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Mechanical properties of cryogenic epoxy adhesives: Effects of mixed curing agent content

Yu Liu, Guo Yang, Hong-Mei Xiao, Qing-Ping Feng*, Shao-Yun Fu*

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

Phenyl glycidyl ether was used to react with solid metaphenylene diamine (MPDA) to produce N-(3-phenoxy-2-hydroxypropyl)-1,3-benzenediamine (NPHB). MPDA was intentionally formulated to have an excessive amount to obtain a new liquid MPDA–NPHB mixture. The mixed curing agent was indicated to have a few advantages over MPDA. The mixed curing agent was then used to cure diglycidyl ether of bisphenol A as cryogenic epoxy adhesive. The effects of the MPDA–NPHB content were systematically studied on the impact strength and shear strength at both room temperature and cryogenic nitrogen temperature of the epoxy adhesive. Moreover, two coupling agents with various contents were used to further enhance the shear strength of the optimal cryogenic epoxy adhesive. Finally, differential scanning calorimetry analysis showed that the modified adhesive showed a higher glass transition temperature than the unmodified adhesive.

1. Introduction

Epoxy resins have many merits such as high strength, excellent dielectric properties, good chemical and solvent resistance etc., hence they have been widely used in many engineering applications [1–3]. Moreover, epoxy resins have also been employed in cryogenic engineering applications as adhesives, impregnating resins and matrices for fiber reinforced composites [4–10]. However, epoxy resins are intrinsically brittle especially at cryogenic temperatures. Therefore, it is important to attain high fracture resistance for epoxy resins. Moreover, as adhesives for cryogenic engineering applications, it is necessary to optimize their shear strength at both room temperature and cryogenic temperature.

Metaphenylene diamine (MPDA) is one of the widely used aromatic amine hardeners for curing epoxy resins to get good mechanical properties [2,11–16]. Nevertheless, it is not convenient to use MPDA as curing agent since it is a solid material at room temperature (RT) and has to be melted to mix with epoxies [2,11]. Moreover, when epoxy resins are cured with MPDA alone, the highly crosslinked epoxy networks would be formed, leading to a relatively low fracture resistance of cured epoxy resins [11]. Diglycidyl ether of bisphenol A (DGEBA) is one of the most important epoxy resins for cryogenic engineering applications [17,18]. The mechanical performance of DGEBA epoxy can be improved by polypropylene glycol diglycidyl ether (PPGDGE) and hydroxyl-terminated polyether diglycidyl ether (JEf-0211) especially at cryogenic temperatures [9,19]. This modified DGEBA will be used in the present work.

Herein the purpose of this work is to produce a new hardener for developing cryogenic adhesive resins based on modified DGEBA. MPDA suffers a disadvantage of aromatic diamine toxicity [20], so a low toxic phenyl glycidyl ether (PGE) was used to react with MPDA of an excessive amount to get N-(3-phenoxy-2-hydroxypropyl)-1,3-benzenediamine (NPHB), resulting in an MPDA–NPHB mixture as the mixed curing agent. The impact strength and shear strength at both room temperature (RT) and liquid nitrogen temperature (77 K) of the cured epoxy resins were studied by taking into account the effects of the MPDA–NPHB content. Then, two coupling agents of 3-aminopropyltrimethoxysilane (APTMS) and γ-(2,3-epoxypropoxy) propyltrimethoxysilane (EPTMS) with various contents were used to further increase the shear strength of the modified cryogenic epoxy adhesive. The glass transition temperature of the epoxy resins with various MPDA–NPHB contents was also examined.

2. Experimental

2.1. Materials

The epoxy resin used was liquid DGEBA (YueYang Baling Petrochemical Technology Ltd., China) with an epoxide equivalent weight (EEW) of 212–244. PPGDGE (EPG-207, Tohto Kasei Co., Ltd., Japan) with an EEW of 300–350 and hydroxyl-terminated polyether diglycidyl ether (JEf-0211, Changshu Jiafa Chemistry

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* Corresponding authors. Tel./fax: +86 10 82543752.
E-mail addresses: fengqp@mail.ipc.ac.cn (Q.-P. Feng), syfu@mail.ipc.ac.cn (S.-Y. Fu).

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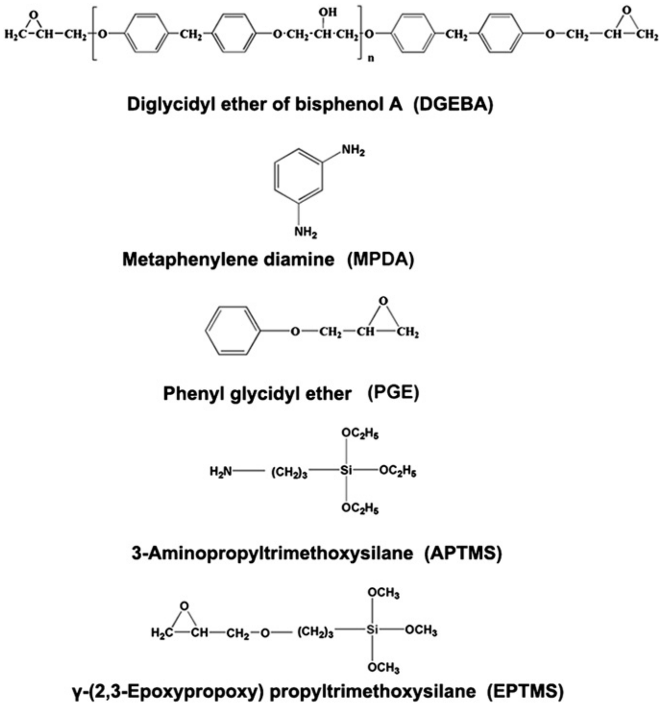

Fig. 1. Chemical structures of DGEBA, MPDA, PGE, APTMS and EPTMS.

Co., Ltd., China) with an EEW of 250–285 were used as the flexible modifiers for the epoxy system [9,21]. MPDA (Beijing Chemical Works, China) was used as one component of the mixed curing agents. PGE (JX-016, Changshu Jiafa Chemistry Co., Ltd., China) was used to react with MPDA to get NPHB which then became another component of the mixed curing agent. Two coupling agents of APTMS and EPTMS were purchased from Shen Da Co. Ltd. (Beijing, China). The chemical structures of DGEBA, MPDA, PGE, APTMS and EPTMS are shown in Fig. 1.

2.2. *Preparation of MPDA–NPHB mixture*

MPDA was placed in a four-neck round-bottom flask fitted with a condenser, overhead stirrer, thermometer and gas inlet tube and melt at 65 °C under a gentle nitrogen sweep. After stirring for 30 min, PGE was added to the flask. PGE was employed to react with MPDA to get NPHB. The molar ratio of MPDA and PGE was 2:1 with an intentionally excessive amount of MPDA and an MPDA–NPHB mixture would thus be obtained as the mixed curing agent. The mixture was heated to 80 °C and then maintained at 80 °C for 4 h. Finally, a black and viscous liquid of a mixed curing agent was obtained.

2.3. *Preparation of samples*

The DGEBA, PPGDGE and JEf-0211 were first blended thoroughly. A constant DGEBA:PPGDGE:JEf-0211 weight ratio of 100:20:20 was used. Then the as-synthesized MPDA–NPHB mixed curing agent was added to the blend and the MPDA–NPHB content varied from 14 to 32 phr. For the purpose of comparison with using MPDA alone, unmodified MPDA with a stoichiometric amount (11 phr) was used to react with the epoxy. The EEW of the epoxy resin mixture was about 244. The amine hydrogen equivalent weight (AHEW) of the new liquid hardener could be obtained as 52.3. At the stoichiometric point, the initial number of epoxy groups equals the initial number of amine hydrogens. At this composition, all amine and epoxy functionalities may be reacted. The parts of mixed hardener can be calculated according to the following equation:

$$G = 100 \times (\mathrm{AHEW}/\mathrm{EEW})$$

where G is the parts by weight of amine to react with 100 parts by weight of mixed epoxy, then, the result is 21.4 g (relative to 100 g mixed epoxy system). The content of curing agent with non-stoichiometric amount influences the mechanical properties of cured epoxy systems [11].

The cure schedule was optimized through the study of the epoxy resin with the stoichiometric MPDA using the differential scanning calorimeter (DSC). In order to eliminate the effect of curing condition, all the samples were cured under the same curing condition. The resultant materials were completely mixed by a mechanical stirrer and degassed with a vacuum pump to eliminate air bubbles. The bubble-free mixtures were then poured into the steel mold preheated in an oven. The inner dimensions of the steel mold for making impact specimens are 4 mm × 10 mm × 80 mm. The obtained samples are then used for measurement of impact resistance.

The specimens for the shear strength testing are made according to the recommendation of ASTM D 1002-01. The adherends used were LY12-CZ aluminum alloy sheets with a yield point of greater than 300 MPa. The aluminum sheets are 2 mm thick and 80 mm long. They were polished with emery papers and the polished surfaces were greased with acetone and then dried. Afterwards, two rectangular aluminum alloy sheets with an overlap length of 20 mm were fixed with the as-prepared epoxy adhesives. This overlap length is not ideal but is acceptable since it is much less than the maximum permissible overlap length (about 40 mm at a shear strength of 10 MPa according to the ASTM D 1002-01). The selection of such an overlap length is to get a large contact area between two aluminum sheets so that an enough large tensile force is needed for precious measurement of a force under a 2-ton load cell used. A designed fixture was used to assemble the adhesive joints and control the adhesive thickness. The actual adhesive thickness of the cured joint was measured by a Digimatic Caliper. All the samples were cured at 60 °C for 5 h, then cured at 80 °C for 1 h, and post-cured at 100 °C for 2 h. The resultant adhesive thickness for all specimens was controlled at 0.1 ± 0.02 mm. In order to enhance the shear strength, two coupling agents (APTMS and EPTMS) were separately introduced into the epoxy adhesive with the optimal curing agent content.

2.4. *Measurement and characterization*

The MPDA–NPHB product was analyzed by gas chromatography–mass spectrometry (GC–MS). The analysis was processed using a trace GC ULTRA Thermo Gas Chromatograph coupled with the mass selective detector (DSQ, Italia).

Charpy impact strength of the samples was measured with a REGER RG-30 impact tester according to the recommendation of GB-T 2571-95 (equivalent to ISO 179:2000) for un-notched specimens. Charpy impact testing was conducted at both room temperature (RT) and 77 K as done previously [23].

The shear strength testing was performed referring to GB-T 7124-86 (equivalent to ASTM 1002-05) with a crosshead speed of 2 mm/min at both RT and 77 K. The cryogenic temperature condition was also achieved by immersing the specimens in a liquid nitrogen filled cryostat. The number of specimens for each composition was not less than five for the above mechanical tests.

The glass transition temperatures (T_g) of the samples were measured by DSC under nitrogen atmosphere with a heating rate of 10 °C/min using a NETZSCH STA 409PC. The elastic modulus in the rubbery state of the epoxy resins with different MPDA–NPHB contents for evaluating the crosslink density were monitored by dynamic mechanical analyzer (DMA 2980, TA Instruments). All specimens were performed at 1 Hz and a heating rate of 5 °C/min.

The typical DSC curves of uncured epoxy resin system with MPDA (solid line) and cured epoxy resin system with MPDA (dot line) at 10 °C/min heating rate are shown in Fig. 2. The observed exothermic peak of uncured epoxy resin represents the released heat of epoxy-amine reaction [22]. But no exothermic peak is observed in the DSC curve for the cured DGEBA/MPDA epoxy system and also for the cured DGEBA/MPDA–NPHB system (not shown). This indicates that the curing reaction is complete. Thus, the curing schedule is adequate for the investigated epoxy systems.

3. Results and discussion

3.1. GC–MS detection of MPDA–NPHB mixture

Fig. 1 demonstrates that MPDA and PGE are a primary amine and an epoxide, respectively. The combination of a primary amine and an epoxide would lead to the following possible reactions that are shown in Fig. 3 [22,24,25]. In this work, the molar ratio of MPDA to PGE is 2:1. This means that there is a four-fold excessive amount of amine in the mixture. When the DGEBA/MPDA mixture contained a several fold excess of amine, Sbirrazzuoli et al. [22,26] indicated that the reaction of the primary amine with epoxide was predominant. So, the main reaction would be the type of reaction 1 as shown in Fig. 3 and the main product was NPHB, a primary and secondary amine. Its chemical structure is shown in Fig. 4. Because MPDA is in large excess, only a part of MPDA would react with the whole PGE. Thus, the as-prepared liquid is a mixture of the un-reacted MPDA and the obtained NPHB. This is confirmed below by the GC–MS detection.

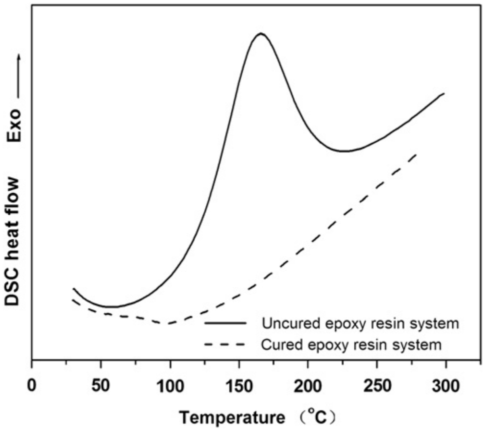

Fig. 2. DSC curves for uncured epoxy resin system with MPDA (solid line) and cured epoxy resin system with MPDA (dot line) at 10 °C/min heating rate.

GC–MS detection was employed to analyze the as-prepared liquid as shown in Fig. 5. Two main peaks are gained at different retention times as shown in Fig. 5A for the GC result, representing two substances of the mixture. Fig. 5B and C are the mass spectra results respectively for the two substances at the main peeks. According to the National Institute of Standards and Technology (NIST) MS database, the substances were MPDA at 11.58 min and NPHB at 27.67 min, respectively. The PGE was not defected in the mixture, which indicated that the PGE was exhausted after the chemical reaction. In the resultant liquid mixture, only MPDA and NPHB existed. Namely, a liquid mixed MPDA–NPHB curing agent was finally obtained.

3.2. Mechanical properties

Impact strength can be regarded as a fracture resistance of materials [27,28]. Impact strengths of the epoxy resins cured with the MPDA–NPHB mixed curing agent of various contents at both RT and 77 K are shown in Table 1. For a chosen confidence level (95%), an impact strength of 27 kJ/m^2 at RT could be 32 or 22 kJ/m^2 according to ISO 2602 – 1980 (E) (Statistical interpretation of test results–Estimation of the mean–Confidence interval). Thus,

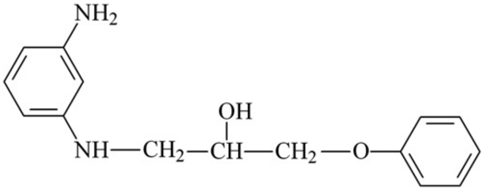

Fig. 4. Chemical structure of NPHB.

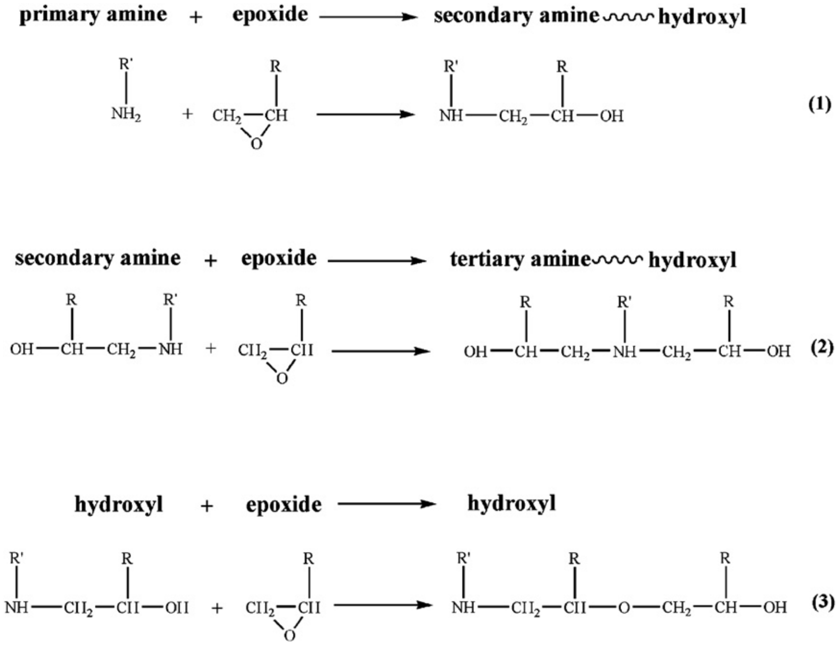

Fig. 3. Reaction schemes of primary amine and epoxide.

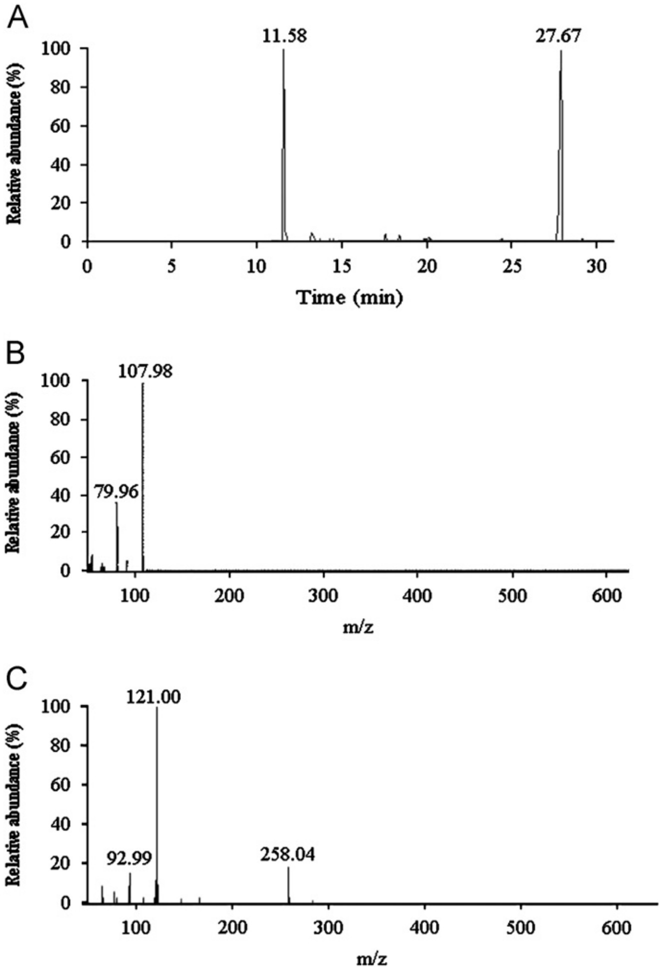

Fig. 5. The GC–MS results of the MPDA–NPHB mixture: (A) the total chromatogram, (B–C) the mass spectra at 11.58 and 27.67 min, respectively.

only average values of impact strength are discussed and its changing tendency is briefly summed up below.

The impact strength initially increases up to the 25 phr curing agent content at both RT and 77 K and afterwards decreases with further increasing of the MPDA–NPHB content. The average impact strength of the epoxy resins with 25 phr MPDA–NPHB is 35.0% and 12.5% higher respectively at RT and 77 K than for the unmodified epoxy system. The impact strength of the epoxy resin cured with MPDA alone is 16 ± 5 kJ/m^2 at 77 K, which shows an obviously larger scatter than for the modified adhesive. This is also true for other mechanical properties such as flexural strength, modulus and fracture toughness of unmodified epoxy resins using MPDA as curing agent [11]. In addition, Table 1 shows that the impact strength at RT is larger than that at 77 K with the same composition. This is mainly due to the fact that the molecules have less mobility at 77 K than at RT [10]. So, the deformation of polymer molecules during the impact testing absorbs less energy at 77 K than at RT.

It is shown above that the impact strength achieves the maximum values at the 25 phr MPDA–NPHB content. This is the case that the MPDA–NPHB mixture has some excess (namely 25 phr content) over the 21 phr stoichiometric amount. Residual thermal stress would take place while epoxy resins are cooled from a high temperature to RT during curing [10]. The appropriate excess of MPDA–NPHB mixture could reduce the internal stress due to the decrease of the crosslink density and toughen the epoxy resins at RT and 77 K. However, when the MPDA–NPHB content is higher than 25 phr, the impact strength is decreased slightly. The decrease in the impact strength may be due to structural weakness associated with the un-reacted MPDA–NPHB curing agent (un-reacted amines) [29,30].

Table 1
Impact strength and shear strength at RT and 77 K of the epoxy resins with stoichiometric MPDA and various MPDA–NPHB contents[a].

MPDA–NPHB content (phr)[b]	Impact strength (kJ/m^2)		Shear strength (MPa)	
	RT	77 K	RT	77 K
Stoichiometric MPDA (11 phr)	20 ± 6	16 ± 5	4.7 ± 0.2	8.5 ± 0.5
14	12 ± 4	10 ± 1	3.1 ± 0.3	5.2 ± 0.9
18	16 ± 4	14 ± 1	4.3 ± 0.5	8.4 ± 1.1
21	24 ± 4	17 ± 1	6.4 ± 0.3	8.9 ± 0.5
25	27 ± 4	18 ± 2	8.1 ± 0.1	10.0 ± 0.9
29	21 ± 2	14 ± 2	7.2 ± 1.2	9.3 ± 0.4
32	19 ± 4	13 ± 2	4.4 ± 1.1	7.2 ± 0.4

[a] *Note*: Data are expressed as average value ± standard error.
[b] *Note*: Relative to 100 parts of mixed epoxy resins.

The results for the shear strength at RT and 77 K of the epoxy resins with various MPDA–NPHB contents are also shown in Table 1. It is observed that the shear strength is very sensitive to the MPDA–NPHB content. The changing trend of the shear strength is similar to that shown above for the impact strength. It can be noticed that the shear strength of the epoxy resins cured with the optimal MPDA–NPHB content is higher than that with the MPDA alone. The relative enhancements in average shear strength are respectively 72.0% and 17.6% at RT and 77 K. Moreover, we can observe from Table 1 that the shear strength at 77 K is larger than that at RT with the same MPDA–NPHB content. This result is consistent with that reported by Hu and Huang [31]. This is because the binding force and intermolecular force at 77 K are greater than those at RT due to thermal shrinkage [10,17], which would contribute to the increase of the shear strength. Also, it can be noticed that there is a large change (100%) for the un-modified adhesive but a small change (20%) for the modified adhesive in the shear strength between RT and 77 K. Namely, the RT shear strength for the unmodified adhesive is relatively low. As a cryogenic adhesive, its RT shear strength should also be good since the adhesive is used not only at 77 K but also at RT. Moreover, MPDA can be dissolved in the excellent solvent: N-methyl-2-pyrrolidone. If using this “liquid” curing agent, the solvent has to be carefully taken out during the curing reaction of epoxy resins. Otherwise, too many voids due to addition of the solvent will exist in the final samples. Finally, the solvent will definitely affect the properties of the cured samples. Thus, the modified adhesive is a better candidate than the unmodified adhesive as a cryogenic adhesive.

In order to attain higher shear strength, two coupling agents (APTMS and EPTMS) were introduced into the epoxy adhesive with the optimal (25 phr) MPDA–NPHB content. Tables 2 and 3 show the results for the shear strength of epoxy resins after the addition of APTMS and EPTMS at various contents, respectively. Table 2 shows that the addition of APTMS obviously increases the shear strength. The shear strength increases with increasing the APTMS content and reaches the maximum at 6 phr APTMS content. Afterwards, the shear strength decreases with further increasing of the APTMS content. Table 3 shows a similar changing tendency for the effect of EPTMS content on the shear strength to that for APTMS and the only difference is that the maximal shear strength occurred at the 4 phr EPTMS. Consequently, it is clear that the addition of some amount of coupling agents to cryogenic epoxy adhesives is necessary to further increase the shear strength for practical applications.

Table 2
Shear strength of epoxy resins after addition of coupling agent APTMS[a].

APTMS content (phr)	Shear strength (MPa)	
	RT	77 K
0	8.1 ± 0.1	10.0 ± 0.9
2	8.4 ± 1.2	10.5 ± 2.3
4	9.9 ± 0.5	12.7 ± 0.6
6	10.2 ± 0.4	14.1 ± 1.2
8	9.8 ± 0.5	13.8 ± 1.1
10	8.6 ± 0.4	12.3 ± 1.0

[a] *Note*: Data are expressed as average value ± standard error.

Table 3
Shear strength of epoxy resins after addition of coupling agent EPTMS[a].

EPTMS content (phr)	Shear strength (MPa)	
	RT	77 K
0	8.1 ± 0.1	10.0 ± 0.9
2	9.0 ± 0.1	11.2 ± 0.2
4	10.0 ± 0.6	13.0 ± 0.6
6	9.4 ± 0.5	12.1 ± 0.2
8	8.5 ± 0.2	11.3 ± 0.4
10	7.6 ± 0.7	10.9 ± 0.5

[a] *Note*: Data are expressed as average value ± standard error.

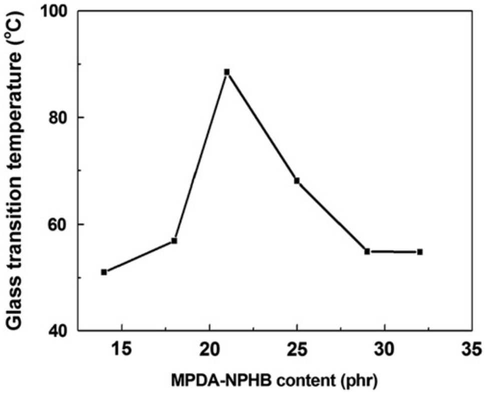

Fig. 6. Glass transition temperatures of the epoxy resins with various contents of MPDA–NPHB.

3.3. Glass transition temperature and crosslink density

The results for the T_g of the epoxy resins with various MPDA–NPHB contents are shown in Fig. 6. T_g of the epoxy resins increases with increasing MPDA–NPHB content, and attains a maximum value at the stoichiometric 21 phr MPDA–NPHB content, and then decreases with further increasing of the MPDA–NPHB content. The similar result was reported previously [32,33], in which stoichiometric formulation corresponded to the highest T_g. It is well known that T_g is related to crosslink density. For examining the crosslink density, the elastic modulus (G_r) in the rubbery state was measured by DMA. The elastic properties of dense epoxy networks can be described by the following equation [32]:

$$\log G_r = 6 + 293d/M_c$$

where d is the density and M_c the average molecular weight of chain segments between crosslink points. The crosslink density, μ, is then given by

$$\mu = dN/1.5M_c$$

where N is Avogadro's number. Fig. 7 shows the results for the crosslink density of the epoxy resins with various MPDA–NPHB contents. The epoxy resins attained the maximal crosslink density at 21 phr MPDA–NPHB content. As a result, the stoichiometric MPDA–NPHB content would lead to the highest T_g.

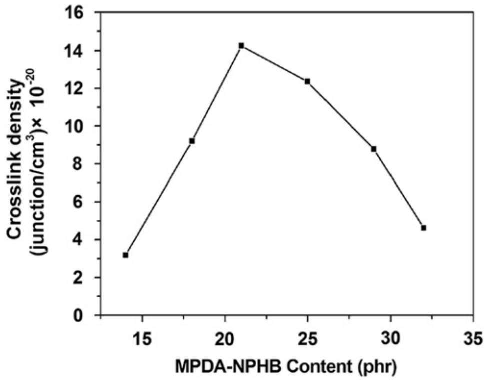

Fig. 7. The crosslink density of the epoxy resins with various contents of MPDA–NPHB.

4. Summary and conclusions

In this paper, a new liquid mixed curing agent (MPDA–NPHB) has been prepared by using PGE to react with MPDA with an excessive amount. The mixed curing agent has a few advantages over MPDA. First, as cryogenic adhesives, the RT shear strength is also important since they are used not only at cryogenic temperatures but also at room temperature. The RT shear strength (8.1 ± 0.1 MPa) for the modified adhesive is much higher than that (4.7 ± 0.2 MPa) for the unmodified adhesive. Second, the hardener for the modified adhesive is a liquid while the hardener for the unmodified adhesive is a solid. It is more convenient to use a liquid curing agent than a solid curing agent. Third, the cryogenic impact strength has a smaller scatter for the modified adhesive than for the unmodified adhesive. Fourth, the hardener for the unmodified adhesive due to high toxicity of MPDA has a higher toxicity than for the modified adhesive. Finally, the modified adhesive has a higher glass transition temperature than the unmodified adhesive. The as-prepared MPDA–NPHB liquid mixture was used to react with modified DGEBA to prepare cryogenic epoxy adhesives. The modified adhesives at proper MPDA–NPHB contents showed improved impact strength and shear strength at both RT and 77 K compared to the unmodified adhesive. Consequently, the as-prepared cryogenic epoxy adhesive possessing high overall cryogenic mechanical performance shows great potential for practical applications in cryogenic engineering areas.

Acknowledgments

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