of *p*-BAB and SPB were shown in Fig. 3 and their chemical structure were analyzed using a nuclear magnetic resonance spectrophotometer (^{1}H NMR) and the results were shown in Figs. 4 and 5. Fig. 4 shows the ^{1}H NMR spectrum of *p*-BAB and the signals at δ_{ppm}=4.3 and 7.3 are due to methylene H and aromatic H, respectively. The numbers below the signals depict the intensity of each signal and show ratio of the methylene H and aromatic H are 1:1. These are in good agreement with the chemical structure of *p*-BAB. Fig. 5 shows the ^{1}H NMR spectrum of SPB and the signals at δ_{ppm}=3.3 from acetyl group H, 4.8 from methylene H, 7.2 from aromatic H next to the ether group, and 7.9 from aromatic H next to sulfonyl group. The numbers below the signals depict the intensity of each signal and show ratio of each H is 1 (3.3 ppm):2 (4.3 ppm):2 (7.2 ppm):2 (7.9 ppm). These are in good agreement with the chemical structure of SPB. Both in Figs. 4 and 5, all the signals are due to the Hs of the *p*-BAB or SPB or solvent (DMSO), suggesting both *p*-BAB and SPB have very high purity
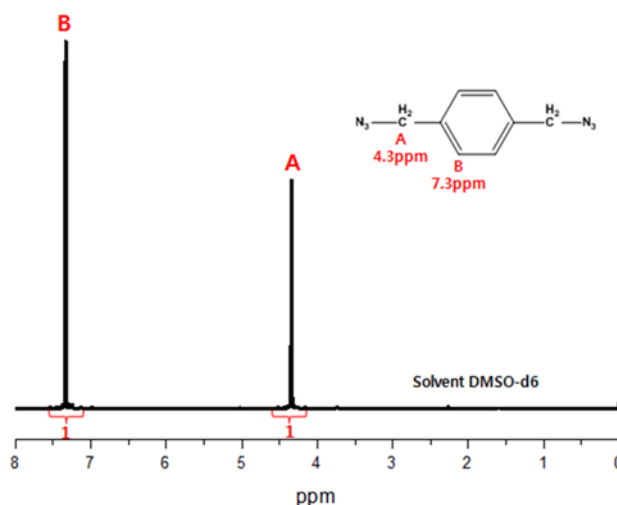

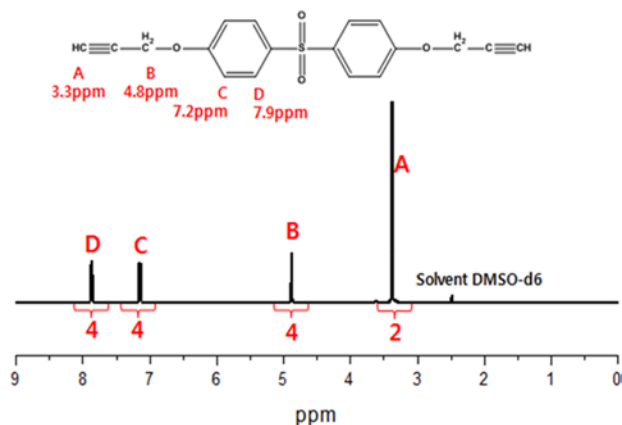**Fig. 4.** ^{1}H NMR spectrum of the novel toughening agent monomer, *p*-BAB.

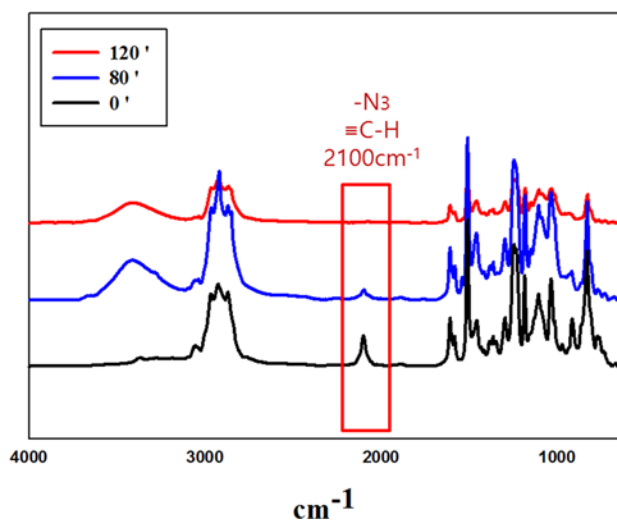**Fig. 5.** ^{1}H NMR spectrum of the novel toughening agent monomer, SPB.

Fig. 6. FT-IR spectra of the epoxy resin mixture at each curing step: 0' (no curing), 80' (the first curing at 80°C for 4 h) and 120' (the second curing at 120°C for 12 h).

Fig. 7. Flexural properties of the prepared composites. (a) Flexural test results, (b) calculated toughness from the flexural tests.

without any byproduct.

As mentioned earlier, the novel toughening agent monomers, *p*-BAB and SPB, are expected to be polymerized to polytriazolesulfone through azide-alkyne click reaction during the epoxy curing reaction. To confirm the polymerization of polytriazolesulfone, the matrix resin mixture of epoxy resin, curing agent, *p*-BAB and SPB was prepared and cured at 80°C for 4 h and 120°C for 12 h. In each step, FT-IR analysis was carried out and the changes in chemical structure were investigated. Fig. 6 shows the infrared spectra of the matrix resin mixture at 0 h (no curing, 0'), 80°C for 4 h (the first curing step, 80'), and 120°C for 12 h (the second curing step, 120'). The absorption band at 2100 cm^{-1} is due to azide and acetylene groups. As the curing proceeds, this band is disappeared due to the formation of the triazole groups and the new broad band around 3300 cm^{-1}, which is due to N related bands from cured epoxy and triazole groups [31]. Therefore, the novel toughening agent, polytriazolesulfone, can be polymerized from *p*-BAB and SPB monomers in the matrix resin mixture system during the curing reaction through the azide-alkyne click reaction.
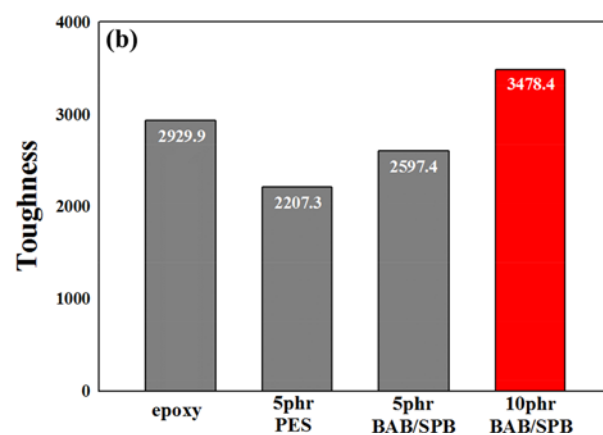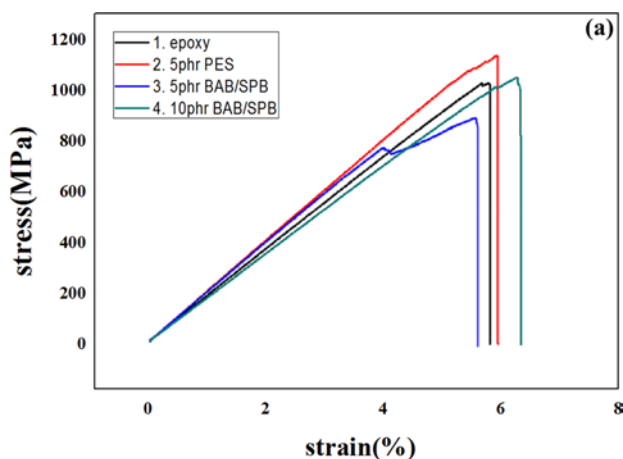
3.2. Mechanical properties of the prepared carbon fiber-epoxy composites with the novel toughening agent

The carbon fiber-epoxy composites were prepared using VIP and the matrix resin systems were neat epoxy resin, 5 phr of PES added epoxy resin, 5 phr of *p*-BAB and SPB added epoxy resin, and 10 phr of *p*-BAB and SPB added epoxy resin. With the conventional thermoplastic toughening agent, PES, 5 phr was the maximum loading, whereas 10 phr was the maximum loading with the novel toughening agent, the mixture of *p*-BAB and SPB monomers.

The flexural test results are shown in Fig. 7 and flexural strength, modulus, and toughness calculated from the area of the stress-strain curve are compared. When 5 phr of PES is added to the resin mixture, the flexural strength is increased, the modulus is decreased and the toughness is increased. When 5 phr of *p*-BAB and SPB is added, the flexural strength, modulus, and toughness are decreased. When 10 phr of *p*-BAB and SPB is added, the flexural strength and toughness are increased and the modulus is maintained.

The drop weight test results are shown in Fig. 8 and the energy required to destroy the sample, which can show the toughness of the sample, was compared. All the composites prepared with the toughening
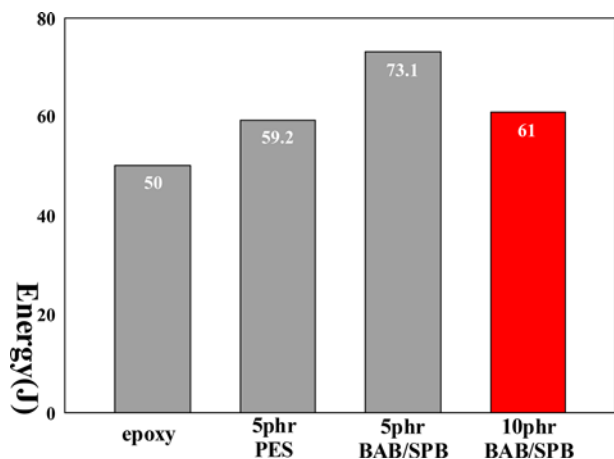
Fig. 8. Drop weight test results of the prepared composites.

Fig. 9. Schematic diagram of the Soxhlet extraction of the prepared composites.

agent have the improved toughness compared to neat epoxy based composites. Unlike, the flexural test results, when 5 phr of *p*-BAB and SPB is added, the toughness increased most. When 5 phr of PES and 10 phr of *p*-BAB and SPB is added, the toughness is almost similar.

TMA results showed T_gs of the matrix resin in the prepared composites, neat epoxy resin had T_g of 88.5℃, 5 phr of PES added resin had T_g of 88.6℃, 5 phr of p-BAB and SPB added resin had T_g of 83.4℃, and 10 phr of p-BAB and SPB added resin had T_g of 86.0℃. When the novel toughening agent was added to the matrix resin, T_g was dropped, whereas T_g was maintained when PES was added.

Before the mechanical tests, it is expected that the novel toughening agent shows better toughening effect than the conventional toughening agent, because more toughening agent can be loaded in *p*-BAB and SPB monomer form. And it is not expected that the flexural properties of the composite are diminished when 5 phr of *p*-BAB and SPB is added. Therefore, the next section shows the process to reveal the reason of the unexpected results.

3.3. Analyses of mechanical properties of the prepared composites

When the conventional toughening agent, PES, is used, the toughness is improved, as the amount of the PES increases up to 30 phr. When the novel toughening agent is used, the toughness is improved or diminished, with the addition of 5 phr of *p*-BAB and SPB, whereas the toughness and flexural properties of the composite is improved with the addition of 10 phr of *p*-BAB and SPB. To investigate the reason of this unexpected results, the toughening agent in the prepared composite is extracted using the Soxhlet extraction with methylene chloride, as shown in Fig. 9.

After the Soxhlet extraction of the prepared composites with 5 and 10 phr of *p*-BAB and SPB, the extracted products were analyzed using FT-IR and ^{1}H NMR. The FT-IR spectra of the extracted products, epoxy resin, curing agent, *p*-BAB and SPB are shown in Fig. 10. The band at 2100 cm⁻¹ is observed in the spectra of the extracted products and this is due to the azide and acetylene groups from *p*-BAB and SPB. ^{1}H NMR spectra of the extracted products are shown in Fig. 11 to confirm the chemical structure of the extracted products more precisely. Fig. 11a and b is the ^{1}H NMR spectrum of the extracted product from the composites with 5 and 10 phr of *p*-BAB and SPB. When compared with Fig. 4,
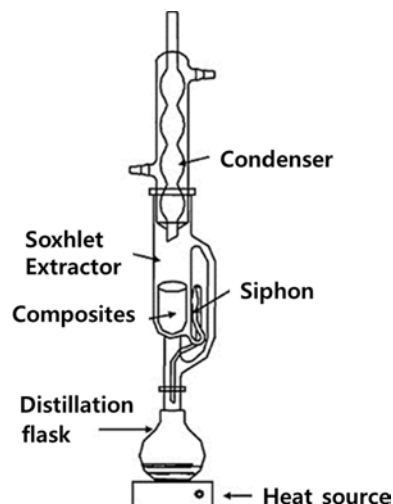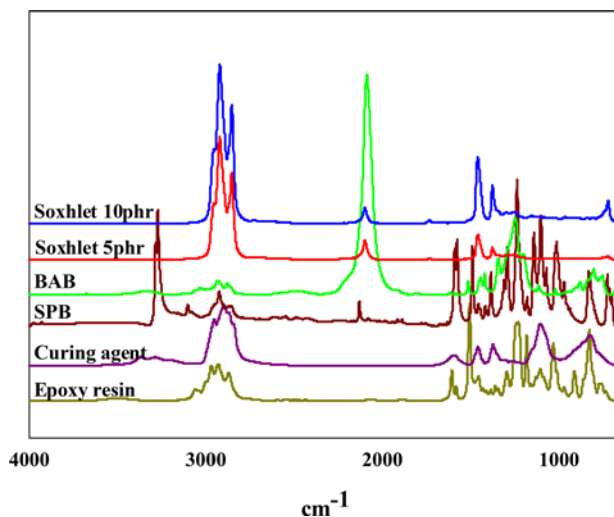

Fig. 10. The FT-IR spectra of the extracted products, epoxy resin, curing agent, *p*-BAB and SPB.

the major chemical is *p*-BAB. Fig. 11c is the expanded spectrum of the extracted product from the composite with 10 phr of *p*-BAB and SPB. Unlike the spectrum of the extracted composites with 5 phr of *p*-BAB and SPB, the weak signals from the polytriazolesulfone are observed in Fig. 11c, showing the presence of the polytriazolesulfone.

As mentioned earlier in the experimental section, *p*-BAB is liquid, whereas SPB is solid and only *p*-BAB was extracted from the prepared composites. This suggests that the liquid of *p*-BAB can be easily infiltrated into the layered carbon fabrics, whereas the solid of SPB may be filtered by the layered fabrics like nano particle type toughening agent. When 5 phr of *p*-BAB and SPB was added, the infiltrated amount of solid SPB was too little to contact liquid *p*-BAB and to be polymerized to polytriazolesulfone, which is the actual toughening agent. And *p*-BAB acted as a plasticizer, resulting in the lowered T_g, deteriorated flexural properties and significantly improved toughness in the drop weight test.
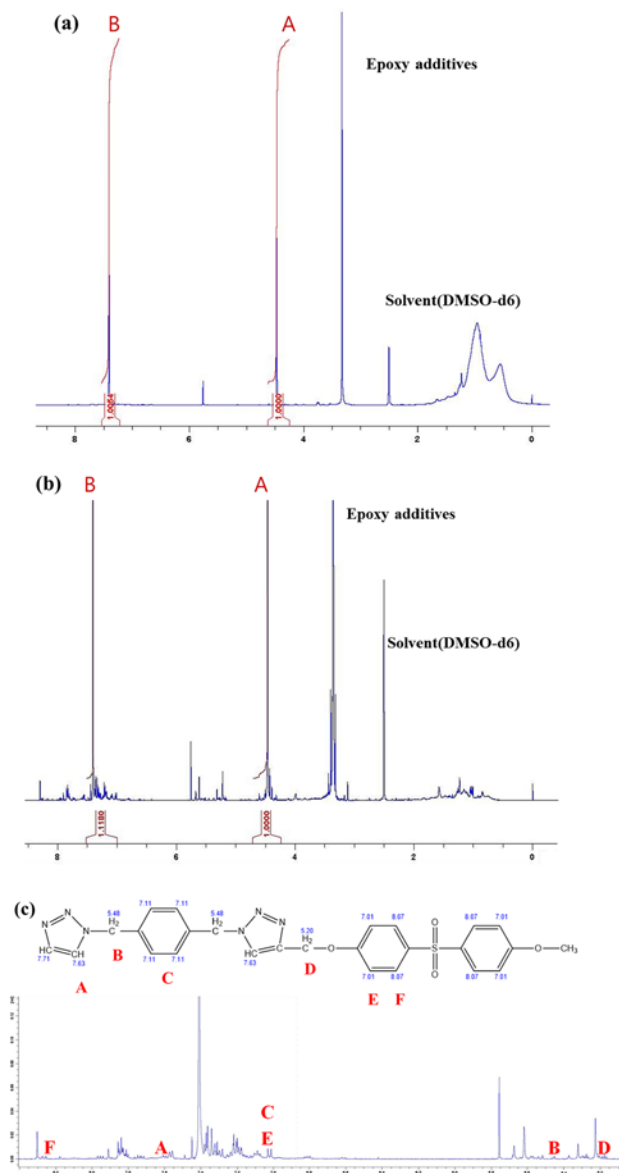
Fig. 11. ^{1}H NMR spectra of the extracted products. (a) The extracted product with 5 phr of *p*-BAB and SPB, (b) the extracted product with 10 phr of *p*-BAB and SPB, (c) the expansion of (b).

When the amount of *p*-BAB and SPB was increased to 10 phr, the infiltrated amount of solid SPB was also increased and could be contact with liquid *p*-BAB and polymerized to polytriazolesulfone, resulting in the improved flexural properties and toughness. This was a very surprising result because the matrix resin mixture seems homogeneous dispersion during the VIP and no carbon fabric filtering effect was expected. To figure out this issue, the solubility parameters of DGEBA, PES, and SPB were compared. The solubility parameter of DGEBA is usually calculated as 21.0–21.6 MPa$^{1/2}$ and that of PES is calculated as around 23.28 MPa$^{1/2}$ [32]. The solubility parameter of SPB cannot be calculated accurately, because no cohesive energy of the acetyl group was found yet. However, it can be a little larger than the solubility parameter of PES, which has the similar chemical structure. The difference in the solubility

parameters of DGEBA and SPB is more than 1.7 MPa$^{1/2}$ and it should be less than 0.5 MPa$^{1/2}$ to be dissolved. Therefore, solid SPB is not dissolved in DGEBA and remained as a dispersant and filtered by the layered carbon fabrics. However, when 10 phr of *p*-BAB and SPB is added, the flexural properties are improved, maintaining the modulus as well as the toughness is improved, even with a small amount of polytriazolesulfone polymerized. This suggests that the novel toughening agent has a potential to be used for the composites prepared from viscosity sensitive process, such as RTM and VIP. For example, the most popular epoxy resin in aerospace applications, TGAP (triglycidyl aminophenol) has the solubility parameter of 23.83 MPa$^{1/2}$ which is similar to that of PES or SPB and can dissolve the solid SPB, suggesting no filtering effect of the layered carbon fabrics or carbon preform [32].

4. Conclusions

The novel toughening agent is successfully synthesized. This can be mixed with epoxy resin and curing agent in monomer forms, *p*-BAB and SPB and polymerized to polytriazolesulfone during the epoxy curing reaction through azide-alkyne click reaction. When 10 phr of *p*-BAB and SPB is added, the flexural properties are improved, maintaining the modulus and the toughness is also improved, whereas the conventional toughening agent PES can be added only 5 phr and resulted in diminished flexural properties and improved toughness of the resulting composites. Even with a small amount of polytriazolesulfone polymerized, due to the filtering effect of the solid SPB by the layered carbon fabrics during the VIP, the toughening and strengthening effect were observed from the novel toughening agent, which could be added in monomer forms, *p*-BAB and SPB. This suggests that the novel toughening agent has a potential to be used for the composites prepared from viscosity sensitive process, such as RTM and VIP.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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