

## Development of High $T_g$ Epoxy Resin and Mechanical Properties of its Fiber-Reinforced Composites

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**ABSTRACT:** A new epoxy resin with high glass transition temperature ( $T_g$ ) ( $\sim 180^\circ\text{C}$ ) and a viscosity low enough for infiltration into dry reinforcements at  $40^\circ\text{C}$  was developed for the vacuum-assisted resin transfer molding process. To study the curing behavior and viscosity, several blends were formulated using multifunctional resin, aromatic hardener, and reactive diluents. Effects of these components on the viscosity and  $T_g$  were investigated by thermomechanical analysis, dynamic scanning calorimetry, and rheometer. Experimental results showed that a liquid aromatic hardener and multifunctional epoxy resin should be used to decrease the viscosity to  $<1\text{ Pa}\cdot\text{s}$  at  $40^\circ\text{C}$ . Moreover, the addition of a proper reactive diluent decreased the viscosity and simultaneously minimized the deterioration of  $T_g$ . Mechanical properties of the composite produced with the optimized blend were evaluated at both room-temperature and high-temperature conditions. According to the results, the composite showed comparable mechanical properties with that of the current commercial resin. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** thermosets; thermal properties; mechanical properties; viscosity; glass transition

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### INTRODUCTION

High-performance polymer composites have been applied in a variety of fields such as aerospace, transportation, construction, electronics, and sports owing to their outstanding physical properties. There have been increasing demands for composites of enhanced durability under severe conditions<sup>1–4</sup> and a cost-effective processing method for large and complex structures.

As an alternative process to the cost-demanding autoclave process,<sup>5,6</sup> the vacuum-assisted resin transfer molding (VARTM) has been applied to fabricate composite structures with high performance and affordability. VARTM process is a type of RTM process, which involves the assistance of vacuum to infiltrate liquid resins into dry reinforcements. This process normally requires the resin to have low viscosity of  $<1\text{ Pa}\cdot\text{s}$  for it to flow through the reinforcement fibers. Common epoxy resins used for VARTM have very low viscosity at room temperature, but most of them have low glass transition temperature ( $T_g$ ), for instance,  $<120^\circ\text{C}$ .<sup>7,8</sup> On the other hand, epoxy resins with high  $T_g$  over  $180^\circ\text{C}$  generally have a semi-solid phase at room temperature, requiring a high temperature to lower its viscosity for infiltration.<sup>9–12</sup> It usually takes much time to decrease the viscosity by applying an initial heating temperature, and cost is also incurred to maintain the high temperature within the heat-

ing equipment. Besides, the expensive bagging and sealing materials for high-temperature usage are required in the VARTM process, resulting in the increased overall cost. Therefore, to produce cost-effective composite parts, it is necessary to develop a high  $T_g$  epoxy resin system that can be infiltrated at near room temperature. This resin system can also be used in any composite fabrication processes such as filament windings<sup>13</sup> or pultrusion processes which require low-viscosity resin.

Several studies have been performed on the development of low-viscosity and high  $T_g$  epoxy resin. Varley<sup>14,15</sup> evaluated three different low-viscosity additives as epoxy resin tougheners and reported that an epoxy-terminated hyperbranched polyester polymer had the best balance of properties, increasing the toughness, while affecting minimally the mechanical properties,  $T_g$ , and viscosity. Reactive diluents were used to decrease the resin viscosity and improve the impact strength of epoxy resin.<sup>16</sup> However, these approaches may seriously decrease the  $T_g$  of epoxy resin systems. As an effective reactive diluent, trimethylolpropane triglycidyl ether<sup>17</sup> was added at several percentages to diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin cured with diethyl toluene diamines (DETDA). These formulations showed a moderate  $T_g$ , but their viscosities exceeded  $1\text{ Pa}\cdot\text{s}$  at nearly room temperature, indicating the difficulty of

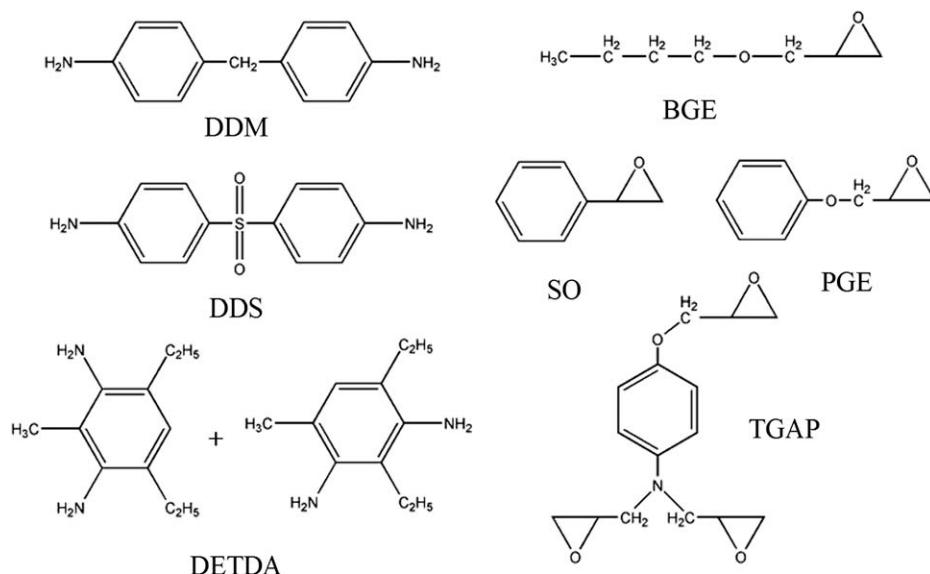


Figure 1. Chemical structure of materials.

infiltration of the resins. To improve the thermal properties of epoxy resin, multifunctional epoxy resins and aromatic amine hardeners have been widely employed.<sup>18–20</sup> Frigione<sup>21</sup> reported a very high  $T_g$  value of 245.4° and a low viscosity of <0.5 Pa·s using triglycidyl *p*-amino phenol (TGAP) as a base resin with DETDA. Recently, new multifunctional epoxy resins were synthesized to perform high thermal resistance with a good flowability.<sup>22,23</sup> The introduction of these multifunctional resins is very effective to increase the  $T_g$ . However, the optimization in regards to the costs as well as the resin properties should be required. Moreover, any results for the long-term stability of physical properties of composites including the newly developed resins with multifunctional epoxy resins were not reported.

Depending on the processing methods and applications of composites, there are several physical and chemical property requirements that an epoxy resin should fulfill. These requirements can be met by formulating base epoxy resins, curing agents, and additives. As the viscosity and  $T_g$  have a trade-off relationship, it is very important to choose proper reagents and right contents ratios. In this article, several curing agents, reactive diluents, and multifunctional resins were blended to modify the DGEBA-based epoxy resin system for the optimal properties. The purpose of this study is to obtain a resin blend with a high  $T_g$  of approximately 180°C and a low viscosity, which allows it to be infiltrated at near room temperature of 40°C. Effects of the chemical structure of additives on the viscosity and  $T_g$  were also studied. Curing behavior of epoxy systems was examined by differential scanning calorimetry (DSC). Mechanical properties of the composite manufactured using the optimum resin were also compared with a commercially available high  $T_g$  epoxy resin<sup>24–27</sup> at room temperature and high temperature.

## EXPERIMENTAL

### Materials

The general DGEBA-based epoxy resin, YD-128, was supplied by Kukdo Chemical (South Korea). The curing agents such as

4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), and a mixture of DETDA (Ethacure-100) were purchased from Kukdo Chemical, Huntsman (South Korea), and Albemarle (South Korea), respectively. Styrene oxide (SO, Aldrich, South Korea), *n*-butyl glycidyl ether (BGE, Kukdo Chemical) and phenyl glycidyl ether (PGE, Aldrich) were used as a reactive diluent. TGAP (Araldite MY-0510, Huntsman) was added to enhance the  $T_g$  of epoxy resin blends. Figure 1 shows the chemical structures of these materials. For comparison, a commercial resin of high  $T_g$ , RTM-6 from Hexcel, was also tested. Plain woven carbon fabrics (TR50S fiber, Mitsubishi, 12k) were used as the composite reinforcements.

### Blend Preparation and Characterization

YD-128, TGAP, curing agents, and reactive diluents were mixed with different formulations as summarized in Table I. All reagents were blended with the stoichiometric balance. The mixtures were agitated for 20 min at room temperature by a mechanical stirrer and were degassed for 60 min at 40°C under vacuum condition to remove trapped air. After degassing, the mixtures were cured at 100°C for 60 min, then at 150°C for 90 min and finally at 177°C for 120 min. Postcuring was performed at 200°C for 120 min. In the case of the blend including DDS and DDM, YD-128 was first heated to a temperature between 60 and 120°C. Then, the curing agents were added and stirred moderately until they were completely clear. In this study, all the blends, epoxies, and related composites underwent the same curing cycle.

The curing behavior of the formulated mixtures was studied using a DSC (Perkin Elmer, USA). Approximately, 2 mg of each sample was sealed in an aluminum pan and was dynamic-scanned from 50 to 300°C at a heating rate of 5°C/min. To measure  $T_g$  of the resin mixtures and RTM-6 resin, the thermomechanical analysis was conducted using a thermomechanical analyzer (TMA, Perkin Elmer). The cured samples were cut into 8 × 8 × 8 mm<sup>3</sup> and then placed in a temperature-controlled

**Table I.** Formulations of Epoxy Resin Blends

Sample code	DGEBA	TGAP	DDS	DDM	DDM	DETDA	BGE	SO	PGE
1	100		35						
2	100			29					
3	100	5		30					
4	100	10		32					
5	100	20		36					
6	100				25				
7	100	5		27					
8	100	10		29					
9	100	20		34					
10	100	20		36		5			
11	100	20		37		10			
12	100	20		40		20			
13	100	20		36			5		
14	100	20		37			10		
15	100	20		40			20		
16	100	20		36				5	
17	100	20		37				10	
18	100	20		40				20	
19	100	20		40				10	
20	100	20		44				20	

chamber equipped with a penetration type probe.  $T_g$  data were obtained at a heating rate of 5°C/min.

The viscosity of formulated epoxy mixtures was measured using a parallel-plate type rheometer (Gemini 200, Bohlin, UK). During the measurement, the shear rate was constantly maintained at 3.15 s<sup>-1</sup> and the temperature was varied from room temperature to 200°C at a heating rate of 5°C/min. The viscosity at 40°C was taken for comparison.

#### Composite Fabrication and Evaluation of Mechanical Properties

Fiber-reinforced composites were fabricated via a VARTM process using the developed epoxy blend. Infiltration temperature of the formulated epoxy was 40°C. Curing for the composites was carried out at the same cycle as mentioned earlier. The fiber volume fractions of all the composite samples were 51% approximately. Tensile specimens of the blend were also produced to compare the properties of the neat resin with RTM-6.

The mechanical characterization such as tensile, compressive, and shear testing for composites were performed at room temperature according to the ASTM standard D3039, D3410, and D3518, respectively. Modulus of specimens was measured using a strain gauge (FCA-5-11-1L, Tokyo Sokki Kenkyujo, Japan). The mechanical properties for a comparison of high-temperature characteristics were also evaluated at elevated temperature (ET) of 72°C. For the condition of elevated temperature wet (ETW), composite specimens were aged at 72°C and relative humidity of 95% until the moisture absorption was saturated. The point of saturation was determined such that the moisture

level did not change by more than 0.01% of its previous value when measured after 7-day period. The mechanical testing was carried out at 72°C, and data were taken from an average of at least five specimens.

## RESULTS AND DISCUSSION

### Effect of Multifunctional Resin on the Viscosity and $T_g$

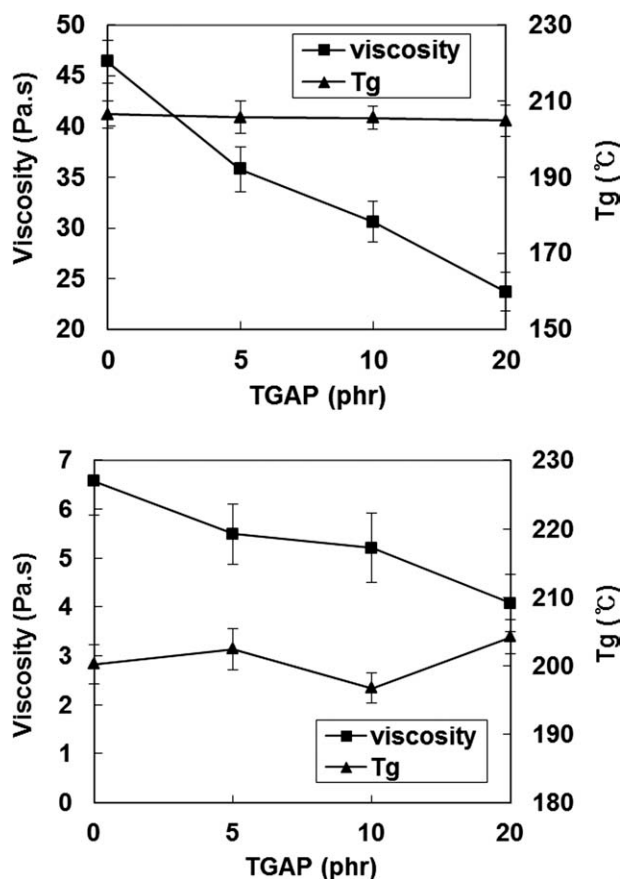
For the selection of the proper curing agent, the 1 : 1 stoichiometric mixtures of DDS, DDM, and DETDA with DGEBA-type resin were prepared based on the formulation summarized in Table I.  $T_g$  values of curing agents were 210, 207, and 200°C, respectively. As DDS and DDM showed higher  $T_g$ , they were expected to have excellent thermal performance. However, a high temperature of approximately 120°C was required to dissolve them into the epoxy base resin. Moreover, the epoxy resin containing DDS and DDM exhibited relatively high viscosity as compared to the resin with DETDA. Therefore, DETDA was selected as a curing agent in the experiment.

As compared to common epoxy resins, the multifunctional epoxy resins retain more epoxy groups, resulting in large functionalities and high crosslinking. It is well known that they can exhibit good thermal stability, chemical resistance, and mechanical properties. Although tetraglycidyl diaminodiphenyl methane (TGDDM), for instance, has been utilized commercially in the high-temperature epoxy resin, there are some drawbacks including the high cost. As the resin is solid like at room temperature, it is very difficult to infiltrate into fiber reinforcements even at a high temperature of around 100°C. Moreover, large amount of heat is generated during the curing reaction. Therefore, it is critical to control the heat of reaction when a thick and large structure is to be produced.

Another type of high  $T_g$  multifunctional epoxy resins is TGAP, which has a nitrogen atom linked to two glycidyl groups and an oxygen atom linked to one glycidyl group. Unlike TGDDM, TGAP has liquid-like phase with the viscosity of 0.5–0.8 Pa·s at room temperature. Although it is more expensive than DGEBA type resin, the optimal dosage level for economical feasibility can decrease the viscosity of epoxy systems while maintaining  $T_g$ . Figure 2 shows the effect of TGAP contents on the viscosity and  $T_g$ . With the increased amount of TGAP, the viscosity decreased effectively, and  $T_g$  was maintained regardless of the curing agent types. From this result, 20 phr of TGAP was added for the optimal condition.

### Effect of Reactive Diluents

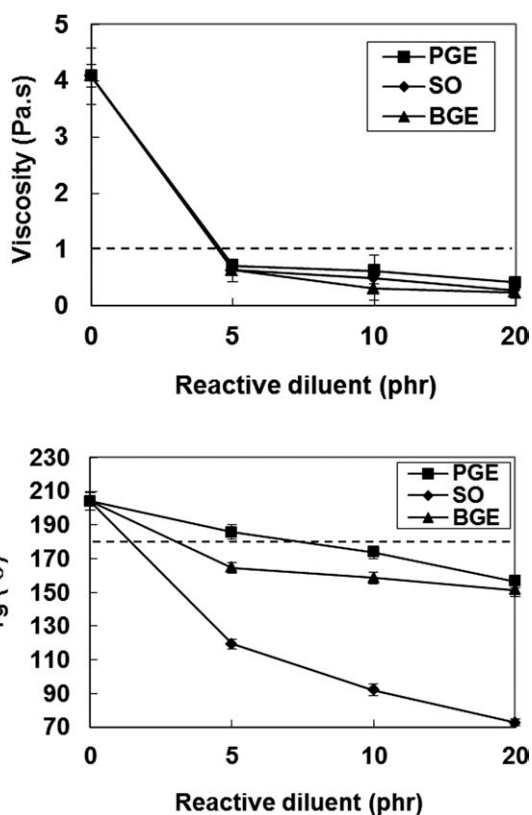
Addition of reactive diluent is one of the common methods to lower the viscosity of epoxy systems, whereas the thermal and mechanical properties deteriorate. This is because of the imperfection of network structure in the reactive diluents having a mono-epoxy group, where the growth of polymer chains is terminated during the curing reaction. In addition,  $T_g$  of the blend resin decreases owing to the fact that the reactive diluents usually have flexible aliphatic chains, which act as an internal plasticizer. Therefore, it is necessary to determine the optimal content of reactive diluent to achieve the balance between viscosity and thermal/mechanical properties.



**Figure 2.** Effect of TGAP contents on the viscosity and  $T_g$ : (a) DDM (Code, 2–5), (b) DETDA (Code, 6–9).

Another important consideration is that a reactive diluent should have a similar chemical reactivity to the base resin to minimize the deterioration of physical properties. It is believed that the reactivity strongly depends on the chemical structure of the reactive diluent. In many cases, the difference of the chemical structure may be practically considered as negligible. However, if the chemical reactivity between the reactive diluent and the base resin is very different, the heat of curing reaction ( $\Delta H_{cr}$ ) might reduce owing to the unreacted resin or diluent.

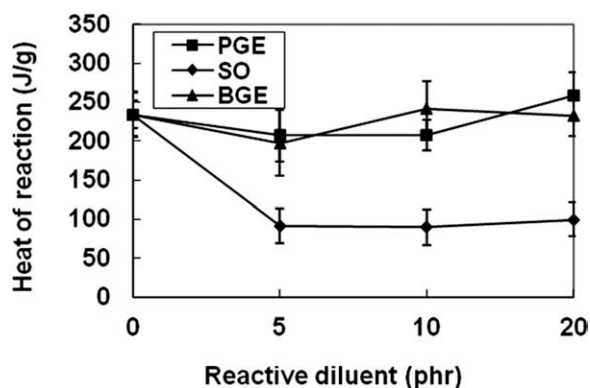
In this study, three kinds of general reactive diluents are considered, namely BGE, SO, and PGE. Figure 3(a,b) shows the variations of viscosity and  $T_g$  of DETDA-cured epoxy blends, respectively, with respect to the increased amount of each reactive diluent. In Figure 3(a), there was no significant difference in the viscosity caused by the reactive diluent types. The critical viscosity for the VARTM process, which is  $<1$  Pa·s, was achieved when more than 5 phr of any reactive diluents was added. On the other hand, very different trend of  $T_g$  values is shown in Figure 3(b). The epoxy blend containing PGE showed the highest value of  $T_g$ . As PGE has one glycidyl ether and one phenyl group, its chemical structure is similar to that of TGAP. Thus, it may have a similar reactivity with the blend resin of DGEBA/TGAP. However, SO shows a significant difference in reactivity because it is also an epoxy derivative linked with a phenyl group but is not a glycidyl ether structure. Although BGE has a



**Figure 3.** (a) Viscosity and (b)  $T_g$  of epoxy blends with different reactive diluents (Code, 10–18).

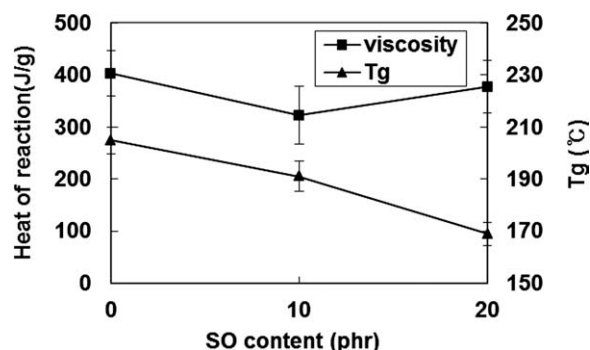
glycidyl group, *n*-butyl end group may contribute to the decrease of  $T_g$ .

Figure 4 shows  $\Delta H_{cr}$  calculated from the DSC curves of the DETDA-cured epoxy resin blends. When compared with PGE or BGE, the epoxy blend with SO obviously possessed a lower  $\Delta H_{cr}$ . This indicates that there were some resin or diluent molecules which did not participate in the curing reaction. This may result in the decrease of  $T_g$  and mechanical properties. Figure 5 shows  $\Delta H_{cr}$  and  $T_g$  of DDM-cured epoxy blend with SO. Contrary to the DETDA-cured blend, it can be seen that the addition of SO to DDM-cured system slightly reduced  $\Delta H_{cr}$  and the decrease in  $T_g$  was equivalent with other diluents. This result



**Figure 4.** Heat of curing reaction with different reactive diluents.





**Figure 5.** Heat of reaction and  $T_g$  of DDM-cured epoxy as a function of SO content (Code, 19, 20).

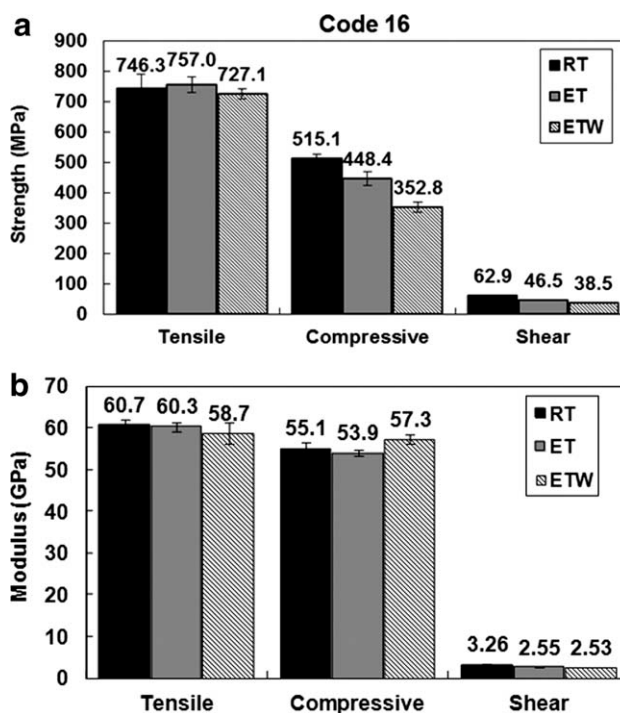
indicates that  $\Delta H_{cr}$  may also be related with the reactivity of the curing agent. It is known that DDM has higher reactivity than DETDA because the diethyl and methyl groups of DETDA sterically hinder the amine functional groups.<sup>13</sup> One possible implication of this result is that the unbalanced chemical structure between the TGAP and the SO may be negligible owing to the high reactivity of DDM. However, the lower reactivity of DETDA can accelerate the influence of the unbalanced chemical structure, which results in the low  $\Delta H_{cr}$  and  $T_g$ .

### Comparison of Mechanical Properties

From the experimental results, sample code 16 in Table I was selected as the optimum formulation of epoxy blends. Table II summarizes the mechanical and thermal properties of two resin system: Code 16 and RTM-6. The formulated resin showed comparable tensile properties and  $T_g$  with RTM-6. The composite samples for mechanical testing were fabricated via VARTM process using the newly formulated resin. The resin was infiltrated into carbon fabrics at 40°C by vacuum.  $T_g$  of the composite was measured as 185.8°C. Tensile, compressive, and shear properties were evaluated at room temperature, ET, and ETW conditions. The results are shown in Figure 6. Under the ET and ETW conditions, the mechanical strength and modulus were maintained without significant reduction. These basic data can offer possible alternative usage of the epoxy resin for high-performance composites.

### CONCLUSIONS

Three reactive diluents and one multifunctional resin (TGAP) were evaluated, and their effects on the viscosity and  $T_g$  of DGEBA/DETDA epoxy systems were compared. These properties were measured using a TMA and a rheometer. Curing behavior of the epoxy blends was also studied using DSC.



**Figure 6.** Mechanical properties of composites for the sample code 16 resin at room temperature, ET, and ETW conditions.

Experimental results suggested that the addition of TGAP was found to be effective in reducing the viscosity of resin while maintaining its  $T_g$ . To reduce the viscosity of resin to be low enough for infiltration into reinforcement fibers at 40°C, the optimal content of reactive diluent was determined. According to the experiments, decrease in  $T_g$  was probably dependent on the chemical structure of reactive diluent. To minimize the decline in  $T_g$ , the reactive diluent retaining the similar structure to TGAP was applied. From the experimental results, a novel resin formulation was established based on DGEBA, TGAP, DETDA, and PGE, showing a viscosity of 0.71 Pa·s at 40°C and  $T_g$  of 185.8°C. Mechanical properties of composites containing the optimized epoxy blend were tested at room temperature, ET, and ETW. Under both the ET and the room temperature testing conditions, the mechanical properties were maintained without significant reduction.

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**Table II.** Mechanical and Thermal Properties of Neat Resins

Sample	Tensile strength <sup>a</sup> (MPa)		Tensile modulus <sup>a</sup> (GPa)		$T_g$ (°C)	
	Room temperature <sup>b</sup>	72°C <sup>b</sup>	Room temperature	72°C	Cured at 177°C	Postcured at 200°C
Code 16	73.1 ± 5.6	69.5 ± 5.4	3.6 ± 0.2	2.81 ± 0.03	181.3 ± 3.9	185.8 ± 4.2
RTM-6	75 <sup>c</sup>	-	2.9 <sup>c</sup>	-	174.2 ± 4.0	193.5 ± 5.5

<sup>a</sup>Standard test specification: ASTM D 638, <sup>b</sup>Test condition, <sup>c</sup>From RTM-6 product data.<sup>9</sup>

composites for aircraft structure) of the Ministry of Knowledge Economy, Republic of Korea.

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