# Accepted Manuscript

Development of a supramolecular accelerator simultaneously to increase the cross-linking density and ductility of an epoxy resin

Jiae Seo, Nobuhiko Yui, Ji-Hun Seo

Please cite this article as: J. Seo, N. Yui, J-H. Seo, Development of a supramolecular accelerator simultaneously to increase the cross-linking density and ductility of an epoxy resin, *Chemical Engineering Journal* (2018), doi: https://doi.org/10.1016/j.cej.2018.09.020

Title: Development of a supramolecular accelerator simultaneously to increase the cross-linking density and ductility of an epoxy resin

Corresponding Authors: [1] Prof. Ji-Hun Seo, Email: seojh79@korea.ac.kr
                        Tel: +82-2-3290-3263, Fax: 82-2-928-3584

Corresponding Author's Institutions: [1] Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841

First Author: Jiae Seo[1]

Order of Authors: Jiae Seo, Nobuhiko Yui, Ji-Hun Seo

# Development of a supramolecular accelerator simultaneously to increase the cross-linking density and ductility of an epoxy resin

Jiae Seo[1], Nobuhiko Yui[2], Ji-Hun Seo[1]*

[1] Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

[2] Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Tokyo 101-0062, Japan.

* E-mail: [1] seojh79@korea.ac.kr

**Abstract:**

The development of a novel accelerator capable of simultaneously enhancing the cross-linking density and ductility of an epoxy resin without sacrificing the reaction rate is reported. The basic concept comprises the synthesis of a tertiary amine-functionalized polyrotaxane (PRX_NR1) accelerator: a molecular necklace structure that induces a high cross-linking density as well as active molecular movement. Fourier transform infrared spectroscopy and differential scanning calorimetry measurements confirmed that the PRX_NR1- containing epoxy resin afforded a high reaction rate. Furthermore, the cross-linking density and mechanical properties of the epoxy resin were confirmed by dynamic mechanical analysis and tensile testing. Consequently, the PRX_NR1-containing epoxy resin greatly increased the cross-linking density, thereby resulting in an increase in tensile strength and glass transition temperature. Interestingly, the epoxy resin exhibited a simultaneous increase in ductility which is important to avoid brittle fracture (low toughness) of the epoxy resins. These results indicate that the proposed molecular necklace-like supramolecular PRX_NR1 accelerator is highly effective to overcome the traditional drawbacks of an epoxy resin that pose significant problems in the industrial field.

## 1. Introduction

Epoxy resins are one of the most widely used class of materials in the industrial field because of their cheap and distinct mechanical properties. When properly cured, epoxy resins display excellent mechanical strength, chemical resistance, adhesiveness, heat resistance, and structural stability [1]. Thus, these components show great potential for application as functional organic materials in bonding agents, flame retardants in IT devices, and structural strengthening systems [2-3].

During the epoxy curing process, an accelerator is usually added in suitable proportions to enhance the reaction [4]. In general, an imidazole-based accelerator is widely used to enhance the epoxide conversion rate at high-temperature region [5]. However, an additional accelerator is normally required to enhance the room temperature curing rate. The most widely used room temperature accelerator, 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30), accelerates the initial reaction rate via the catalytic activity of its acidic hydroxyl group and tertiary amine residues [6]. As a nucleophile, the hydroxyl group can initiate the ring opening reaction of the epoxide group, while tertiary amine groups are known to accelerate the reaction by acting as a base to the hydroxyl groups. Because epoxy resins normally display slow initiating reactions, the addition of catalytic molecules such as DMP-30 is inevitable when epoxy resins are employed at room temperature. However, such additions result in bad odor, while the rapidly increasing reaction rates of the curing process decrease the ductility, cross-linking density, and glass transition temperature of the epoxy resin. As a result, many epoxy resins that are cured with small molecular accelerators are brittle and display decreased mechanical strength. This is due to a trade-off between a low cross-linking density and an enhanced reaction rate [7]. Therefore, for the ideal application of epoxy resins, a novel catalytic molecule that can simultaneously increase the ductility and cross-linking density without sacrificing the reaction rate is required. To this end, the use of a polyrotaxane (PRX)-based catalytic molecule is proposed in this study.

4

PRX is a necklace-like supermolecule composed of a ring shaped host molecule, e.g. α-cyclodextrin (α-CD), threaded onto a linear guest molecule, e.g. poly(ethylene glycol) (PEG) [8-11]. Because PRX is a movable supermolecule, PRX has been widely studied to provide flexible nature to the cross-linked materials [12-14]. However, its potential utility for enhancing cross-linking density and the catalytic activity for the synthetic resin was yet to be studied. Because a single α-CD molecule contains 18 epoxide accessible hydroxyl groups, one PRX molecule is theoretically able to create 900 cross-linking points when 50 α-CDs are threaded onto a PEG chain. Therefore, a significant increase in the cross-linking density of the PRX-containing epoxy resin is anticipated. Moreover, cross-linked α-CDs are expected to display molecular mobility so that they can rotate and slide along the linear PEG chain axis [15-20]. Therefore, we hypothesized that this entire structural singularity can be effective to simultaneously increase the mechanical strength (cross-linking density) and ductility of the epoxy resin. By introducing the catalytic activity, i.e. basic tertiary amine residues, to the PRX framework, we propose the novel concept of an accelerator that can satisfy the required mechanical properties while maintaining a high reaction rate. To confirm this hypothesis, we synthesized a partially tertiary amine-functionalized polyrotaxane (PRX_NR). This species, comprising both a tertiary amine and an epoxy-accessible hydroxyl group, provided catalytic activity as an accelerator. Thus, the accelerating performance and changes in the mechanical properties of the epoxy resin were thoroughly investigated.

## 2. Material and methods

### 2-1. Materials

PEG (10,000) and dehydrated chloroform were purchased from Sigma Aldrich (St. Louis, MO, USA). N,N'-Carbonyldiimidazole (CDI), ethylenediamine, α–CD, 4-(4,6-dimethoxy-1,3,5-tiazin-

2-yl)-4-methylmorpholinium chloride (DMT-MM), and car-bobenzoxy L-tyrosine were purchased from Chemical Industrial Co. Ltd. (Tokyo, Japan). Resorcinol diglycidyl ether (resorcinol epoxy) (90 %), epoxy phenol novolac resin (YDPN631 epoxy) (99.99 %) (Table S1.), bis(para-aminocyclohexyl)methane (hardener), 2-ethyl-4-methylimidazole (imidazole), and DMP-30 were received from KCC Central Research Institute (Gyeonggi-Do, Korea). All organic solvents (HPLC grade) were purchased from Samchun Pure Chemical Co. Ltd. (Gyeonggi-Do, Korea).

### 2.2. Synthesis of PEG-bis(amine)

PEG (0.03 M, Mw 10,000) was stirred in dehydrated chloroform until it was completely dissolved. Subsequently, 0.12 M CDI was added and stirred vigorously for 12 h. Next, 0.36 M ethylenediamine was added and the solution was stirred for a further 24 h. The solution was then dropped into diethyl ether to produce PEG-bis(amine) powder. Finally, the afforded polymer was recrystallized from a small amount of dichloromethane to completely remove the residual reactants.

### 2.3. Synthesis of polyrotaxane and tertiary amine-introduced polyrotaxane

First, 5 g α-CD was dissolved in 35 mL distilled water and 1 g PEG-bis(amine) was then added and allowed to mix for 1 d. The afforded white paste was freeze-dried and dispersed in 40 mL ethanol. Next, DMT-MM and car-bobenzoxy L-tyrosine (1 g each) were added and the mix-ture was stirred for 24 h. The resultant solution was placed in a dialysis bag (MWCO 12k), dialyzed with DMSO, methanol, and distilled water for 3 d, and subse-quently freeze dried to afford the polyrotaxane powder. The tertiary amine was introduced into PRX as follows: 100 mg PRX was dissolved in 2 mL DMSO and 1 mmol CDI. Next, 0.5 mmol N,N-dimethyl ethylenediamine was

added to the solution. After stirring for 24 h, the mixture was dialyzed in DMSO and D.I. water

for 2 d. Finally, the tertiary amine induced-PRX powder was collected by freeze-drying.

*2.4. Preparation of the epoxy resin*

The epoxy, hardener, and additives in the epoxy resin mixtures were mixed homogeneously

according to the ratios listed in Table 1. The different accelerators were then dissolved in a

minimum amount of DMSO and mixed with the epoxy resin. The uniformly mixed epoxy resin

was cured at 25 °C for 24 h in an oven and post cured at 80 °C for 16 h. Once the curing process

was begun, PRX derivatives were homogeneously dissolved in the resin by forming the networked

resin plastics. The cured red epoxy resin was afforded after this series of processes.

*2.5. Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC)*

   *analysis*

FT-IR spectrometry (Spectrum 100, PerkinElmer Inc., Massachusetts, USA) and DSC (DSC-Q20,

TA Instruments, New Castle, USA) in $N_2$ atmosphere measurements were recorded every 4 h to

determine the conversion of epoxide during the 40 h curing process (25 °C for 24 h + 80 °C for 16

h). For example, when recording FT-IR and DSC data of a sample after 26 h of curing, the sample

was cured at 25 °C for 24 h and at 80 °C for 2 h. Next, the reaction was stopped with liquid nitrogen

and the FT-IR and DSC data were recorded. Threefold FT-IR measurements were recorded

(attenuated total reflectance, ATR) per sample for accuracy. For DSC analysis, the sample was

heated at a rate of 10 °C/min and fully scanned to determine the exothermic peaks. Threefold

measurements were recorded for each sample and statistical processing was performed using the

t-test.

*2.6. Dynamic mechanical analysis (DMA)*

The epoxy resin mixtures were placed in a mold and cured at 25 °C for 24 h and subsequently, at 80 °C for 16 h. The fully cured specimens were then subjected to DMA treatment (Seiko Exstar 6000, SEICO INST., Japan), under bending mode, at a frequency of 1 Hz and an elevating temperature of 5 °C/min. The sample size was determined according to ASTM D4065. Threefold measurements were recorded for each sample and statistical processing was performed using the t-test.

## 2.7. Measurement of water contact angle

The water contact angles were measured to examine the hydrophilicity of cured epoxy resin. The contact angles were measured using a goniometer (Phoenix 150, Surface Electro Optics CO. Suwon, Korea). Three positions on each surface were analyzed. Threefold measurements were recorded for all samples and statistical processing was performed using the t-test.

## 2.8. Micro tensile test

The sample for microtensile testing was synthesized using the same procedure described above, except for the sample size (ASTM D1708-13638). The cured specimen was then subjected to tensile testing (E3000LT, Instron corp., UK) at a speed of 0.12 mm/min. Threefold measurements were recorded for all samples and statistical processing was performed using the t-test.

## 2.9. Izod impact test

The sample for impact test was synthesized using the same procedure described above, except for the sample size (ASTM D 256). The cured specimen was then subjected to izod impact tester (T0-700DC, Test one, Korea) at a speed of 3.46 m/sec. Threefold measurements were recorded for all samples and statistical processing was performed using the t-test.

## 3. Results and discussion

In this study, the supramolecular accelerators PRX_NR1 and PRX_NR4, comprising both tertiary amines and hydroxyl groups, were synthesized to provide basic catalytic tertiary amine residue and large amount of epoxy-accessible hydroxyl groups to enhance reaction rate and cross-linking density (Fig. 1). The success of the synthetic procedure was confirmed by $^1$H nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC; Table 2, Fig. S1). Data in Table 2 confirms that the number average molecular weight of the PRX derivatives ($M_n$) estimated by GPC falls within the range of 44000–68000. The number of α-CD molecules threaded on the PEG chain was calculated ($^1$H-NMR) as ~42, suggesting a theoretical molecular weight of the PRX derivatives of ~50000. This value is well in agreement with the range of the relative molecular weights determined by GPC [9].

In this work, we assumed that the synthesized tertiary amine-containing PRX additives would accelerate the initial epoxide ring opening process arising from nucleophilic activity of the hydroxyl group and the catalytic activity of the tertiary amine residues (Fig. 1). Moreover, the highly dense hydroxyl groups threaded on the PEG chain are expected to form a significant amount of mobile cross-linking points [21]. As a result, the cross-linking density and ductility of the epoxy resin is expected to simultaneously increase (Fig. 2). In this work, we examined how the substitution of DMP-30, small molecular accelerator, with tertiary amine-functionalized PRX, a supramolecular accelerator, influenced the reaction rate of the epoxide and the mechanical properties of the cured resins.

To confirm this hypothesis, we first employed FT-IR spectroscopy to the effect of the curing time on the rate of epoxide ring-opening (Fig. S2) [22]. FT-IR data was collected every 4 h during both

the room temperature (R.T.) precuring process (25 °C for 24 h) and the subsequent post (complete) curing process (80 °C for 16 h). Fig. S2 reveals that the absorption peak gradually became broader in the range of 3500–3000 cm$^{-1}$ as the epoxide opened further along the curing time. To calculate the reaction rate of the epoxide, the area of the 914 cm$^{-1}$ peak arising from C–O stretching of the epoxide ring was compared to the area of the invariant 1450 cm$^{-1}$ peak arising from C–C stretch of the benzene ring in the epoxy resin [23-24]. The real-time epoxy conversion was calculated from Equation 1:

$$\text{Conversion (\%)} = \frac{\frac{A_{914,0}}{A_{1450,0}} - \frac{A_{914,t}}{A_{1450,t}}}{\frac{A_{914,0}}{A_{1450,0}}} \times 100 \tag{1}$$

where $A_{x,t}$ is the area in 'x' cm$^{-1}$ at curing time 't'. Fig. S3 illustrates that during the precuring process (25 °C), the percentage conversion for each specimen was significantly different. Conversely, no difference was observed among the specimens in the post curing (80 °C) process. Fig. 3, which extracts the main points in Fig. S3, reveals that after 4 h at 25 ℃, DMP-30, PRX_NR1, and

PRX_NR4 exhibited a fast epoxide ring opening initiation rate, with DMP-30 and PRX_NR1 maintaining the highest reaction rates until the precuring process was completed (8 h to 24 h). From the viewpoint of the ring-opening reactivity of the epoxide, the PRX_NR1 and DMP-30 species exhibited the best acceleration performance both at the initiation stage and during the overall R.T. precuring process. In the case of the epoxy resin without DMP-30 or PRX-based accelerator (Neat) and the PRX-added sample, no accelerating effect was observed during the initiation step (4 h). Because the tertiary amine residues in the accelerator contribute towards the increase in the nucleophilic activity of the hydroxyl groups, samples without tertiary amine residues are thought to exhibit very limited initiation reaction rates. This was the main reason for selecting an accelerator containing tertiary amine residues. Interestingly, PRX_NR4, with the

highest substitution rate with tertiary amines, displayed the highest initiation reaction rate ($\leq$4 h) but the lowest persistence in reaction rate throughout the 24 h precuring process. As shown in Tables 1 and 2, primary hydroxyl group in PRX-NR1 and PRX_NR4 were partially functionalized with tertiary amine group. As shown in Table 2, there was a little difference (96.3% vs. 85.6%) in the residual hydroxyl group in PRX-NR1 and PRX_NR4, but the ratio of the primary hydroxyl group to the secondary one was significantly different (41.7% vs. 16.7% ). In general, primary hydroxyl groups are much more reactive than secondary ones when participating in the ring opening reaction of the epoxy. As a result, PRX_NR4, which has a large number of catalytic tertiary amines but has a small number of primary hydroxyl groups, exhibits the highest initiation reaction rate until 4 hours due to the large number of catalytic tertiary amines. However, during subsequent room temperature curing process (4-24 h), it shows a lower epoxide-conversion rate, which may be attributed to the small number of primary hydroxyl groups. In any case, the proper ratios of the tertiary amine and primary hydroxyl groups on the PRX backbone significantly affect the persistence of the epoxide reactivity throughout the precuring process.

To characterize the reactivity of the epoxide more precisely, DSC analysis was additionally conducted [24]. The total heat value could be calculated from the integrated value of the heat flow of each sample (Fig. 4). Additionally, epoxide conversion ($\alpha$ index) could be evaluated from Equation 2:

$$\alpha(t) = \frac{H_T - H(t)}{H_T} \tag{2}$$

where $H_T$ is the total heat and $H(t)$ is the remaining enthalpy at a specific time 't' [25]. The $\alpha$ index was calculated for each sample and the afforded values were compared. Fig. 4 illustrates that the total heat values of the samples were similar when the epoxy resins were completely cured. This

indicates that the contents of the total reactive epoxide group in the different samples were near identical. Interestingly, PRX shows almost similar value of initial ($T_i$) and peak ($T_p$) temperature with DMP-30 samples in 10 °C/min elevated temperature condition. The acidic phenol group in DMP-30 is known to accelerate the epoxide ring-opening reaction, which is well-expected to result in a decrease in $T_i$ and $T_p$ of DMP-30. In the case of PRX sample, the catalytic multivalent reactivity of the dense hydroxyl group is thought of as a cause of the decreased $T_i$ and $T_p$ [26]. Because catalytic activity of the imidazole is maximized at higher temperature region, PRX derivatives containing largest number of the primary hydroxyl group is thought to reveal low $T_i$ and $T_p$ values. Based on the total amounts of the reactive epoxide groups, real time monitoring for the ratio of the reacted epoxide was conducted along a curing time of 24 h at 25 °C followed by a post curing process (80 °C for 16 h; Fig. S4). Fig. 5, which extracts the main points in Fig. S4, reveals that the DMP-30, PRX_NR1, and PRX_NR4 samples displayed fast initiation reaction rates after 4 h. However, only DMP-30 and PRX_NR1 maintained high reactivity throughout the precuring process. These tendencies are well in agreement with the results afforded from FT-IR analysis [24]. To compare the reliability of these values, the conversion values of the epoxide evaluated by both FT-IR and DSC analysis are displayed in a single graph (Fig. 6). The epoxide conversions calculated from the different methods exhibited a strong correlation with R2 values >0.95. The calculated epoxide conversion based on the different experimental methods (FT-IR and DSC) were highly reliable. Fig. 6 confirms that PRX_NR1 can be an alternative additive with a similar level of accelerating performance as DMP-30.

As previously explained, there is a trade-off problem between the reaction rate and the cross-linking density and brittleness of the cured epoxy resins. The most significant problem posed by the use of a small molecular accelerator such as DMP-30 is the decreased cross-linking density,

which is the main cause of the decreased mechanical strength and glass transition temperature. Therefore, the determination of the degree of internal cross-linking density is important to discuss the effect of the accelerator on the mechanical properties of the epoxy resin. To this end, DMA was carried out to evaluate the cross-linking density of the epoxy resins after completion of the curing process. DMA is a method that observes the viscoelastic behavior of a sample by analyzing the waveform that returns to the solid sample after a vibration of a specific wavelength is applied. Mechanical properties, expressed as a function of time, temperature, and vibration, can be measured using DMA [27-28]. Based on these values, glass transition temperatures ($T_g$), tan δ values, and the cross-linking density of the material can be calculated from Equation 3:

$$\rho = \frac{E'_r}{3RT} \tag{3}$$

where $\rho$ is the cross-linking density (mol/cm$^3$), R is 8.314 (cm$^3$·MPa/mol·K), T is $T_g$ +50 in the rubbery state (K), and E'$_r$ is the storage modulus in the rubbery state (MPa). DMA analysis was conducted for each sample and the cross-linking density was calculated as described above. Fig. 7 (a) indicates that the storage modulus of the 'Neat' and 'DMP-30' samples were significantly decreased at temperatures $>T_g$. This indicates that at elevated temperatures, intermolecular slip easily takes place in these samples. Conversely, PRX and PRX_NR1 samples exhibited a negligible decrease in storage modulus with temperature changes. This indicated that intermolecular slip is negligible. Fig. 7 (b) illustrates the cross-linking density of each sample calculated from Equation 3. Compared to the Neat and DMP-30 samples, the PRX and PRX_NR1 samples display increasing cross-linking density. Interestingly, the cross-linking density of the PRX_NR1 sample is 11.62 x 10$^{-3}$ mol/cm$^3$, which is 79.5% higher than that of the Neat sample and 159% higher than that of DMP-30. In previous results, the epoxide conversion rate for the PRX_NR1 sample was near identical to that of the DMP-30 sample. This marked difference in

cross-linking density is quite abnormal because accelerated epoxy curing processes commonly induce low cross-linking density due to the increased rigidity. In this work, the increased cross-linking density of the PRX_NR1 sample was attributed to the structural singularity of the PRX structure. The large amounts of epoxide accessible hydroxyl groups present on the PRX chain afford highly dense cross-linking points that propagate the epoxide ring opening reaction by sliding through the PEG axis. Consequently, the final PRX_NR1 cured epoxy resin forms dense long-range networks. The $T_g$ values of each sample are listed in Fig. 7 (c). These results indicate that the overall $T_g$ trend is similar to that of the cross-linking density. According to literature [29-30], the glass transition temperature increases with an increasing degree of cross-linking. This is due to the formation of macromolecular networks. Because the $T_g$ value normally increases with the formation of long-range-networked cross-linking, this result can be explained in terms of the increased cross-linking density. These results verified that PRX_NR1 maintains the good accelerating performance of the epoxide groups without sacrificing the high cross-linking density and glass transition temperature.

The changes in surface property (wettability) along to the cross-linking density was also confirmed by the contact angle measurement. However, no significant differences among the samples were observed (Fig. S5.). This indicated that one of the important property, i.e. surface wettability, of the epoxy resin was not significantly changed due to the addition of the supramolecular accelerators.

 Finally, the mechanical properties of the cured epoxy resins were estimated by tensile testing (Fig. 8). The Neat exhibited a tensile strength of about 43.5 MPa, which is a general strength of conventional resorcinol epoxy [31-32]. The tensile strength, Young's modulus and maximum strain at the breaking point of the PRX_NR1 and PRX molecules are noticeably higher than those

of the Neat and DMP-30 samples (Fig. 8b,c). The tensile strength of the PRX_NR1 sample increased by 151.9% and 82.2% compared to those of the respective Neat and DMP-30 samples. Moreover, Young's modulus that represented material's stiffness also increased by 30.3% and 48.7% compared to those of the respective Neat and DMP-30 samples. Interestingly, the maximum strain at the breaking point likewise increased by 128.2% and 59.2% compared to those of the respective Neat and DMP-30 samples. In general, densely cross-linked polymer materials display low ductility and are therefore brittle. However, the PRX_NR1 cured epoxy resin was quite unique and exhibited an increase in cross-linking density with high ductility. This was attributed to the cross-linked αCD molecules that are expected to maintain their molecular mobility along the PEG chain [12-14]. In Fig. 8 d, there are cross-sectional SEM images of the fractured specimens by a tensile test. The PRX_NR1 was very definitely different compared to other samples. According to fractographic analysis, usually the fracture surface of ductile materials represents a modified form, such as PRX_NR1 [33-35]. Therefore, this result could reveal clearly about ductility of the PRX_NR1 sample. The cross-linking density was plotted against the tensile strength (maximum strain at the breaking point) and toughness (Fig. 9). As a result, the tensile strength of the samples tended to increase with an increase in cross-linking density (Fig. 9a). This is a well-known phenomenon for traditional cross-linked polymer materials [36-37]. However, the maximum tensile strain at the breaking point and the subsequent toughness also increased in the PRX and PRX_NR1 samples which cross-linking density is maximized (Fig. 9 b,c). Because an increased cross-linking density is associated with an increase in the brittleness of the cured epoxy resin, the addition of PRX_NR1 suggests an outstanding guide line to avoid the brittleness in an epoxy resin cured in an accelerated manner. The decreased brittle nature of the cured epoxy resin was also confirmed by izod impact test, which afforded similar results (Fig. 10 a). The izod impact tests have been widely used in the study of material toughness. This high izod impact energy can be

interpreted as a result of being able to withstand high plastic deformation in the material. In Fig. 10 b, it was confirmed that the tendency of the toughness of the tensile test and the impact test were almost the same and PRX_NR1 was superior. The possible mechanism of these results has already been explained based on the molecular mobility of the densely cross-linked αCD molecules, a unique property of PRX derivatives. By mimicking the catalytic activity of DMP-30, we confirmed that the PRX_NR1 sample has the ability to stably accelerate the epoxide reaction without sacrificing the cross-linking density and ductility of the resin. This results in a product with enhanced mechanical properties.

## 4. Conclusions

In this study, we successfully introduced the concept of a molecular necklace structured accelerator that can be effectively used in the epoxy curing reaction. In general, the trade-off between a decrease in cross-linking density and a brittle and thermal denatured epoxy resin has been inevitable as a result of accelerating the reaction rate of the epoxy resin. By mimicking the structural singularity of a traditional accelerator, we optimized the molecular structure of the PRX accelerator. The resultant accelerator was capable of simultaneously increasing the cross-linking density and ductility of the resin without sacrificing the accelerating performance of the reaction. We believe that this work contributes towards the formation of the desired epoxy resin as well the development of novel additives that can overcome the traditional drawbacks of cross-linked materials.

**Acknowledgements**

**References**

[1] C. May, Epoxy resins: chemistry and technology, First edition, CRC press, (1987).

[2] Y. L. Liu, C. S. Wu, K. Y. Hsu, T. C. Chang, Flame retardant Epoxy Resins from O- Cresol Novolac Epoxy Cured with a Phosphorus- containing Aralkyl Novolac, J. Polym. Sci. Pol. Chem. 40 (2002) 2329-2339.

[3] C. Czaderski, E. Martinelli, J. Michels, M. Motavalli, Effect of Curing Conditions on Strength Development in an Epoxy Resin for Structural Strengthening, Compos. Pt. B-Eng. 43 (2012) 398-410.

[4] S. Monterrat, C. Flaque, M. Calafell, G. Andreu, J. Malek, Influence of the Accelerator Concentration on the Curing Reaction of an Epoxy-anhydride System, Thermochim. Acta 269 (1995) 213-229.

[5] C. H. Zhao, S. J. Wan, L. Wang, X. D. Liu, T. Endo, Carbonyldiimidazole- accelerated efficient Cure of Epoxidized Soybean Oil with Dicyandiamide. J. Polym. Sci. Pol. Chem. 52 (2014) 375-382.

[6] Yang, T., Zhang, C., Zhang, J., & Cheng, J. (2014). The influence of tertiary amine accelerators on the curing behaviors of epoxy/anhydride systems. Thermochimica Acta, 577, 11-16.

[7] B. L. Burton, Acceleration of Amine-Cured Epoxy Resin Systems, Huntsman Corp. (2013).

[8] G. Wenz, B. H. Han, A. Müller, Cyclodextrins as Building Blocks for Supramolecular Structures and Functional Units, Angew. Chem. Int. Ed. 33 (1994) 803-822.

[9] A. Harada, J. Li, M. Kamachi, Preparation and Characterization of a Polyrotaxane Consisting of Monodisperse Poly (ethylene glycol) and. Alpha.-Cyclodextrins, J. Am. Chem. Soc. 116 (1994) 3192-3196.

[10] G. Wenz, B. Keller, Threading Cyclodextrin Rings on Polymer Chains, Angew. Chem. Int. Ed. 31 (1992) 197-199.

[11] A. Harada, A. Hashidzume, H. Yamaguchi, Y. Takashima, Polyrotaxanes, Encyclopedia of Polymer Science and Technology, 1998.

[12] K. Ito, Novel Cross-Linking Concept of Polymer Network: Synthesis, Structure, and Properties of Slide Ring Gels with Freely Movable Junctions, Polym. J. 39 (2007) 489.

[13] C. Katsuno, A. Konda, K. Urayama, T. Takigawa, M. Kidowaki, K. Ito, Pressure- Responsive Polymer Membranes of Slide- Ring Gels with Movable Cross- Links, Adv. Mater. 25 (2013) 4636-4640.

[14] Y. Okumura, K. Ito, The Polyrotaxane Gel: A Topological Gel by Figure- Of- Eight Cross-links, Adv. Mater. 13 (2001) 485-487.

[15] N. Yui, T. Ooya, Molecular Mobility of Interlocked Structures Exploiting New Functions of Advanced Biomaterials, Chem. Eur. J. 12 (2006) 6730-6737.

[16] T. Ooya, M. Eguchi, N. Yui, Supramolecular Design for Multivalent Interaction: Maltose Mobility along Polyrotaxane Enhanced Binding with Concanavalin A, J. Am. Chem. Soc. 125 (2003) 13016-13017.

[17] C. A. Schalley, K. Beizai, F. Vögtle, On the Way to Rotaxane-based Molecular Motors: Studies in Molecular Mobility and Topological Chirality, Accounts Chem. Res. 34 (2001) 465-476.

[18] J. H. Seo, S. Kakinoki, Y. Inoue, T. Yamaoka, K. Ishihara, N. Yui, Inducing Rapid Cellular Response on RGD-binding Threaded Macromolecular Surfaces. J. Am. Chem. Soc. 135 (2013) 5513-5516.

[19] J. H. Seo, S. Kakinoki, T. Yamaoka, N. Yui, Directing Stem Cell Differentiation by Changing the Molecular Mobility of Supramolecular Surfaces, Adv. Healthc. Mater. 4 (2015) 215-222.

[20] J. H. Seo, N. Yui, The effect of molecular mobility of supramolecular polymer surfaces on fibroblast adhesion. Biomaterials 34 (2013) 55-63.

[21] T. Ooya, H. Utsunomiya, M. Eguchi, N. Yui, Rapid Binding of Concanavalin A and Maltose−Polyrotaxane Conjugates Due to Mobile Motion of α-Cyclodextrins Threaded onto a Poly (ethylene glycol). Bioconjugate Chem. 16 (2005) 62-69.

[22] M. G. González, J. C. Cabanelas, J. Baselga, Applications of FTIR on Epoxy Resins-identification, Monitoring the Curing Process, Phase Separation and Water Uptake. In Infrared Spectroscopy-Materials Science, Engineering and Technology. InTech, (2012).

[23] P. Musto, E. Martuscelli, G. Ragosta, P. Russo, P. Villano, Tetrafunctional Epoxy Resins: Modeling the Curing Kinetics Based on FTIR Spectroscopy Data. J. Appl. Polym. Sci. 74 (1999) 532-540.

[24] S. D. Pandita, L. Wang, R. S. Mahendran, V. R. Machavaram, M. S. Irfan, D. Harris, G. F. Fernando, Simultaneous DSC-FTIR Spectroscopy: Comparison of Cross-linking Kinetics of an Epoxy/Amine Resin System, Thermochim. Acta 543 (2012) 9-17.

[25] N. Sbirrazzuoli, S. Vyazovkin, Learning about Epoxy Cure Mechanisms from Isoconver-sional Analysis of DSC Data, Thermochim. Acta 388 (2002) 289-298.

[26] H. H. Dam, F. Caruso, Formation and Degradation of Layer-by-layer-assembled Polyelectrolyte Polyrotaxane Capsules, Langmuir 29 (2013) 7203-7208.

[27] K. P. Menard, Dynamic Mechanical Analysis: a Practical Introduction, CRC press, (2008).

[28] W. K. Goertzen, Thermosetting Polymer-matrix Composites for Structural Repair Applications, Iowa State University, 2007.

[29] J. S. Chen, C. K. Ober, M. D. Poliks, Y. Zhang, U. Wiesner, C. Cohen, Controlled Degradation of Epoxy Networks: Analysis of Crosslink Density and Glass Transition Temperature Changes in Thermally Reworkable Thermosets, Polymer 45 (2004) 1939-1950.

[30] Y. Sun, Z. Zhang, K. S. Moon, C. P. Wong, Glass Transition and Relaxation Behavior of Epoxy Nanocomposites, J. Polym. Sci. Pt. B-Polym. Phys. 42 (2004) 3849-3858.

[31] H. Ren, J. Sun, B. Wu, Q. Zhou, Synthesis and Properties of a Phosphorus-containing Flame Retardant Epoxy Resin based on Bis-phenoxy (3-hydroxy) phenyl phosphine oxide, Polym. Degrad. Stabil. 92 (2007) 956-961.

[32] M. Tsukada, M. Nagura, H. Ishikawa, H. Shiozaki, Structural Characteristics of Silk Fibers treated with Epoxides, J. Appl. Polym. Sci. 43 (1991) 643-649.

[33] S. C. Kim, H. R. Brown, Impact-modified Epoxy Resin with Glassy Second Component, J. Mater. Sci. 22 (1987) 2589-2594.

[34] R. B. Grubbs, J. M. Dean, M. E. Broz, F. S. Bates, Reactive Block Copolymers for Modification of Thermosetting Epoxy, Macromolecules 33 (2000) 9522-9534.
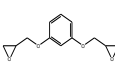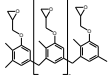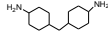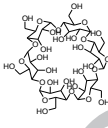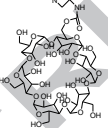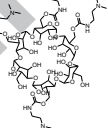
[35] A. Arnebold, A. Hartwig, Fast Switchable, Epoxy based Shape Memory Polymers with High Strength and Toughness, Polymer 83 (2016) 40-49.
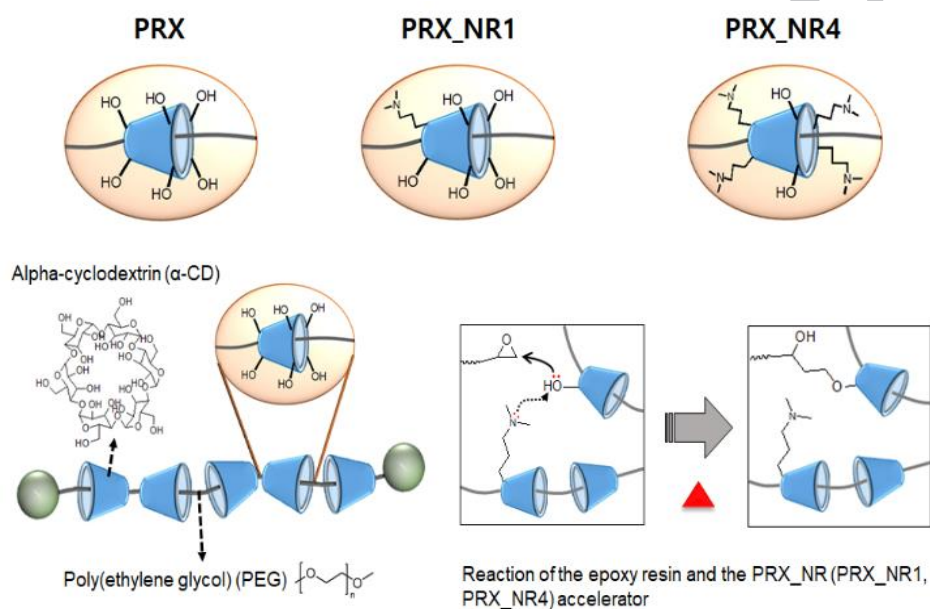
[36] J. P. Yang, Z. K. Chen, G. Yang, S. Y. Fu, L. Ye, Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer, Polymer 49 (2008) 3168-3175.

[37] R. Thomas, D. Yumei, H. Yuelong, Y. Le, P. Moldenaers, Y. Weimin, T. Czigany, S. Thomas, Miscibility, Morphology, Thermal, and Mechanical Properties of a DGEBA Based Epoxy Resin Toughened with a Liquid Rubber, Polymer 49 (2008) 278-294.

**Table 1.** Chemical composition of the epoxy resin and four different accelerators.

| Chemical name | Epoxy resin | | Hardener | Imid-azole | Different type of accelerator (One of these is selected) | | | |
|---|---|---|---|---|---|---|---|---|
| | Resorcinol epoxy | YDPN631 epoxy | | | DMP-30 | PRX | PRX_NR1 | PRX_NR4 |
| Chemical Structure |  |  |  |  |  |  |  |  |
| Ratio | 63.56 | 19.59 | 11.85 | 3.4 | 1.6 | | | |



**Fig. 1.** Schematic explanation of PRX-derivatives and the reaction mechanism with epoxy resin.
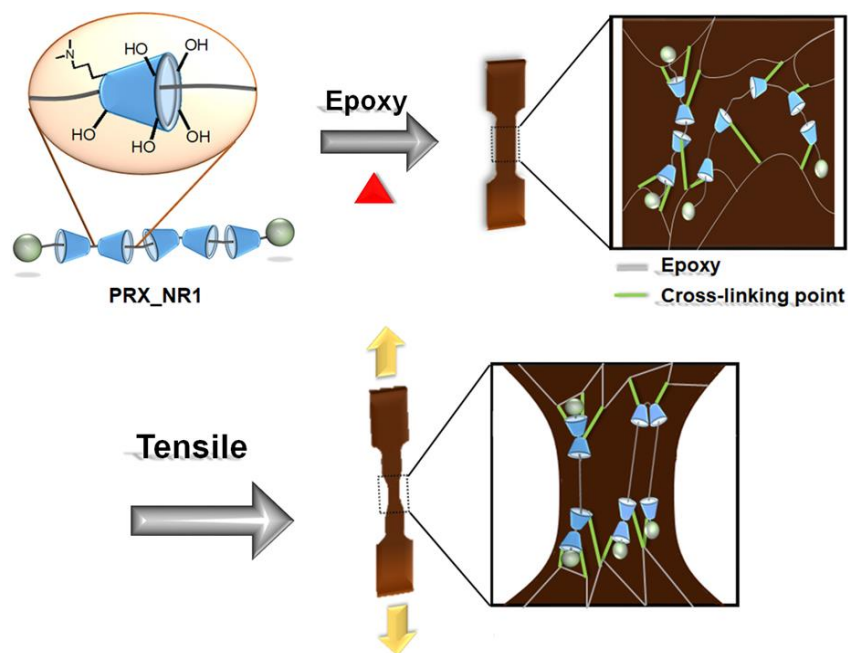
**Fig. 2.** Schematic explanation of the increased ductility by adding PRX derivatives.

**Table 2.** Molecular profile of the synthesized PRX derivatives.

| Symbol | Number of threading α-CDs per PEG (ea, ^{1}H-NMR) | Functional group composition in PRX (%, ^{1}H-NMR) | | Number of tertiary amines per α-CD (ea, ^{1}H-NMR) | $M_n$ (×$10^4$ g/mol, GPC) |
|---|---|---|---|---|---|
| | | Hydroxyl group | Tertiary amine | | |
| PRX | 42 | 100 | - | 0 | 6.7 |
| PRX_NR1 | 42 | 96.3 | 3.7 | 1 | 4.4 |
| PRX_NR4 | 42 | 85.7 | 14.3 | 4 | 4.5 |
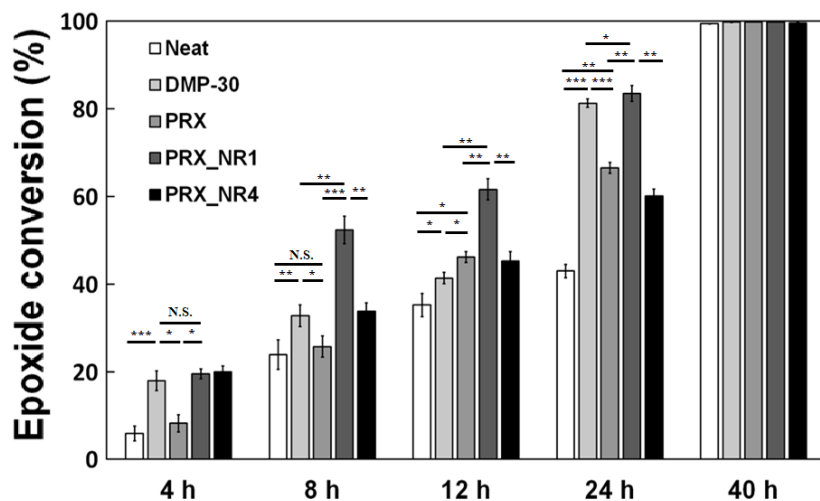
( *** Indicates p < 0.001, ** Indicates p < 0.01, * Indicates p < 0.1,
N.S. indicates no statistical difference )

**Fig. 3.** Comparative analysis of epoxide conversion for different accelerators. The values were calculated by Equation 1. Data are expressed as mean ± SD (n = 3).
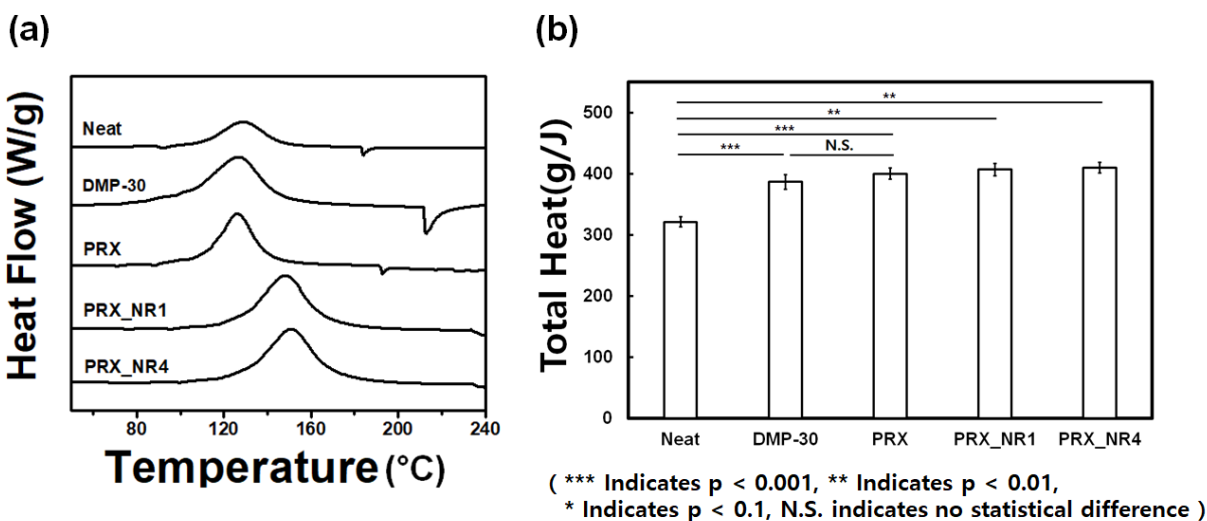


( *** Indicates p < 0.001, ** Indicates p < 0.01,
* Indicates p < 0.1, N.S. indicates no statistical difference )

**Fig. 4.** (a) Changes of heat flow of each sample, (b) amount of total heat. Data are expressed as mean ± SD (n = 3).

25
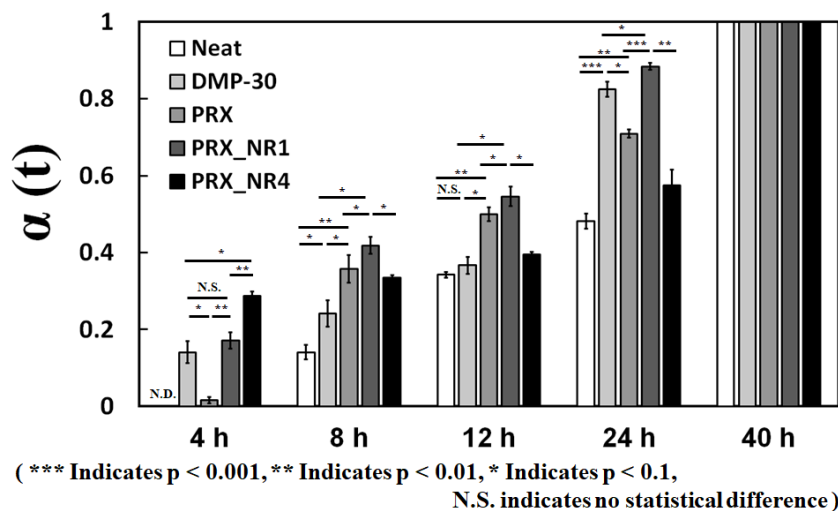
**Fig. 5.** The difference in alpha value of the samples. The values were calculated by Equation 2.
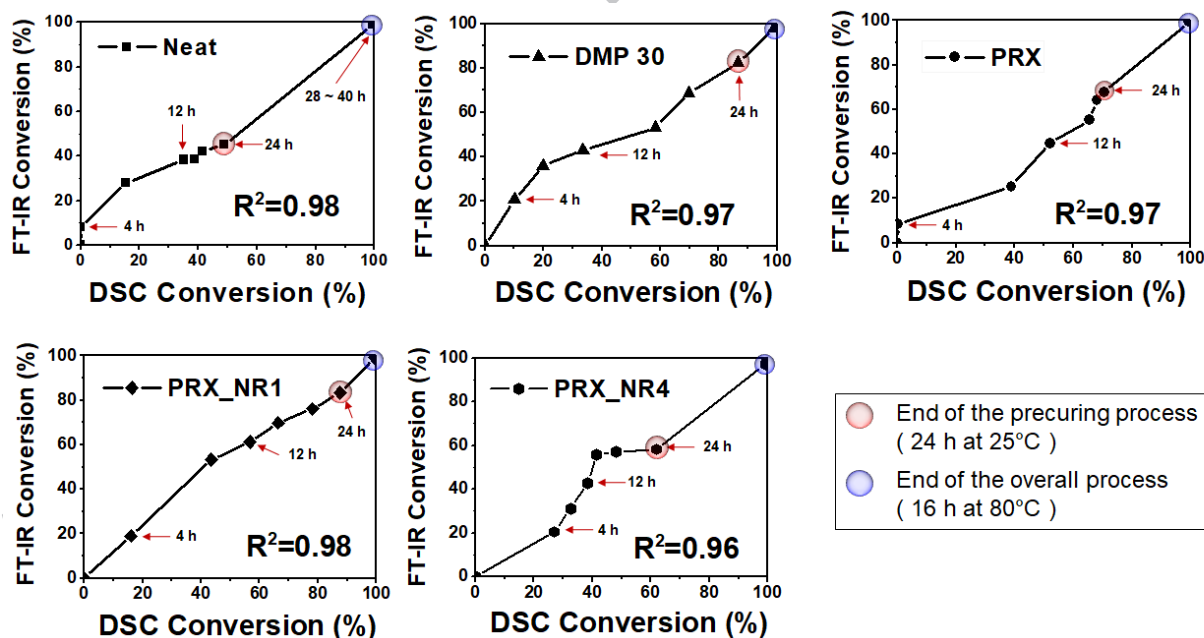
Data are expressed as mean ± SD (n = 3).



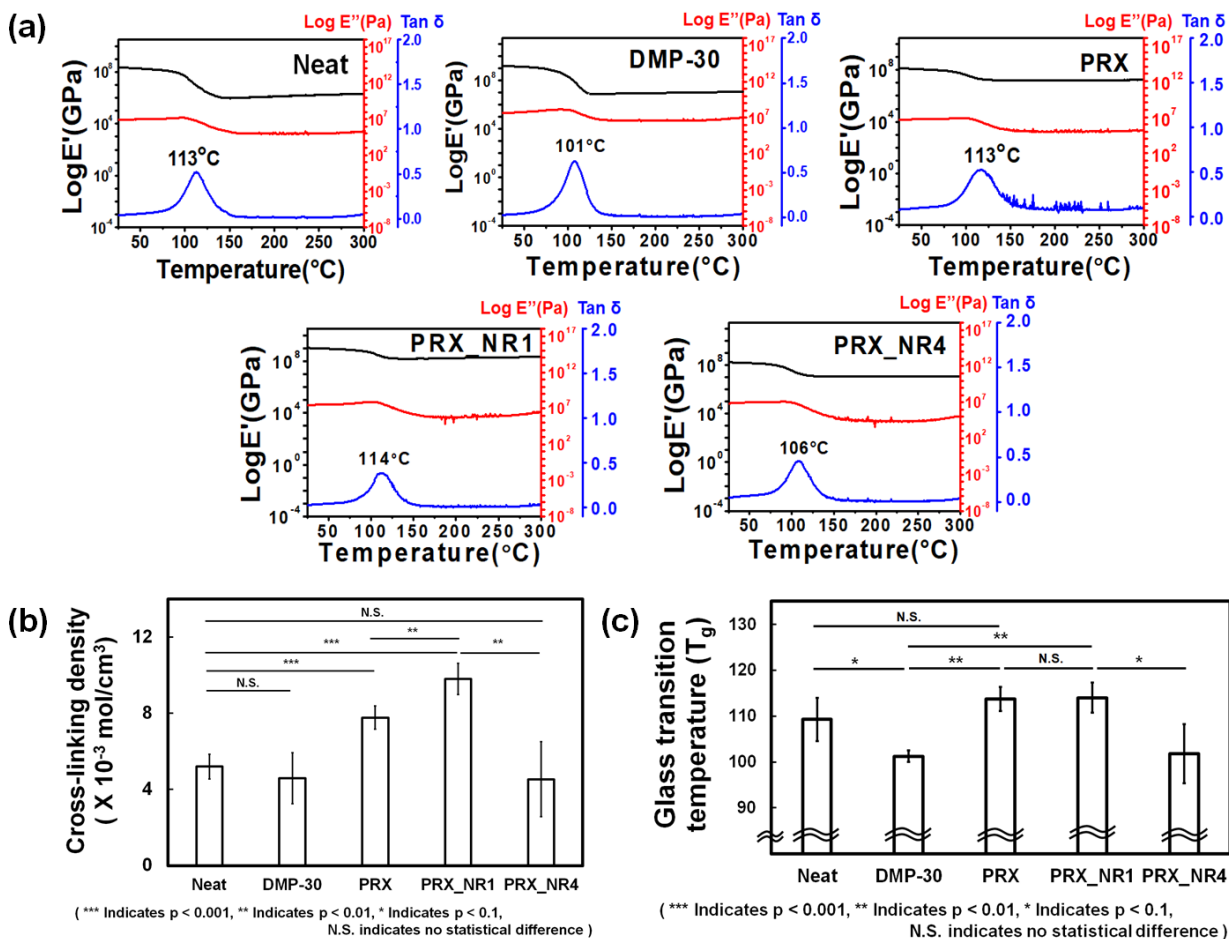**Fig. 6.** The plots of the epoxide conversion calculated by FT-IR and DSC measurement.

**Fig. 7.** (a) The storage and loss modulus with tanδ of each sample obtained from the DMA. (b) Comparison of cross-linking density of the samples calculated by Equation 3. (c) Glass transition temperature of the samples. Data are expressed as mean ± SD (n = 3).
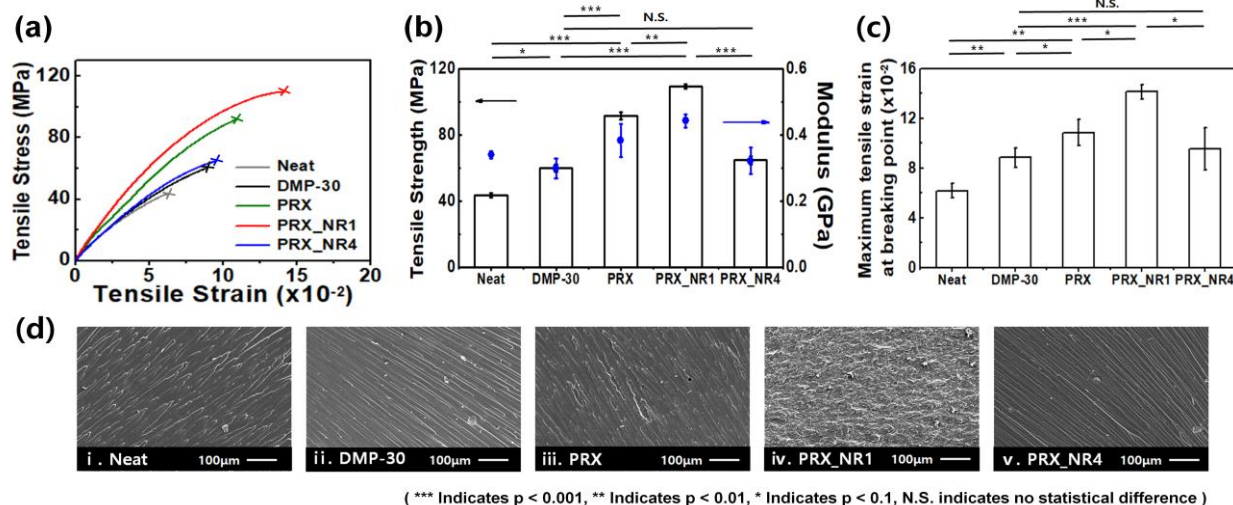
**Fig. 8.** (a) Stress-strain curves of the cured epoxy resins. (b) a tensile strength, a young's modulus and (c) a maximum tensile strain at breaking point. (d) Cross-sectional SEM images of the fractured epoxy specimen by a tensile test. Data are expressed as mean ± SD (n = 3).
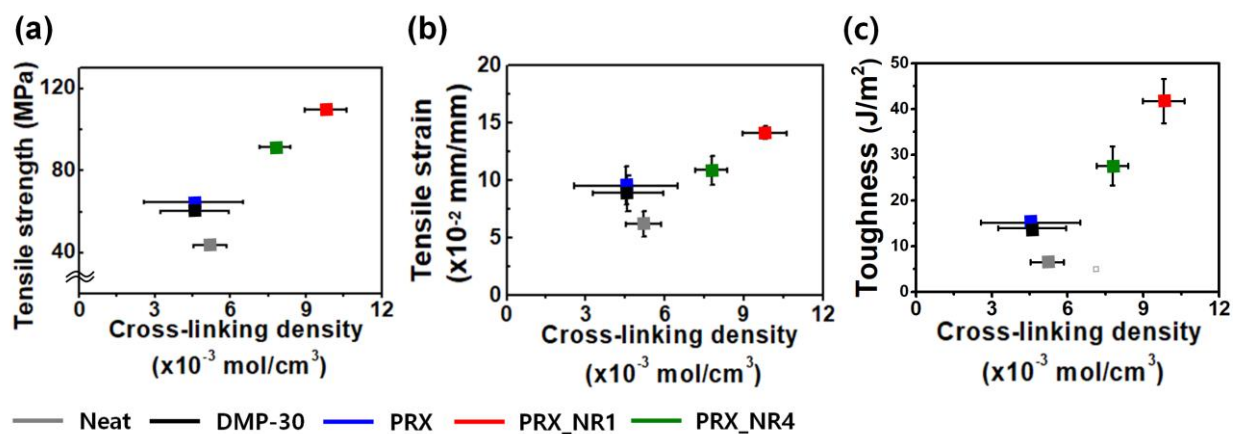


**Fig. 9.** The plots of (a) The crosslinking density vs tensile strength, (b) The cross-linking density vs maximum tensile strain at breaking point, (c) The crosslinking density vs toughness.
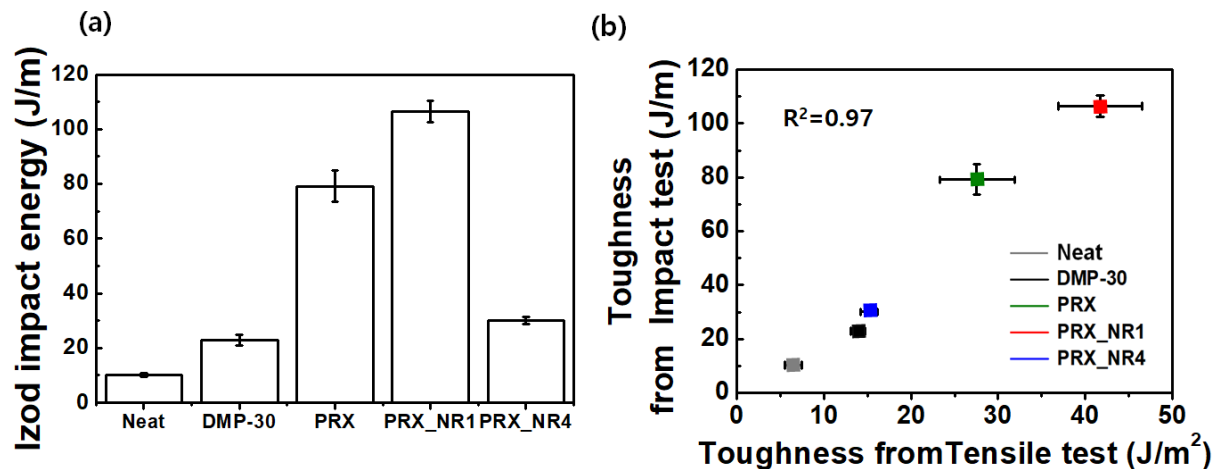
28

**Fig. 10.** (a) The energy of each sample obtained from the impact test. The plots of (b) the cross-linking density from impact test vs S-S curve. Data are expressed as mean ± SD (n = 3).

Highlights

- Molecular necklace-like supramolecular accelerator for epoxy resin was suggested

- The synthesized accelerator displayed fast room temperature curing rate

- The cross-linking density and ductility was simultaneously enhanced