

Studies of Physical Properties Changes of Epoxy Compositions Including Elastomeric Polyurethanes Prepared With Different Polyols

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Abstract: Elastomeric polyurethanes (PUs) were synthesized and added to epoxy resin. This was done to compensate for the brittleness of the epoxy resin. The PUs, which comprises soft segments and hard segments, are often used as a toughener for an epoxy resins. Different types of polyols such as polycarbonate diol, polybutadiene diol, polypropylene glycol, and polytetrahydrofuran have been used to change the soft segments of the PUs. The modified soft segments of the PUs were added to the epoxy resin in order to see how the modified soft segment changed the physical properties of the epoxy resin compositions. The results showed that the introduction of PUs into the epoxy compositions composed with bisphenol A epoxy resin and dicyandiamide curing agent lowered both tensile and flexural strength in general, but significantly increased the impact strength of the cured epoxy composition including ether-type polyol-PUs. Scanning electron microscopy was used to confirm the improved impact resistance by studying the phase separation of the PU in the cured epoxy resins. Furthermore, the existence of polyether polyol-PU in epoxy resin afforded high lap shear strength for steel substrates. Specifically, the epoxy resin containing polytetrahydrofuran-PU showed three times higher T-peel strength than that of epoxy neat resin (i.e., resin without any toughening agent). The results showed that PU can be used to toughen epoxy resins.

Keywords: Polyurethane, Epoxy resin, Adhesive, Physical property, Adhesive property

I. INTRODUCTION

Epoxy resin is one of the most popular thermosetting polymers that are used in wide-ranging industrial fields such as adhesives, coatings, composites, and electronics [1-3]. Cured epoxy resin provides excellent mechanical properties, higher chemical resistance, and lesser shrinkage strain than other thermosetting resins in molding processes. Also, the curing reaction of the epoxy resin does not generate any water as a by-product [4]. However, epoxy resins have certain disadvantages as well, such as short workability time by forming a gel, yellowing of the cured resins, and high brittleness causing breakage on impact. Although epoxy resins show poor adhesion with hydrophobic polymer or crystalline polymer substrates, epoxy resins have been studied for the preparation of high-performance adhesives with high toughness by introducing rubber or thermoplastic polymer as a toughener [5,6]. Elastomeric polyurethanes (PUs) with urethane (-NH-CO-O-) functional groups are one of the most common polymeric tougheners that can compensate for the brittleness of the epoxy resins. PUs are composed of a soft segment made of an alkyl long chain and a hard segment comprising a relatively short chain of diisocyanate. The mechanical properties of the PU can be modified by reacting different types of polyols with diisocyanates or chain extenders [7,8]. Also, polyols can be classified as either polyester or polyether types [9-11]. Polyester polyols can be applied to PU to improve its mechanical properties and abrasion resistance, and polyether polyols can be used to afford high elastic properties to PU. Aromatic or aliphatic diisocyanates function as hard segments of PU and form peptide bond with the hydroxyl group of polyols, resulting in the restriction of rotation of the molecule. Elastomeric PUs are used as adhesives or additives of adhesives to impart toughening effects to the resin [12]. The PUs, which are miscible with epoxy resins, enhance the toughening properties by causing phase separation owing to the high-temperature curing process. For the purpose of enhancing toughness of epoxy matrix, four different types of polyols were used to prepare PUs with different physical properties. Previously, we studied the toughening effects of the PUs in two pot epoxy compositions composed with cycloaliphatic epoxy resin (celoxide 2021P) and methylhexahydrophthalic acid curing agent [13].

In this study, four different types of polyols were used to prepare PUs with different physical properties. The prepared PUs were added into a binder including bisphenol A epoxy resin, dicyandiamide, and a promoter (fenuron) to study the change in the mechanical properties such as tensile strength, flexural strength, or impact resistance of the cured epoxy resin. The fractured surface of the cured epoxy matrix was observed with scanning electron microscopy (SEM). Furthermore, the adhesion performance of the epoxy compositions with PUs was

measured to determine the relation between the mechanical and adhesion properties resulting from the toughness change of the epoxy compositions.

II. EXPERIMENTAL

1.1. Materials

Polycarbonate diol (PCD) was purchased from Nippon Polyurethane. Polybutadiene diol (PBD) was obtained from Mirae Tech. Polypropylene glycol (PPG), polytetrahydrofuran (PTHF), isophoronediiisocyanate (IPDI), dibutyltindilaurate (DBTD), and 2-allylphenol (2-AP) were purchased from Sigma-Aldrich. Diglycidyl ether of bisphenol A (DGEBA, EPIKOTE 828) was obtained from Momentive. Dicyandiamide (DICY) and 1,1-dimethyl-3-phenyl urea (fenuron) were bought from Air Product Co. All reagents were used further purifications.

1.2. Preparation of polyurethanes

The PUs were synthesized with the method described in the patent [14]. Four different types of polyols (PBD, PPG, PTHF, and PCD) were individually reacted with isophoronediiisocyanates (IPDI) at 80 °C to produce their corresponding elastomeric PUs. The terminal –NCO of the PUs, on both sides of the polymer, was capped with 2-AP to stabilize the final PU. The PU prepared was analyzed with Fourier transform infrared spectroscopy (FT-IR) to confirm that there was no remaining –NCO at 2270 cm⁻¹.

1.3. Preparation of epoxy compositions

The formulation data used is presented in Table 1. Reference epoxy resin comprised bisphenol A epoxy resin and a DICY curing agent. The curing temperature was adjusted by fenuron to make the reaction occur at 170 °C for 2 h. The mixtures were blended in a reactor equipped with a vacuum pump and a mechanical stirrer (Eurostar digital, IKA) at 70 °C and 400 rpm for 50 min.

1.4. Characterizations

Gel permeation chromatography (GPC; 1260 Infinity series, Agilent Technologies) was used to analyze the molecular weight of prepared elastomeric polyurethanes. The peak of –NCO terminal group of the polyurethanes shown at 2270 cm⁻¹ was monitored with fourier infrared (FT-IR) (Nicolet 6700/Nicolet Continuum). Differential scanning calorimeter (DSC, Q2000, TA Instruments) was used to determine the reaction activation energy (E_a) of the epoxy compositions made of different types of PUs. The main aim was to determine whether the different polyols would affect the stability of the cured resins. The experiments were carried out using a dynamic method by running DSC at heating rates of 2, 5, 10, and 20 K/min from 25 °C to 250 °C. The dynamic thermal properties of the cured epoxy resins were characterized with dynamic mechanical analysis (DMA, Q800, TA Instruments). The cured resins were used to make a test specimen of size 60 × 12 × 3 mm. The analysis was conducted with a dual cantilever probe at 1 Hz of frequency and 10 μm of amplitude at a heating rate of 5 °C/min in the temperature range of 30–200 °C. The tensile strength of the cured plastics was determined using a universal testing machine (UTM, model 5982, INSTRON). All testing and conditioning procedures were carried out as ASTM D-638. The flexural strength and modulus were obtained according to ASTM D 790M using a 3-point bending at a crosshead speed of 1.2 mm/min. The impact strength was measured with an Izod impact tester (CEAST 9050, INSTRON) according to ASTM D 256. The fractured test specimen obtained from Izod impact tests were studied using scanning electron microscopy (SNE-3000M, SEC). Also, lap shear strength was determined by pulling out test specimen prepared by bonding two SPRC 440 substrates (101 × 25 × 1.6 mm) with each epoxy composition by overlapping 12.7 mm. The test was performed as ASTM D 1002 method with UTM at a cross-head speed of 1.3 mm/min. The T-peel strength test specimen having T-shape was prepared by applying each epoxy composition between two SPCC substrates (150 × 25 × 0.8 mm). The tests were conducted by UTM according to ASTM D-1876 at a cross-head speed of 254 mm/min. The test specimen for determining the adhesive performance was cured at 170 °C for 30 min after epoxy compositions were applied on the substrates.

III. RESULTS AND DISCUSSION

Elastomeric PUs were prepared by using the four different polyols (Fig. 1), with the same molecular weight of 2,000 g/mol and a similar range of number average molecular weight (M_n) of 7,000–9,000 g/mol (PB; 9,200, PolyTHF; 7,150, PPG; 8,151, PCD; 9,026). PUs are known to form round particles that can be useful for absorbing the impacts in the cured epoxy resin. The changed soft segments in PU are predicted to bring about toughening effects when it is added into epoxy resin compositions followed by curing at high temperatures.

Kinetic studies of the epoxy curing process are important to understand the amine reaction with epoxy functional group [15]. Kissinger's equation (equation 1) that deals with the T_{peak} shift caused by variation in the heating rate helps determine the reaction activation energy [16-18]. The epoxy resin compositions shown in Table 1 were run in DSC with four different heating rates to calculate the activation energy (Table 2).

$$-\ln\left(\frac{\beta}{T_{peak}}\right) = \frac{E_a}{RT_{peak}} - \ln\frac{AR}{E_a} \quad (1)$$

(Where β is the heating rate (K/min), and E_a is the activation energy (kJ/mol)).

Fig.2 shows the shift of T_{peak} caused by changing the heating rates from low temperature to high temperature. Fig.3 displays the plot of $-\ln(\beta/T_{peak}^2)$ vs $(1/T_{peak})$ to obtain activation energy as a slope of the linear line. The calculated activation energies for the compositions are presented in Table 2. The activation energies of epoxy compositions with PU were lower than that of EP, except for the composition comprising PCD-PU. The results indicate that the curing reaction of epoxy resin and amine curing agent requires lower energy when PU is added into the epoxy composition.

The physical properties such as tensile or flexural strength of epoxy compositions with PUs prepared with different polyols were compared by curing each composition at 170 °C for 30 min (Fig. 4 and 5). Fig. 4 shows that the tensile strength of epoxy compositions with PUs was lower than that of epoxy composition without PU (EP). The tensile strength of PBD-EP and PTHF-EP sharply decreased as shown in Fig. 4. This may have resulted from the elastic properties of PU that provides flexibility, resulting in the reduction of the brittleness of the cured epoxy matrix. PUs prepared with polyether polyols such as PPG, PTHF, or PBD decreased the tensile strength of the epoxy matrix because of their better rubber properties than those of PU prepared with PCD.

The effects of PUs in the epoxy matrix were further observed by measuring the flexural strength of the cured epoxy matrices containing PUs. Fig. 5a shows that the flexural strength of all epoxy matrices, except for PCD-EP, was 16–26% lower than that of the reference epoxy composition. Hence, introduction of PU containing polyether polyol affords flexibility to the epoxy matrix. On the other hand, PU having a rigid polyester polyol enhances the flexural strength of the epoxy matrix so that the matrix can endure higher stress. The polyester functional group of PCD-PU restrains the rotation of polyester bonded with –NCO and causes the formation of less flexible geometry that improves the stiffness. Fig. 5b shows the flexural modulus of each epoxy composition. PCD-EP shows a higher modulus than those of other compositions. Hence, it supports the claim that polyester-PU can improve the stiffness of the epoxy matrix, while polyether PUs are capable of increasing the flexibility to reduce the brittleness of the matrix.

Fig. 6 shows the results of Izod impact tests of cured epoxy compositions. The epoxy compositions containing polyether-PU showed three times higher impact strength than those of PCD-EP or EP. The results were considered that the flexibility of the polyether PUs lowers the brittleness of the epoxy matrix to enhance the impact resistance. The fractured surface of the impact test specimen was observed by SEM (Fig. 7). Fig. 7d and 7e show that the phase-separated 1–2 μ m PU particles or holes left by the removal of PU particles from the shock are arranged. The round particles are able to absorb impacts from the outside or distribute the impact to prevent crack formation. However, the phase-separated PU particles are not observed on the surface image of PCD-EP or EP. The absence of PU particles on the images explains the low impact resistance of these matrices. Besides, the fractured image of PBD-EP shows that there are no micro particles of size 1–2 μ m beneficial to absorb impacts in Fig. 7c1. Instead, larger particles (10–50 μ m) with smaller surface area in the limited area are formed as shown in Fig. 7c2. Therefore, the impact resistance of PBD-EP was relatively lower than that of PPG-EP or PTHF-EP.

The viscoelastic properties of the cured epoxy compositions were analyzed with DMA at a heating rate of 5 °C/min from 25 to 200 °C. The storage modulus and $\tan \delta$ are presented in Table 3, and the corresponding graphs are presented in Fig. 8. The initial storage modulus of the epoxy compositions prepared with polyether-PU decreased compared to the value of EP, while the value of PCD-EP was higher than that of EP. The $\tan \delta$ values, considered to be glass transition temperature (T_g) [19], were reduced when PU is added in the epoxy resin compositions. Moreover, PCD-EP showed the lowest T_g among the epoxy compositions considered in this work. The rubber properties of PUs provided flexibility to the epoxy compositions. This coincided with a decrease in the T_g values. Polyether PUs added into epoxy compositions are phase separated in the cured matrix. This allows the epoxy functional groups to react with the amine curing agent to form a polymer structure similar to that of EP. In contrast, polyester-PU is not phase separated, but miscible with epoxy resin in the matrix to interrupt from forming pure epoxy-amine reacted polymers. It explains the steep decrease in the T_g value for PCD-EP. Adhesion performance was evaluated by measuring both the lap shear and the T-peel strength of the different epoxy compositions. Fig. 9a shows the results of the lap shear strength of epoxy compositions applied to the steel substrates. Epoxy compositions with polyether-PU improved the lap shear strength when compared to that of EP. In contrast, polyester PU did not affect the shear strength. As shown in Fig. 9b, polyether PUs play an important role in making the T-peel strength of the resin around three times higher than that of EP. The improvement trends of the T-peel strength of each composition look similar to the result of the Izod impact test. PPG-EP and PTHF-EP had the highest T-peel strength, while the T-peel strength of both PCD-EP and PBD-EP decreased compared to that of EP. The results showed that the toughening effects of PUs in epoxy compositions could be determined based on the T-peel strength or impact strength.

IV. CONCLUSIONS

In conclusion, four Pushaving different soft segments were prepared to improve the mechanical properties and adhesion performance of epoxy compositions. To synthesizethe PUs, the polyols species were changed while diisocyanate and capping agent were fixed. The results showed that the addition of PUs into the epoxy composition reduced the reaction activation energy during the curing process and provided flexibility to the cured epoxy composition, except for the rotation-restrained polyester PU. The low flexural strength of the epoxy compositions with polyether PU were owing to the rubber properties of the PUs. Low flexural strength of the epoxy compositions can help improve their application as adhesives, even though such low flexural strength is not suitable for preparing epoxy composites. In contrast, polyester PU increased the flexural strength of epoxy composition. The results of impact strength tests showed that polyether PUs increased the toughness of the epoxy compositions by forming microparticles, as observed in the SEM images of the fractured surface. The results of lap shear strength and T-peel strength showed that polyether PUs improved the adhesion properties. Specifically, PTHF-EP made the T-peel strength three times as high as that of EP.

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REFERENCES

- [1] J.I. Moon, Y.H. Lee, H.J. Kim, S.M. Noh, J.H. Nam, M.S. Kim, J.K. Kim, J.H. Kim, *J. Adhesion Interf.*, **12**, 99(2011).
- [2] B.L. Zhang, G.L. Tang, K.Y. Shi, Y.C. You, Z.J. Du, J.F. Yang, J. Huang, *Eur. Polym. J.*, **36**, 205(2000).
- [3] R. Thomas, S. Durix, C. Sinturel, T. Omonov, S. Goossens, G. Groeninckx, P. Moldenaers, S. Thomas, *Polymer*, **48**, 1695(2007).
- [4] S.G. Hong, C.K. Chan, *Thermochimica Acta*, **417**, 99(2004).
- [5] T. Ashida, A. Katoh, K. Handa, M. Ochi, *J. Appl. Polym. Sci.*, **74**, 2955(1999).
- [6] S. He, K. Shi, J. Bai, Z. Zhang, L. Li, Z. Du, B. Zhang, *Polymer*, **42**, 9641(2001).
- [7] B.Y. Jeong, J.M. Cheon, J.W. Chun, D.Y. Mok, H.M. Lee, *J. Adhesion Interf.*, **10**, 169(2009).
- [8] K.H. Jin, U.R. Cho, *Elastom. Compos.*, **49**, 31(2014).
- [9] R. Gogoi, M.S. Alam, U.K. Niyogi, *Int. J. Res. Eng. Tech.*, **2**, 393(2013).
- [10] A.A. Beltran, L.A. Boyaca, *Lat. Am. Appl. Res.*, **41**, 75(2011).
- [11] L. Zhang, X. Ding, Y. Ou, *Am. J. Chem. Appl.*, **1**, 7(2014).
- [12] D.Y. Mok, I.S. Kim, D.H. Kim, G.N. Kim, *Elastom. Compos.*, **47**, 318(2012).
- [13] T.H. Kim, D.Y. Kim, S.H. Kang, B.K. Seo, C.S. Lim, Toughening epoxy compositions with polyurethanes tougheners, *Sci. Adv. Mater.*, 2016; Manuscript accepted for publication.
- [14] R. Mulhaupt, J.H. Powell, C.S. Adderley, W. Rufenacht, U. S. Patent 5,278,257 (1994) Jan 11.
- [15] Cascaval CN, Rosu D, Mija AM, Rosu L., Kinetics of the curing reaction of selected epoxy resin-amine systems. *Polimery* 2006; 51: 199–205.
- [16] W.S. Ahn, H.S. Lee, *Elastom. Compos.*, **48**, 161(2013).
- [17] B.K. Min, D.R. Park, W.S. Ahn, *Korean Chem. Eng. Res.*, **47**, 169(2009).
- [18] J.J. Park, *Trans. Electr. Electron. Mater.*, **13**, 204(2012).
- [19] M.G. Abiad, O.H. Campanella, M.T. Carvajal, *Pharmaceutics*, **2**, 78(2010)

TABLE CAPTIONS

Table 1. Formulations of the epoxy compositions

Table 2. Calculated activation energy of each epoxy composition

Table 3. Initial storage modulus and tan δ of each composition

Table 1. Formulations of the epoxy compositions

Composition	Sample no.				
	S1	S2	S3	S4	S5
Polyurethane	-	20 (PCD PU)	20 (PBD PU)	20 (PPG PU)	20 (PTHF PU)
Epoxy resin	100	100	100	100	100
Curing agent	10	10	10	10	10
Accelerator	1.3	1.3	1.3	1.3	1.3

※ Unit = phr (part per hundred resin)

Table 2. Calculated activation energy of each epoxy composition

Sample no.	Heating rate (°C /min)				Activation energy (kJ/mol, E _a)
	2	5	10	20	
S1	148.1	160.7	171.5	183.3	97.0
S2	140.6	151.5	161.5	172.9	101.9
S3	134.6	147.6	158.4	170.6	89.1
S4	133.5	146.4	157.5	170.0	87.4
S5	133.2	147.0	158.6	171.3	83.4

※ Unit = degree Celsius (°C)

Table 3. Initial storage modulus and tan δ of each composition

Sample no.	Initial storage modulus (MPa)	Tan δ(°C)
S1	3257	155.0
S2	3689	105.9
S3	2387	126.2
S4	2560	131.4
S5	2648	132.6

FIGURE CAPTIONS

- Fig. 1. A reaction scheme illustrating the PU synthesis.
- Fig. 2. DSC data of PTHF-EP with different heating rates.
- Fig. 3. Plot of $-\ln(\theta/T_{peak}^2)$ vs $(1/T_{peak})$ for each epoxy composition.
- Fig. 4. Tensile strength for different epoxy-PU formulations.
- Fig. 5. Flexural data of each composition: (a) flexural strength, (b) flexural modulus.
- Fig. 6. Impact strength obtained by Izod impact test for each cured epoxy composition.
- Fig. 7. Fractured surface images observed by SEM (a) S1, (b) S2, (c1) S3-x5000, (c2) S3-x300, (d) S4, (e) S5.
- Fig. 8. DMA data of epoxy compositions: (a) storage modulus, (b) tan δ data.
- Fig. 9. Results of adhesion performance of epoxy compositions: (a) single lap shear strength, (b) T-peel strength.

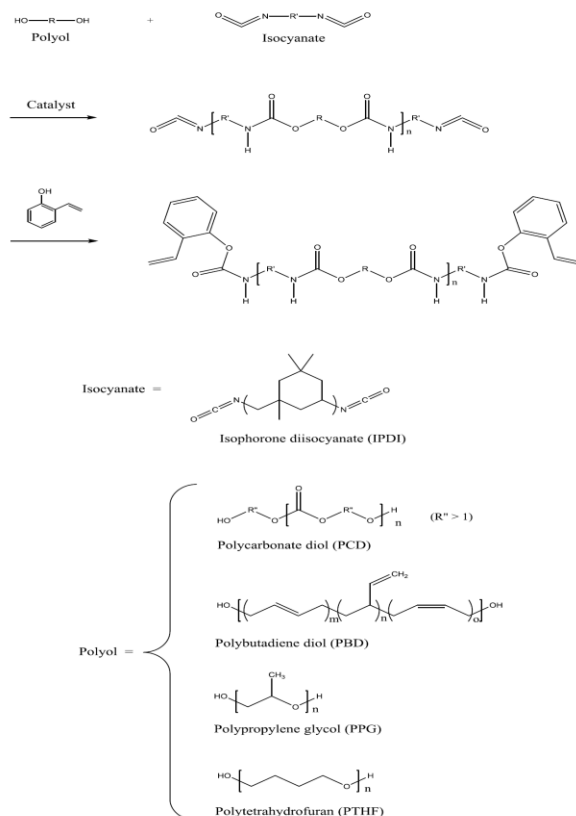


Fig. 1. A reaction scheme illustrating the PU synthesis.

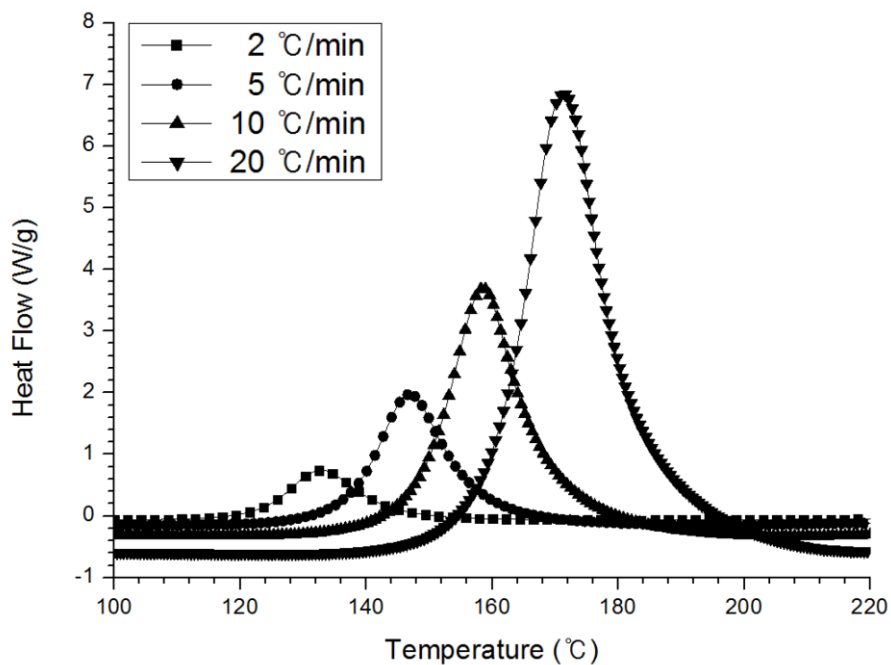


Fig. 2. DSC data of PTHF-EP with different heating rates.

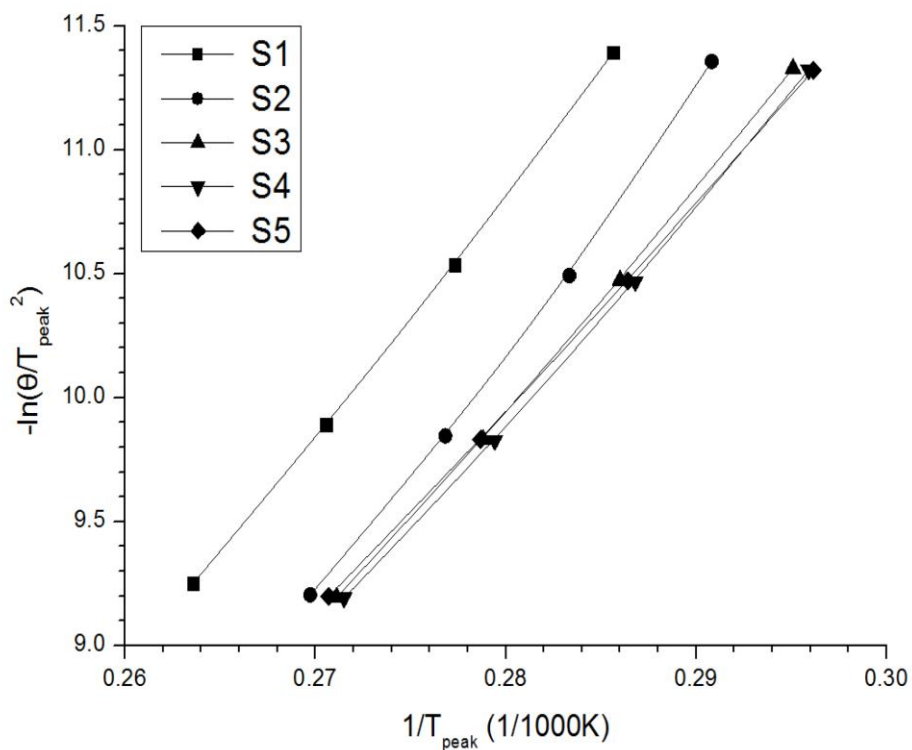


Fig. 3. Plot of $-\ln(\theta/T_{peak}^2)$ vs $(1/T_{peak})$ for each epoxy composition.

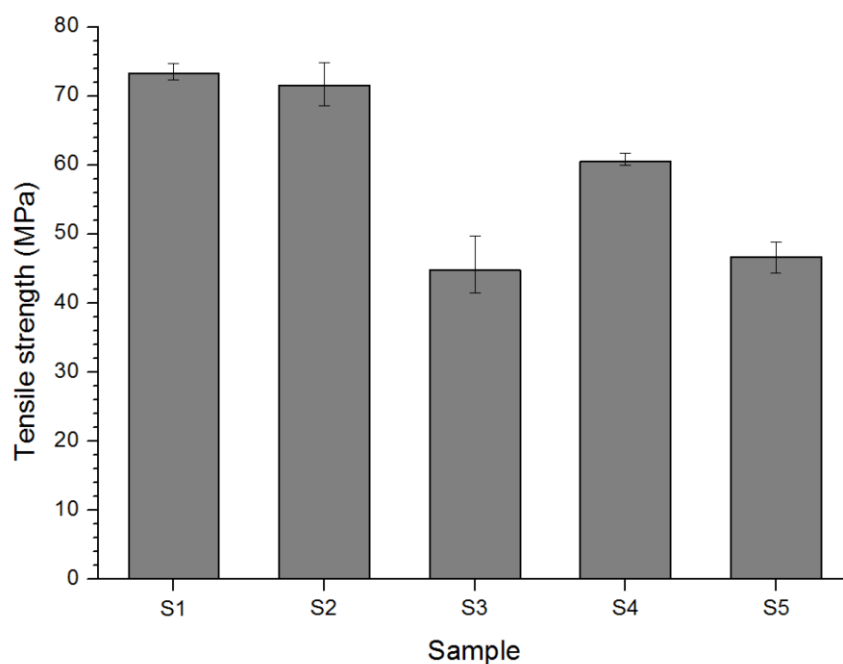


Fig. 4. Tensile strength for different epoxy-PU formulations.

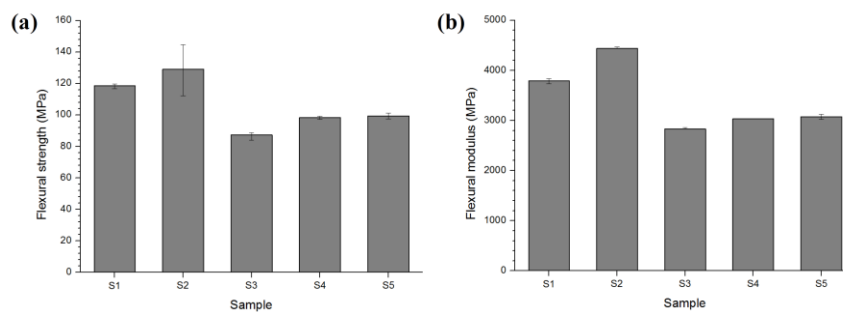


Fig. 5. Flexural data of each composition: (a) flexural strength, (b) flexural modulus.

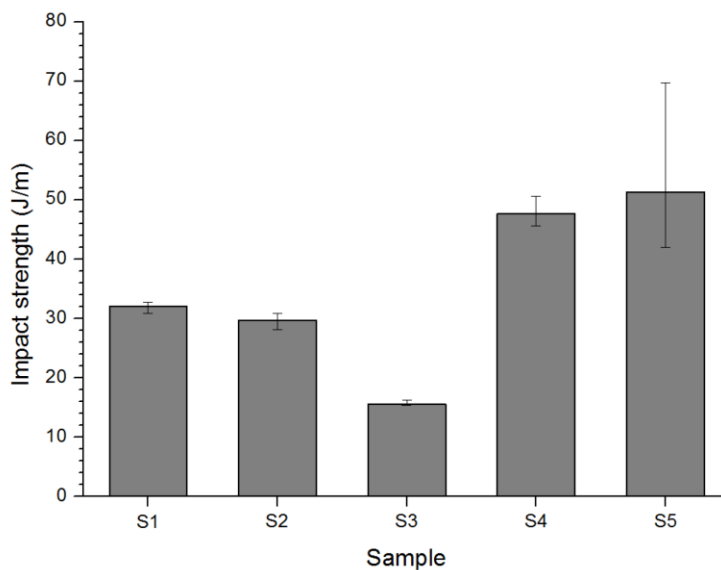


Fig. 6. Impact strength obtained by Izod impact test for each cured epoxy composition.

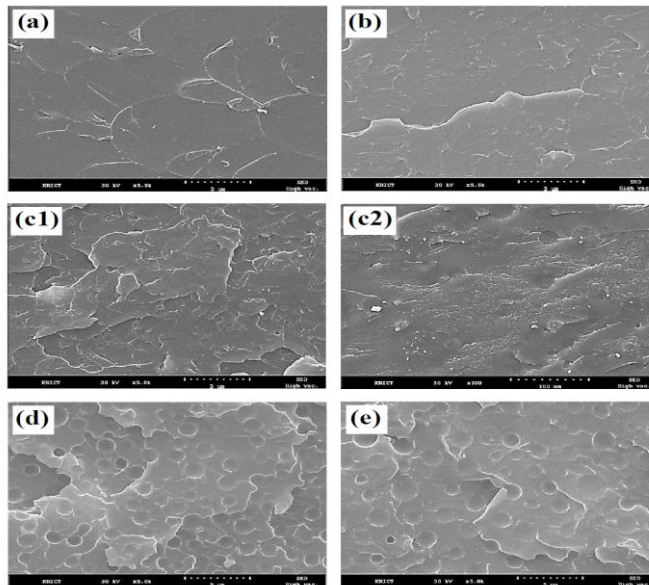


Fig. 7. Fractured surface images observed by SEM (a) S1, (b) S2, (c1) S3-x5000, (c2) S3-x300, (d) S4, (e) S5.

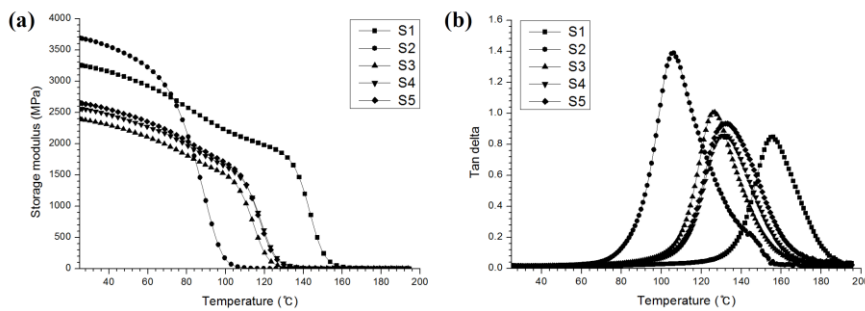


Fig. 8. DMA data of epoxy compositions: (a) storage modulus, (b) tan δ data.

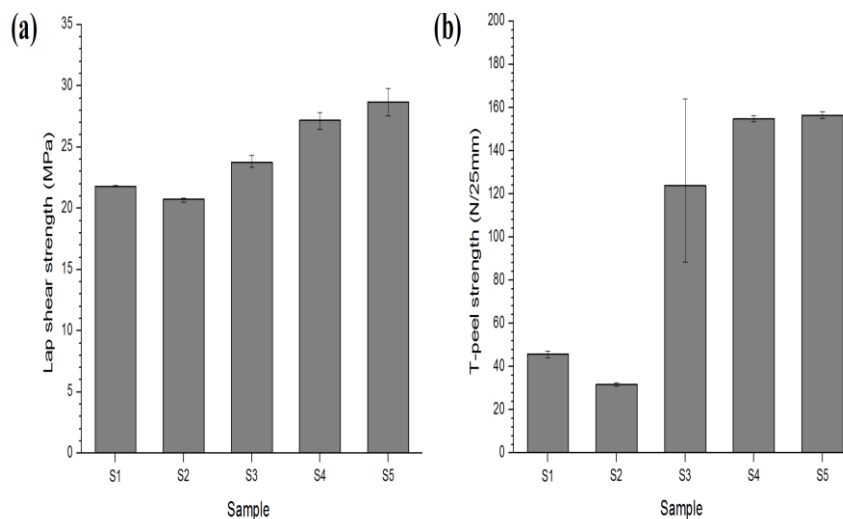


Fig. 9. Results of adhesion performance of epoxy compositions: (a) single lap shear strength, (b) T-peel strength.