Research Article

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Developing an epoxy resin with high toughness for grouting material via co-polymerization method

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Abstract: In order to improve the toughness of epoxy resin for grouting material, the flexible hexamethylene diisocyanate (HDI) was utilized to manufacture a new kind of epoxy resin with high toughness via co-polymerization method. In the procedure of preparing bisphenol A epoxy resin, before the reaction between bisphenol A (BPA) and epichlorohydrin (ECH), HDI was introduced to react with BPA for embedding flexible segments into the chain of epoxy resin, then modified epoxy resin (HDI/EP) was manufactured. The mechanical properties, especially the toughness of the HDI/EP, are significantly increased – the fracture elongation is up to 124%. In addition, the compressed specimens can fully recover to their original shape in a few minutes. Thermal performance and corrosion resistance of the HDI/EP specimen were also investigated, which showed that the specimen can be used under 258°C, and can remain stable in H₂SO₄, NaOH and NaCl solutions with 10 wt% for 100 h, respectively. The present work provides a convenient avenue pathway to prepare an epoxy resin with high toughness, which may be used in many technologies.

Keywords: epoxy resin; high toughness; flexible chain; hexamethylene diisocyanate; co-polymerization

1 Introduction

Among the chemical grouting materials, epoxy resins (EP) has been attracted tremendous interest owing to their excellent thermal and chemical resistance, convenient processing characteristics, superior electrical resistance properties, relatively lower shrinkage and satisfactory mechanical properties on curing as well as strong adhesion to many substrates (1-3). Nonetheless, they suffer one main drawback: the inherent brittleness of the cured resin. As highly cross-linked rigid thermoset, epoxy resins are of poor toughness and impact resistance comes from the fact that their molecule contains many rigid groups, such as benzene ring, which becomes the crucial reason impaired the compatibility of the grouting system (4-7). Therefore, researchers try to settle the significant issue by adding second phase modifier – for example inorganic nanoparticles (8-10), rubber particles (11,12), thermoplastic polymers (13-15), rigid particles (16-19), core-shell polymers (20-22) have been reported to show satisfactory improvement in the fracture toughness of epoxy resins. Unfortunately, enhancing the toughness of epoxy resins through above methods is always accompanied by the enlargement of operation difficulty because it is very difficult to control the phase separation between the matrix resin and modifier polymer (23,24). Based on the above questions, it is considered as an efficient method to toughen epoxy resins by introducing flexible groups directly into the molecular chain of epoxy resin during the synthesis of epoxy resins (25,26). This method is expected to synthesize an epoxy resin which itself contains soft segments in the molecular chain. Carbamate group (-NHCOO-) as a flexible group can be obtained easily by means of the react between bisphenol A (BPA) and hexamethylene diisocyanate (HDI) (27-29). In addition, the flexible aliphatic chains (30,31) in the molecular structure of the HDI is also a soft segment. Hence, it is considered a practicable strategy that epoxy resin containing flexible segments are prepared

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by block reaction of BPA with HDI and grafted with epichlorohydrin (ECH) to achieve double toughening effect (32,33).

In this paper, in the traditional preparation process of epoxy resin, HDI was reacted with BPA at first for embedding flexible segments, then ECH was added to obtain modified epoxy resin (HDI/EP). The HDI/EP was analyzed by NMR, FITR, DSC, TG, mechanical tests and SEM, and corrosion resistance was also tested in H_2SO_4 , NaOH and NaCl solutions respectively.

2 Experimental

2.1 Materials

ECH, HDI, BPA and tetramethylammonium bromide were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China); sodium hydroxide, acetone, concentrated hydrochloric acid were provided by Jinshan Chemical Reagent Co., Ltd. (Sichuan, China); ether of bisphenol A type EP (E-51, room temperature viscosity = 11-15 Pa·s, EEW = 210-240 g/eq), low-molecular-weight polyamide was chosen as a low temperature curing agent and it was obtained from Baling Petrochemical Co., Ltd. (Hunan, China). All materials were used as received without further purification.

2.2 Preparation of flexible epoxy resin (HDI/EP)

Under nitrogen atmosphere, BPA and ECH were mixed in 500 mL four-necked flask at 50°C, after BPA was dissolved, HDI was slowly added into the flask, the mixture solution was stirred continuously. Tetramethylammonium bromide was not added into four-necked flask until the reaction between HDI and BPA was completed. The temperature was raised to 70°C and kept for 3 h. Then the solution was cooled down to 50°C, sodium hydroxide solution was added dropwise into the flask and the temperature was kept at 50°C continuously for another 3 h. After recovering the solvent, the salt that produced during the reaction was filtered off and the filtrate was washed with excessive water, then with the volatiles evaporated (including solvent and water) under reduced pressure, the flexible epoxy resin (HDI/EP) was obtained as a light yellow liquid product. The formulations are listed in Table 1.

2.3 Curing

The HDI/EP was mixed uniformly with curing agent in certain proportion. The mixture was removed bubbles in a vacuum oven and poured into a Teflon mold, then cured at room temperature for a period of time. For comparison, control group (neat EP, epoxy E-51) was cured in a similar procedure, and then fully cured specimens of neat EP and HDI/EP for tests were achieved. Figure 1 shows the synthetic process of cured specimens.

2.4 Characterization

The chemical structure of the HDI/EP was examined by 1H -NMR and ^{13}C -NMR at room temperature on a Bruker Avance 400 NMR spectrometer using DMSO- d_6 as the solvent, and FTIR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer (Germany). The spectra were acquired by KBr pellet method within the wavelength from 4000 cm^{-1} to 500 cm^{-1} .

The viscosity of the HDI/EP was measured by rotational digital viscosimeter (NDJ-5S, Shanghai Heng Ping Scientific Instruments Co., Ltd. China) at 25°C.

DSC was carried out on a DSC Q2000 (Netzsch Corporation, Germany) under nitrogen using 2-6 mg composites in aluminum pans. Thermal scan at a constant heating rate of 5°C·min $^{-1}$ was conducted in the temperature range of 20-200°C.

TG were carried on a STA 449 C (Netzsch Corporation, Germany) equipped with a thermal analysis data station at a heating rate of 10°C·min $^{-1}$ under Ar atmosphere, the sample was heated from 25 to 600°C.

Tensile strength with dumbbell-shaped samples and compressive strength with a sample size of 20 mm × 20 mm × 10 mm were carried out according to the standard of GB/T2567-2008 on a universal testing machine (Metes Industrial Systems Co., Ltd, China) at room temperature. The impact test was accomplished by using a pendulum impact testing machine (Jinan Tianchen Testing Machine

Table 1: Formulations of HDI/EP composites.

Sample	Molar ratio of ECH to BPA	BPA (mol)	ECH (mol)	HDI (mol)
HDI/EP-14	14	1	14	0.5
HDI/EP-18	18	1	18	0.5
HDI/EP-22	22	1	22	0.5
HDI/EP-26	26	1	26	0.5

Figure 1: Schematic illustration of the preparation of the cured specimens.

Manufacturing Co., Ltd, China) and sample dimensions were 200 mm × 20 mm × 10 mm. Consideration for data accuracy, the results of all mechanical properties were presented as averages of five test specimens.

The surficial morphologies of the fracture surface were observed by using a JEOL JSM 5900 LV scanning electronic microscope (SEM, Japan) at the accelerating voltage of 20 kV.

The cured epoxy resin were soaked in water, sodium chloride solution (10 wt%), sodium hydroxide solution (10 wt%) and sulfuric acid solution (10 wt%) for 100 h, respectively, then the compressive strength and impact strength were tested.

3 Results and discussion

3.1 Synthesis and structure characterization of HDI/EP

HDI/EP was synthesized via the reaction between BPA, HDI and ECH, as shown in Scheme 1. First, in ECH solvent, the block reactant was obtained from the reaction between BPA and HDI at molar ratio 2:1. Next, the block reactant

reacted with ECH under the condition of adding catalyst and NaOH solution. Last, the HDI/EP was synthesized. The chemical structure of the HDI/EP, HDI and block reactant were characterized by FTIR (as shown in Figure 2). As compared to HDI, there is an absence of absorption peak at around 2270 cm^{-1} in the FTIR spectrum of block reactant (which is the characteristic absorption peak of the isocyanate group), meanwhile peak at 1720 cm^{-1} ascribed to C=O band is observed, indicating the successful reaction between HDI and BPA. In the FTIR spectrum of HDI/EP, peaks at 1450, 1500, and 1600 cm^{-1} confirm the presence of benzene ring in HDI/EP. It is rather remarkable that an additional peak at 914 cm^{-1} appears in the spectrum of HDI/EP which is attributed to C-O-C absorption.

The chemical structure of the HDI/EP was also studied by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (as shown in Figure 3). The chemical shift at 9.26, 8.0 and 7.64 ppm are assigned to phenolic, aromatic and amide protons. The peak at 7.08 ppm corresponds to the hydrogen of benzene rings, meanwhile the neighboring weak peak at 6.67 ppm is attributed to the amino groups. There is also the chemical shift representing the protons in the epoxy group, which appeared at $\delta = 5.61$ ppm. In addition, two peaks located at 127 and 69 ppm in the $^{13}\text{C-NMR}$ spectrum can be clearly observed and they are associated to the carbon atoms on

Scheme 1: Synthetic pathway of HDI/EP.

Figure 2: FTIR spectra of the HDI/EP, block reactant and HDI.

benzene rings and epoxy groups. The presented results indicate that the flexible epoxy resin (HDI/EP) has been synthesized successfully.

3.2 Epoxy value and viscosity

The epoxy value and viscosity of HDI/EP were determined according to the standard of GB/T1677-2008 and GB/T2794-2013, respectively. The obtained image was shown in Figure 4. The epoxy values of HDI/EP are 0.19, 0.29, 0.32 and 0.32, and the viscosity values are 10.27, 4.11, 2.56 and 2.78 Pa·s. It can be seen that the former increase gradually, while the latter decrease extremely with increase of molar ratio ECH to BPA. Meanwhile, HDI/EP showed lower viscosity than the E-51 (11~15 Pa·s). When the molar ratio close to 22:1, the epoxy value and viscosity are basically unchanged.

3.3 Thermal properties analysis

Figure 5 shows the TG curves of the cured neat EP and HDI/EP-22 under argon, and the corresponding

Figure 3: ¹H (a) and ¹³C (b) NMR spectra of the HDI/EP-22.

data were listed in Table 2. Cured neat EP exhibited one-stage degradation process, whereas HDI/EP-22 presented two weightless processes. Thermal decomposition temperatures of neat EP are higher than that of HDI/EP-22. The difference may be due to lower decomposition temperatures of the flexible chain segments in HDI/EP-22 than that of neat EP. As grouting

Figure 4: Epoxy value and viscosity of the HDI/EP.

material, the initial decomposition temperature is still far higher than the application requirements.

The glass transition temperatures were also obtained from DSC (as shown in Figure 6). It was observed obviously that the T_g of neat EP and HDI/EP-22 are 145.3°C and 136.7°C, respectively. A possible explanation for this result is that the presence of aliphatic flexible chains in

Figure 5: TG curves of cured neat EP and HDI/EP-22 under argon.

Table 2: Thermal properties of the cured neat EP and HDI/EP-22.

Sample	T _{5%} ^a (°C)	T _{15%} ^b (°C)	T _{50%} ^c (°C)	W ₆₀₀ ^d (%)
neat EP	285	346	412	7.0
HDI/EP-22	258	315	389	9.5

^a the temperature where 5 wt% of weight was lost.

^b the temperature where 15 wt% of weight was lost.

^c the temperature where 50 wt% of weight was lost.

^d the residual weight at 600°C.

Figure 6: DSC curves of cured neat EP and HDI/EP-22 under argon.

the structure of the HDI/EP, leading to the molecule chain movement, is easier than neat EP as the temperature increased. Therefore, the cured HDI/EP-22 showed a slightly lower T_g than the neat EP.

3.4 Mechanical properties

Mechanical properties of the cured HDI/EP and neat EP, including compressive strength, tensile strength, elongation at break, impact strength were shown in Figure 7. The specimens curing HDI/EP exhibited intriguing flexibility as shown Figure 7a, bending had

no injure to the specimen. The compressive strength of different specimens were showed in Figure 7b, the pure EP specimens cracked at the beginning of compression, and its compressive strength is only 29.97 MPa. On the contrary, HDI/EP specimens shown no obvious crack after compression for 70% and maintained satisfactory compressive strength with a value of 84.08 MPa. Furthermore, after removing the pressure, the specimens can fully recover to its original shape in a few minutes, which proves its outstanding elasticity. In addition, tensile properties also tested to explore the toughness of the modified epoxy, the typical tensile stress-strain curves of cured neat EP and HDI/EP can be seen in Figure 7c.

Figure 7: Mechanical properties of cured neat EP and HDI/EP. (a) Image of bending curing HDI/EP specimen. (b) Compressive strength of HDI/EP at 70% compression state. (c) Typical stress-strain curve of cured neat EP and HDI/EP in the process of stretching. (d) Impact toughness of neat EP and HDI/EP. Data are expressed as mean $\pm$ SD ($n = 5$).

The elastic deformation of neat EP occurs only during the stretching process, the tensile strength and fracture elongation are 14.30 MPa and 5%, respectively. Different from cured neat EP, two stages are clearly displayed during the same stretching process of the cured HDI/EP, showing an approximately linear relationship between stress and strain. This is observed at the first stage, indicating that the material is subjected to elastic deformation, the tensile strength and elastic elongation are up to about 25 MPa and 20%, respectively. With the increase of the force, the material begins to change from elastic deformation to plastic deformation at the second stage. Compared with neat EP, HDI/EP has higher tensile strength and fracture elongation. Significantly, the optimal tensile strength of HDI/EP-22 is 40.31 MPa, the value corresponds to the results of Chen's (34), but the fracture elongation in this result is 124%, which is much higher. The excellent toughness and strength of cured HDI/EP were further proved in an impact test. It can be concluded from Figure

7d that the maximum impact strength of cured HDI/EP-22 is 51.74 kJ/m², which is much higher than the control sample. This result is better than 11.8 kJ/m² in the Zhou's study and 18.51 kJ/m² in the Kou's study (35,36).

In conclusion, as shown in Figure 7, the HDI/EP has better mechanical properties compared with neat EP. This might be due to the fact that the flexible groups were embedded in the molecular structure of the resin successfully (37). What is noteworthy, the changed trend of the strength value and elongation at break of different samples are similar with the epoxy values (as shown in Figure 4). This may be due to the influence of mechanical properties on the epoxy value: the higher content of epoxy value in the system, the stronger chemical bonds between the HDI/EP and curing agent is, the greater interfacial adhesion can be formed. Because of this, the mechanical properties keep pace with the epoxy value, when the molar ratio of ECH to BPA is close to 22:1. The optimal performance of HDI/EP can be achieved.

Figure 8: SEM images of tensile fracture and impact fracture of cured neat EP and HDI/EP-22.

3.5 SEM analysis

The tensile fracture and impact fracture surface morphologies of the cured neat EP and HDI/EP-22 were obtained by SEM (Figure 8). As can be seen, the tensile fracture and impact fracture surface morphologies of neat EP, large area smooth and flat surface with no lumps or rough parts, the cracking textures on the observed surface are uniform and developed into one-way extension, as expected displays typical characteristics of brittle fracture (38,39). In contrast, the fracture surface of the cured HDI/EP is obviously inhomogeneous and rough, considerable curls can be observed in the tensile fracture morphology, which may possibly be caused by the rebound after fracture of the soft segments. Besides, extensive river-like lines were observed in the impact morphology of the HDI/EP, which presents a typical characteristics

of flexible fracture (40,41). These morphologies can be attributed to the soft segments as the HDI was introduced into the molecular structure of the epoxy resin, which can obviously absorb and dissipate energy when the material was damaged. That is why the fracture toughness of the cured HDI/EP was improved.

3.6 Corrosion resistance test

Taking into account the corrosion of the repairing material that may occur and change the performances during some applications, the corrosion resistance was conducted and shown in Figure 9. The samples were dipped in H_2SO_4 , NaOH and NaCl solution with 10 wt% for 100 h, control samples were obtained by soaking for the same time in water. It can be seen from Figure 9b that

Figure 9: The images of corrosion resistance under H_2SO_4 , NaOH and NaCl solutions.

Figure 10: Mechanical properties of corroded samples. (a) The impact strength of HDI/EP under H_2O , H_2SO_4 , NaOH and NaCl solutions. (b) The compressive strength of HDI/EP under H_2O , H_2SO_4 , NaOH and NaCl solutions. Data are expressed as mean $\pm$ SD ($n = 5$).

there is no obvious change in appearance under different solutions. The mechanical properties of soaked samples were tested and shown in Figure 10. According to impact and compression tests, the mechanical properties of HDI/EP remain stable before and after corrosion. These results proved that the grouting material has an excellent corrosion resistance.

4 Conclusions

In summary, for the first time, a novel bisphenol A epoxy resin as grouting material with high toughness and flexibility was prepared through co-polymerization method from HDI, BPA and ECH. The carbamate groups ($-\text{NHCOO}-$) and flexible aliphatic chains were successfully embedded into the chains of modified epoxy resin, just for the reason, the modified epoxy resin showed excellent mechanical properties, including compressive strength, impact strength, tensile strength and fracture elongation, which are critical for grouting material. With the molar ratio of ECH to BPA close to 22:1, the impact strength of the HDI/EP are significant increased to 51.74 kJ/m^2 . It is much higher than the control sample, and the fracture elongation is up to 124%. The compressive strength and tensile strength reached a higher number of 84.08 MPa and 40.31 MPa, respectively. In addition, the modified epoxy resin has an excellent heat resistance and corrosion resistance. The present work provides a simple and convenient avenue to prepare a high toughness epoxy resin, which may have potential applications in wide fields.

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References

1. Demir B., Beggs K.M., Fox B.L., Servinis L., Henderson L.C., Walsh T.R., A predictive model of interfacial interactions between functionalised carbon fibre surfaces cross-linked with epoxy resin. *Compos. Sci. Technol.*, 2018, 159, 127-134.
2. Sari M.G., Saeb M.R., Shabanian M., Khaleghi M., Vahabi H., Vagner C., et al., Epoxy/starch-modified nano-zinc oxide

- transparent nanocomposite coatings: A showcase of superior curing behavior. *Prog. Org. Coat.*, 2018, 115, 143-150.
3. Wu H., Zhu M., Liu Z., Yin J., Developing a polymer-based crack repairing material using interpenetrate polymer network (IPN) technology. *Constr. Build. Mater.*, 2015, 84, 192-200.
4. Zhang Y., Pang H., Wei D., Li J., Li S., Lin X., et al., Preparation and Characterization of Chemical Grouting Derived from Lignin Epoxy Resin. *Eur. Polym. J.*, 2019, 118, 290-305.
5. Liu Y.L., Wang Y.S., Fang G., Alrefaei Y., Dong B., Xing F., A preliminary study on capsule-based self-healing grouting materials for grouted splice sleeve connection. *Constr. Build. Mater.*, 2018, 170, 418-423.
6. Anagnostopoulos C.A., Sapidis G., Papastergiadis E., Fundamental properties of epoxy resin-modified cement grouts. *Constr. Build. Mater.*, 2016, 125, 184-195.
7. Manjula Dhevi D., Jaisankar S.N., Pathak M., Effect of new hyperbranched polyester of varying generations on toughening of epoxy resin through interpenetrating polymer networks using urethane linkages. *Eur. Polym. J.*, 2013, 49, 3561-3572.
8. Zhang Y., Zhang Z., Li J., Sui G., (3-aminopropyl) triethoxysilane grafted poly(dopamine) $@\text{Fe}_3\text{O}_4$ nanoparticles and their epoxy composites for functional application. *Compos. Part B-Eng.*, 2019, 169, 148-156.
9. Chabane H., Livi S., Benes H., Ladavière C., Ecorchard P., Duchet-Rumeau J., et al., Polyhedral oligomeric silsesquioxane-supported ionic liquid for designing nanostructured hybrid organic-inorganic networks. *Eur. Polym. J.*, 2019, 114, 332-337.
10. Prasad T., Halder S., Dhar S.S., Imidazole-supported silica one-pot processed nanoparticles to enhance toughness of epoxy based nanocomposites. *Mater. Chem. Phys.*, 2019, 231, 75-86.
11. Yahyaei H., Ebrahimi M., Tahami H.V., Mafi E.R., Akbarinezhad E., Toughening mechanisms of rubber modified thin film epoxy resins: Part 2 - Study of abrasion, thermal and corrosion resistance. *Prog. Org. Coat.*, 2017, 113, 136-142.
12. Ricciardi M.R., Papa I., Langella A., Langella T., Lopresto V., Antonucci V., Mechanical properties of glass fibre composites based on nitrile rubber toughened modified epoxy resin. *Compos. Part B-Eng.*, 2018, 139, 259-267.
13. Wu X., Yang X., Yu R., Zhao X.-J., Zhang Y., Huang W., Highly crosslinked and uniform thermoset epoxy microspheres: Preparation and toughening study. *Polymer*, 2018, 143, 145-154.
14. Seo J., Yui N., Seo J.-H., Development of a supramolecular accelerator simultaneously to increase the cross-linking density and ductility of an epoxy resin. *Chem. Eng. J.*, 2019, 356, 303-311.
15. Yu M., Qi S., Fu J., Zhu M., Chen D., Understanding the reinforcing behaviors of polyaniline-modified carbonyl iron particles in magnetorheological elastomer based on polyurethane/epoxy resin IPNs matrix. *Compos. Sci. Technol.*, 2017, 139, 36-46.
16. Meng Q., Wang T., An improved crack-bridging model for rigid particle-polymer composites. *Eng. Fract. Mech.*, 2019, 211, 291-302.
17. Rotbaum Y., Parvari G., Eichen Y., Rittel D., Mechanical reinforcement of methylcellulose hydrogels by rigid particle additives. *Mech. Mater.*, 2019, 132, 57-65.
18. Zhou G., Wang W., Peng M., Molecular-level dispersion of rigid-rod sulfonated aromatic polyamides in epoxy resin for extraordinary improvement in both strength and toughness. *Polymer*, 2019, 163, 20-28.
19. Yu M., Qi S., Fu J., Zhu M., Chen D., Understanding the reinforcing behaviors of polyaniline-modified carbonyl iron particles in

- magnetorheological elastomer based on polyurethane/epoxy resin IPNs matrix. *Compos. Sci. Technol.*, 2017, 139, 36-46.
20. Chen S., Bedia J., Li H., Ren L.Y., Naluswata F., Belver C., Nanoscale zero-valent iron@mesoporous hydrated silica core-shell particles with enhanced dispersibility, transportability and degradation of chlorinated aliphatic hydrocarbons. *Chem. Eng. J.*, 2018, 343, 619-628.
 21. Chen S.H., Li X.-F., Boundary and concentration effects on the creeping motions of core-shell particles. *Chem. Eng. Sci.*, 2019, 203, 122-137.
 22. Lee J.Y., Chin I.-J., Choi H.J., Effect of particle size and crosslinking on the toughening of core-shell-type rubber-modified poly(lactic acid) composites. *Polym. Test.*, 2018, 65, 440-449.
 23. Barua S., Dutta G., Karak N., Glycerol based tough hyperbranched epoxy: Synthesis, statistical optimization and property evaluation. *Chem. Eng. Sci.*, 2013, 95, 138-147.
 24. Saikia A., Karak N., Renewable resource based thermostable tough hyperbranched epoxy thermosets as sustainable materials. *Polym. Degrad. Stabil.*, 2017, 135, 8-17.
 25. Xu P., Cong P., Li D., Zhu X., Toughness modification of hyperbranched polyester on epoxy asphalt. *Constr. Build. Mater.*, 2016, 122, 473-477.
 26. Xu P., Zhu X., Cong P., Du X., Zhang R., Modification of alkyl group terminated hyperbranched polyester on paving epoxy asphalt. *Constr. Build. Mater.*, 2018, 165, 295-302.
 27. Cao Y., Li H., Qin N., Zhu G., Kinetics of the decomposition of dimethylhexane-1,6-dicarbamate to 1,6-hexamethylene diisocyanate. *Chin. J. Chem. Eng.*, 2015, 23, 775-779.
 28. Cao Y., Li H., Li X., Wang L., Zhu G., Tang Q., Heterogeneous synthesis of dimethylhexane-1,6-dicarbamate from 1,6-hexanediamine and methyl carbonate in methanol over a CeO₂ catalyst. *Chin. J. Chem. Eng.*, 2015, 23, 446-450.
 29. Zhao L., He P., Wang L., Ammar M., Cao Y., Li H., Catalysts screening, optimization and mechanism studies of dimethylhexane-1,6-dicarbamate synthesis from 1,6-hexanediamine and dimethyl carbonate over Mn(OAc)₂ catalyst. *Catal. Today*, 2017, 281, 392-401.
 30. Zhuang Y., Seong J.G., Lee Y.M., Polyimides containing aliphatic/alicyclic segments in the main chains. *Prog. Polym. Sci.*, 2019, 92, 35-88.
 31. Zhu J., Tsona N.T., Mellouki A., Du L., Atmospheric initiated oxidation of short chain aliphatic ethers. *Chem. Phys. Lett.*, 2019, 720, 25-31.
 32. Ma C., Qiu S., Wang J., Sheng H., Zhang Y., Hu W., et al., Facile synthesis of a novel hyperbranched poly(urethane-phosphine oxide) as an effective modifier for epoxy resin. *Polym. Degrad. Stabil.*, 2018, 154, 157-169.
 33. Wang J., Jin X., Li C., Wang W., Wu H., Guo S., Graphene and graphene derivatives toughening polymers: Toward high toughness and strength. *Chem. Eng. J.*, 2019, 370, 831-854.
 34. Hu C., Xiao J.-D., Mao X.-D., Song L.-L., Yang X.-Y., Liu S.-J., Toughening mechanisms of epoxy resin using aminated metal-organic framework as additive. *Mater. Lett.*, 2019, 240, 113-116.
 35. Zhou S., Chen Z., Tusiime R., Cheng C., Sun Z., Xu L., et al., Highly improving the mechanical and thermal properties of epoxy resin via blending with polyetherketone cardo. *Compos. Commun.*, 2019, 13, 80-84.
 36. Kou Y., Zhou W., Li B., Dong L., Duan Y.-E., Hou Q., et al., Enhanced mechanical and dielectric properties of an epoxy resin modified with hydroxyl-terminated polybutadiene. *Compos. Part A-Appl. S.*, 2018, 114, 97-106.
 37. Yang P., Ren M., Chen K., Liang Y., Lü Q.-F., Zhang T., Synthesis of a novel silicon-containing epoxy resin and its effect on flame retardancy, thermal, and mechanical properties of thermosetting resins. *Mater. Today Commun.*, 2019, 19, 186-195.
 38. Deng W., Zhao X., Ren Y., Hao E., Han J., An Y., et al., Influence of epoxy resin on the microstructure and cavitation erosion of as-sprayed 8YSZ coating. *Ceram. Int.*, 2019, 45, 5693-5702.
 39. Zhang P., Kan L., Zhang X., Li R., Qiu C., Ma N., et al., Supramolecularly toughened and elastic epoxy resins by grafting 2-ureido-4[1H]-pyrimidone moieties on the side chain. *Eur. Polym. J.*, 2019, 116, 126-133.
 40. Yang Z., Zhang X., Liu X., Guan X., Zhang C., Niu Y., Flexible and stretchable polyurethane/waterglass grouting material. *Constr. Build. Mater.*, 2017, 138, 240-246.
 41. Zhang X., Qiao L., Lu X., Jiang L., Cao T., Preparation and Properties of Toluene-Diisocyanate-Trimer-Modified Epoxy Resin. *Polymers*, 2019, 11(3), 416.