Functional dendritic curing agent for epoxy resin: Processing, mechanical performance and curing/toughening mechanism

Chunhua Lou, Xijun Liu

PII: S1359-8368(16)31148-9

DOI: 10.1016/j.compositesb.2017.09.073

Reference: JCOMB 5321

To appear in: *Composites Part B*

Received Date: 26 June 2016

Revised Date: 27 September 2017

Accepted Date: 28 September 2017

Please cite this article as: Lou C, Liu X, Functional dendritic curing agent for epoxy resin: Processing, mechanical performance and curing/toughening mechanism, *Composites Part B* (2017), doi: 10.1016/j.compositesb.2017.09.073.

Functional dendritic curing agent for epoxy resin: processing, mechanical performance and curing/toughening mechanism

Chunhua Lou[1,2,*] and Xijun Liu[1]

1 College of Materials Science and Engineering of Qiqihar University, Qiqihar 161006, China

2 Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409-3121, USA

* Corresponding author: Chunhua Lou E-mail: chunhua.lou@ttu.edu

Abstract: A functional curing agent was synthesized with imidazole blocked 2,4-tolulene diisocyanate (TDI) by using dendritic polyester polyol as branching unit and toughening segment, which toughening and curing the bisphenol A type epoxy resin (E-44). The effect of dendritic polyester polyol content on the morphology of fracture surface and properties of the cured epoxy resin was investigated, which results in the multiple curing mechanism for the curing process. With the increasing of dendritic polyester polyol content, the surface fracture of the cured epoxy turns to more ductile. The mechanical properties from tensile shear and impact strength tests showed that 1% of dendritic polyester polyol (the molar percentage of isocyanate) was the optimum content to get cured epoxy with desired tensile shear strength and impact strength. The curing and toughening mechanism was proposed based on the experimental results.

Key words: Epoxy resin; Toughening; Blocked isocyanate; Dendrimer

1. Introduction

Epoxy resins are commonly used as protective coatings, structural adhesives, high-performance composite matrices, insulating materials and moulded articles etc. in a wide variety of areas such as aerospace, energy, chemical engineering and automobile industries. The widespread use of epoxy resins is due to their high performance, particularly the thermal and dimensional stabilities. However, the brittleness, poor crack resistance and low fracture toughness because of the highly cross-linked structures, greatly limit their applications in certain areas [1-6]. Hence, toughened-epoxy has been the challenging task around the world[7,8].

Previous studies have shown that the toughening process for epoxy resin has transitioned from using toughening agent additives to modifying the molecular structures[9-16]. Kinloch, Pearson and many others did a lot of research work in this area[17-23]. Among numerous of structural modification methods, toughening epoxy resin with dendrimers or molecules with hyperbranched structure is a novel and effective means.

Dendrimers belong to well-defined tree-like structures, each repeating units consisting of “branches” emanating from a central core[24],which are obtained by step-growth reaction of branch units[6,25-27]. Due to their distinctive chemical and physical properties such as exceedingly high functionalities, universal tunability, unparalleled rheology properties, extraordinary optical-enhancement effects, self-assembly, and host–guest particulates, dendrimers have been attracting enormous interests in the recent 30 years since the first successful achievement of poly(amidoamine) (PAMAM) dendrimers by Tomalia and co-workers[24]. Dendrimers have also been used increasingly in epoxy resins. Todd Emrick etc. prepared hyperbranched aliphatic polyether epoxies via an A2 + B3 approach [28], then, blended with the commercial epoxy resin bisphenol F diglycidyl ether (BPFG) and cured with 2-ethyl-4-methylimidazole (EMI) [29].The ability of a hyperbranched polymer to function as an effective component in adhesive formulations has been established. Jintao Wan etc.[24,30-32] systematically investigated an acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4) and a novel butyl-glycidylether-modified poly(propyleneimine) dendrimers (PPIs) cured for bisphenol A epoxy resin (DGEBA). Based on the experimental results, they concluded that PAN4 and PPIs had a high potential as new curing agents for high-performance epoxy adhesives. These curing agents not only reduced volatility and toxicity, but also improved flexibility, surface appearance and mechanical performances, etc. Analogously, Jianfei Che etc.[33] used single-walled carbon nanotubes functionalized with generation (n) 0-2 dendritic poly(amidoamine) (PAMAM) to reinforce epoxy. Moreover, some other people did similar research work [35-42]. Recently, Felix N. Nguyen etc.[25] discussed processing challenges and hot-wet performance of novel core-shell (dendrimer) (CSD) particles epoxy tougheners. These particles are made from a block copolymers such as polybutadiene (PB)/polystyrene (PS) as core and acrylic polymer, e.g., polymethylmethacrylate (PMMA), as shell. However, a flaw in these or similar systems is that softer materials added to increase toughness causes corresponding decrease in desired stiffness. Meanwhile, Tang etc.[42] and Xu etc.[43] used hyperbranched polyurethane (HBPU) to toughen epoxy. The toughness of the modified thermosets was significantly improved without sacrificing their processability, thermal and mechanical properties to a large extent. Although this was still a method of adding tougheners, it has turned to more focusing on the use of functionalized curing agents for curing and toughening epoxy resins.

In our previous work, the functionalized curing agent, modified m-phenylene diamine with soft ether chain was synthesized by designing molecular structure, which improved the toughness properties of the cured epoxy matrix[44]. It has been found that the curing agent with polyfunctionality was the ideal product. Namely, some functional groups remain their reactivity with epoxy groups after modification.

Polyisocyanates are just these materials to meet this requirement. However, the high reactivity of isocyanates limits their storage and use in one-component systems. Blocking isocyanate groups and then deblocking them at certain temperature would have satisfactorily overcome this problem. Blocking agent is a compound containing an active hydrogen atom. It reacts with isocyanate to form carbamate with labile bond which will regenerate isocyanate and blocking agent functionality at a higher temperature [45-49]. Nevertheless, conventional blocked isocyanate curing agents have no soft segments, which can lead to brittleness of the cured epoxy. For this reason, usually blocked isocyanate curing agents are modified chemically to increase toughness, and they are frequently modified by materials of soft chain.

Considering the advantage of dendrimers, such as high density of functional terminal groups, greater solubility in resins, we proposed to use them as modifying agents to prepare functionalized curing agents for curing and toughening epoxy resins. In this work, a functional curing agent was synthesized with imidazole blocked 2,4-tolulene diisocyanate (TDI) by using dendritic polyester polyol (p1000) as the toughening segment, which had an multiply role in the toughening and curing of bisphenol A type epoxy resin (E-44). The introducing of dendritic toughening segment (p1000) can effectively overcome the inherent drawbacks of epoxy resin and significantly improve the mechanical properties of cured epoxy resin.

2. Materials and methods

2.1 Materials

The aromatic epoxy, bisphenol-A diglycidyl ether (E-44) (epoxy equivalent weight=212-244), was purchased from Wuxi Guangming Chemical Engineering Co., Ltd. (China). The 2,4-tolulene diisocyanate

(TDI) was purchased from ICI company (Britain). The dentridic polyester polyol (p1000), in which the hydroxy value is 490 mg KOH/g, was purchased from Yonghe Chemical Reagent Co., Ltd. (China). The other reagents, including N,N-dimethyl formamide (DMF) and imidazole were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China). All chemicals except the epoxy resin were of reagent grade and used as received.

2.2methods

2.2.1 Preparation of blocked isocyanate curing agent and curing conditions

A certain amount of TDI and corresponding p1000 (the molar ratio of —NCO/—OH was 100:(1~13)) were transferred to a 250ml flask. The solvent, DMF, 150 wt% related to TDI, was added to the reacting system. The system were heated to 50℃ in a constant temperature bath. The blocking agent (imidazole) (the molar ratio of —NCO/(—OH+ —H) was 1:1.1) was added into the reacting system after 1 hour in the constant temperature bath. Then the temperature was gradually increased to 60℃ and maintained at this temperature for 2 hours under the stirring condition. The reaction system was purged with nitrogen gas throughout the reacting process.

To cure the epoxy resin, the above prepared functional curing agent was mixed into the curing system with different ratios. The samples were poured into the molds and cured at 100℃ for 2 hours after intense mixing. The final imidazole /epoxy ratio was set to 4:100 by weight after optimization.

2.2.2 Characterizations and Measurements

The structural characterization was accomplished by real-time FTIR scan using Frontier FTIR

(PerkinElmer Corporation, USA) analyzer in the range of 4000-400 cm^{-1}. The samples were compressed to the desired tablet form with potassium bromide (KBr).

The thermodynamic and kinetic behavior of the cured samples were monitored by DSC 204F1 (Netzsch, Germany) and DMA Q800 dynamic mechanical analyser (TA, USA), respectively. For the DSC experiment, approximate 10 mg samples were sealed in aluminum pans and scanned from 50 to 300℃ at a rate of 10℃/min under nitrogen gas purging. The dual cantilever mode with 1Hz was employed to perform the test of DMA, in which the heating rate was 4℃/min and the temperature range was from 40 to 180℃ under a nitrogen atmosphere.

The fracture surfaces of the cured samples were observed using scanning electron microscopy (SEM, S-3400 (Hitachi, Japan)) at an accelerating voltage of 20 kV.

The mechanical performance tests include tensile shear and impact strength tests. The substrate of tensile shear test was aluminum alloy sheet. The bonded area between two substrates was 15×15mm^2 with cured epoxy resin. The tensile shear test was conducted with a NLW-20 shear tester (Languang Co., China). The sample size of impact strength test was 80×10×4mm^3. Impact strength test was carried out by an unnotched charpy memorable impact tester (JJ-20, Changchun Intelligent Instrument Equipment Co. Ltd., China) at room temperature. (Note: The energy of the pendulum is 25J, which is higher than normal one used for plastic.)

3. Results and discussion

3.1 Synthesis of functional curing agent

In the present study, isocyanate was blocked by imidazole, after the isocyanate reacted with flexible molecules to form isocyanate prepolymer. Then, the functional curing agent was obtained because imidazole is not only the blocking agent of isocyanates, but also the most widely used curing agent in epoxy curing. A rapid reaction between a multifunctional isocyanate and a hydroxyl terminated oligomer leaded to form an urethane bond (—NH—CO—O—).

When polyol having dendritic structure reacted with polyisocyanate, the isocyanate prepolymer with dendritic structure would be prepared. During the process of curing epoxy resins, this functional curing agent could release imidazole and free —NCO groups. Imidazole would react with epoxy groups and finally form —OH. The formed —OH could react with —NCO groups to form new carbamate bond (—NH—CO—O—) and this reaction would be recycled constantly. So, the dendrimer would be introduced in the epoxy matrix. Thus, the epoxy resin could be toughened by the imidazole blocked isocyanate having dendrimer (p-Im-b-TDI) due to its high degree of branching, available internal cavities and the induced phase separations.

Scheme 1 summerized the synthesis of functional curing agents (p-Im-b-TDI)which were synthesized through 2,4-tolulene diisocyanate (TDI), p1000, and blocking agent (imidazole).

3.2 Structural characterizations of the prepared curing agents and cured epoxy resin systems

The real-time FTIR was employed to monitor the reactive degree between TDI and p1000 during the reaction, which can reflect the change of —NCO group. In the reacting system, one part of —NCO groups of TDI can react with the —OH groups in p1000 and the other part of —NCO groups can be blocked by imidazole. Figure 1 shows the real-time FTIR spectra of the blocked isocyanate blocked by p1000. The blocking degree of TDI can be normally evaluated using the intensity of isocyanate band at 2270cm^{-1}, which is assigned to the characteristic absorption peak of isocyanate stretching vibration[50]. From the real-time FTIR spectra, it is obvious that the intensity of the isocyanate band at 2270 cm^{-1} is gradually decreased with increasing reaction time. This indicated that the —NCO groups of the isocyanate molecule was blocked by the —H of imidazole and the —OH of p1000. The blocking reaction was completed after more than 100 minutes reaction, which was indicated by the disappearance of the peak at 2270cm^{-1}. Meanwhile, there appears several strong peaks on the FTIR spectra including C=O stretching peak(1700 cm^{-1}), N—H stretching peak (from 1530 to 1560cm^{-1}) and the C=O stretching vibration peak of carbamate combined with the N—H group (from 1210 to 1240 cm^{-1}) [51]. This further confirms that —NCO groups of TDI were completely consumed after more than 100 minutes reaction.

The characteristic peak of epoxy group at 915 cm^{-1} will be gradually disappeared during the curing process. Therefore, this characteristic peak is usually used as the signal for the degree of curing for epoxy resin. Figure 2 shows the FTIR spectra of cured epoxy resin (E-44) with different curing agents. From Figure 2, it can be apparently seen that this characteristic peak of epoxy group was gradually decreased with an increase in curing time. Meanwhile, the intensity of —OH characteristic peak belonging to the epoxy resin at 3400cm^{-1} was increased gradually. This indicates that the ring of epoxy resin was opened after the resin was cured by curing agent. Moreover, it is worth notifying that there is a new characteristic peak at 1664cm^{-1} when the resin cured by Im-b-TDI and p-Im-b-TDI, which belongs to the C=O of carbamate stretching vibration. This new peak provides the evidence that the blocked isocyanate existed in the curing system and played a role of cross-linking agent. Combining Figure 2 and scheme 1, it can be concluded that the curing ability of the prepared Im-b-TDI and p-Im-b-TDI had more significant curing ability than that of single imidazole for the epoxy resin curing. This advantage could be attributed to the structural specificity.

3.3 Morphological characterization of the fracture surface

As Misaki et al. [52] postulated, a tough or flexible material is conductive to fracture with crack branching and with more uneven fracture surface required large energy to fracture. The morphology of material fracture surface, therefore, can reflect the toughness (or rigidity) to a certain extent. Figure 3 shows the SEM micrographs of epoxy resin cured by different curing agents. The smooth fracture morphological structure is exhibited in the Figure 3a, from which the epoxy resin was cured by neat imidazole. It is well known that imidazole is the ring structure, which has no flexible group in the molecular chain to toughen epoxy. However, cured epoxy resin using synthesized Im-b-TDI as a curing agent gives visibly wrinkled fracture surface as shown in Figure 3b. This is attributed to the existence of urethane, which has a certain toughening effect for the epoxy. However, the desired toughness cannot be achieved by using Im-b-TDI to cure epoxy resin. Figure 3a and 3b are the typical fragile fracture surface. Figure 3c represents the image of the fracture surface of cured epoxy curing with dendritic p-Im-b-TDI curing agent (the mole ratio of —OH (from p1000) to —NCO (from TDI) was 1:100). An obvious rough and wire drawing was observed on the fracture surface. In this curing system, the hyperbranching p1000 can form the dendritic structure to toughen epoxy resin at the presence of TDI as cross-linking monomer. A certain amount of toughening segment of p1000-based dendritic group was released and distributed uniformly into the cured epoxy system and formed the three dimensional net cross-linking structure to induce phase separations via the removal of thermal energy[53], which significantly improves the toughness of epoxy resin. With increasing the molar ratio, the wire drawing disappeared and the fracture surface became rougher as shown in Figure 3d. The surface roughness indicated ductile fracture, caused by the presence of the second phase [54]. The second phase can stop crack propagation via segmented cracking, reduction of the crack propagation rate, and bowing out around dendrimers, thereby improving tension around this second phase due to plastic zone enhancement. A triaxial tension zone change can lead to cavitation, i.e., detachment of added particles, which is an additional toughness mechanism that allows higher energy consumption and consequently a toughening improvement in the epoxy system[54]. There was not apparent sign of phase separation compared with the typical phase separation system which has some toughening segments with size of a few micrometers[42] (Figure 3c and 3d). Based on the microscopic results, we can concluded that the introduction of dendritic p1000 into the epoxy curing system give rise to the dendritic three-dimensional toughening structure, which significantly improves the toughness property of the cure epoxy without sacrificing other properties.

3.4 Dynamic mechanical and thermodynamic analyses

The dynamic mechanical properties were characterized using a TA Instrument DMA 800. The storage modulus (E') represents the ability of material to store energy in a cycle due to the elastic deformation, which is related to the stiffness of the material. The loss modulus (E'') represents the energy dissipated as heat, representing the viscous portion. The loss factor (tanδ) can be obtained by the ratio of loss modulus to storage modulus. The peak value of tanδ curve of DMA test reflects the glass transition temperature (T_g) of polymer.

Figures 4 and 5 show curves of loss factor and storage modulus as a function of temperature for epoxy resin cured with different curing agents. As seen in the Figure 4, the values of T_g (defined as the peak temperature of loss factor curve) of epoxy resin cured with different curing agents are obviously different. The epoxy resin cured by neat imidazole or imidazole blocked TDI has single peak (T_g), which is associated with main chain movement and is defined as alpha transition ($T_α$). Whereas the epoxy resin cured by p-Im-b-TDI has double peak, besides the prominent alpha transition ($T_α$) there appears another transition called beta transition ($T_β$) at lower temperature. The beta transition is associated with the movements of side chain or pendant group and is often related to the toughness of a polymer[55,56]. The stronger perk of beta transition is due to the strong movements of side chain or pendant group from p1000. The higher content of p1000, the lower $T_α$ or T_g the cured resin has. It exhibits a wide range from 108℃ to 129℃ for the resins investigated here. From Figure 4, it can be concluded that the gradually decreased T_g is due to the increasing of three-dimensional dendritic structural group in the cured system introduced by the p1000. As a result, the toughness of the cured resin was significantly improved. This further confirms the conclusion drawn from Figure 3c and 3d.

The storage modulus (material stiffness) of epoxy resin cured by different curing agents is shown in the Figure 5. As seen from the figure that epoxy resin cured by the neat imidazole shows highest E′ (strongest stiffness), which is due to lack of flexible group from imidazole that can toughen the epoxy resin, whereas the curves for the epoxy resins cured by Im-b-TDI and p-Im-b-TDI show a crossover at a certain temperature. The storage modulus of epoxy resin cured by p-Im-b-TDI exceeds that cured by Im-b-TDI at the low temperature. When the temperature reaches a certain point, the opposite behavior was observed and the storage modulus of epoxy resin cured by p-Im-b-TDI was decreased rapidly. This demonstrated that the dendritic structural unit can be used as rigid component to improve the stiffness of epoxy resin at the low temperature. The mobility of the three-dimensional dendritic flexible segment increases with increasing the testing temperature, which results in the rapid decrease of storage modulus of the system of p-Im-b-TDI. With the increasing of p1000 content, the decreasing was more obvious.

Figure 6 displays the DSC curves of epoxy resin cured by different curing agents. It can be seen from the figure that exothermic peak of epoxy resin cured by different curing agent shows slight difference. The imidazole is one of the highly active curing agents in conventional curing agents of epoxy resin. Using imidazole to cure the epoxy resin, the exothermic peak is generally about 115℃. When the epoxy resin was cured by the prepared curing agent, the exothermic temperature is slightly higher than the curing temperature of imidazole. Furthermore, as the content of p1000 increasing, the peak value gradually increased. About this experimental phenomena, it can be illustrated by the curing activity of imidazole that once imidazole was single used to cure the epoxy resin, its activity was greater than other curing agents. Contrarily, when imidazole was firstly used to block isocyanate for the preparation of p-Im-b-TDI curing agent, the imidazole molecule will be fixed on the surface of the three-dimensional dendritic p1000-TDI macromolecule. During the curing process, the deblocking reaction of this curing reactive system initially occurred to release imidazole and —NCO group. After that the curing reaction occurred, in which the epoxy resin was cured by the released imidazole and —NCO group. In this reactive process, the reactive activity of imidazole was equivalent to being reduced.

3.5 Mechanical performance

The brittleness of epoxy resin due to its structural property significantly restricts its application. To overcome this drawback to improve flexibility, toughening epoxy resin is essential. Figure 7 and Figure 8 demonstrated the impact strength and tensile shear strength of epoxy resin with (p1000-Im-b-TDI curing) and without (imidazole curing) toughening treatment. From Figure 7, it is obvious that the impact strength of epoxy resin cured with p1000-Im-b-TDI is higher than that cured by neat imidazole. The effect of p1000 on the impact strength was also shown in the Figure 7. As seen from the figure that there exists an optimal content of p1000 at which the cured system exhibits the highest impact strength of 16.09 kJ/m^2. The optimal value of p1000 is 1% (mol %). The tensile shear strength shown in Figure 8 exhibits the similar trend as that shown in Figure 7 i. e., the tensile shear strength increased first, and reaches maximum value of 10.92 MPa at 1% content of p1000 and then decreased gradually. This further confirms that the three-dimensional dendritic structure introduce by hyperbranching p1000 toughens the epoxy resin. During the curing process, the blocked TDI (p-Im-b-TDI) firstly deblocked to release the imidazole and the naked —NCO group. The —NCO group can react with the —OH group on the epoxy chain, which introduces the dendritic toughening segment from p1000 into the epoxy macromolecule. The toughening segment effectively toughens the epoxy resin and results in improve toughness with appropriate content of p1000. However, the excessive toughening segment had negative effects on the mechanical properties for the epoxy resin. The optimal content of p1000 to achieve the maximum impact and tensile shear strength is 1%.

3.6 Curing and toughening mechanism

Based upon the above design of functional curing agent and the experimental results of epoxy resin, the curing and toughening mechanism of functional p1000-Im-b-TDI was proposed as shown in Scheme 2. In order to cure and toughen epoxy resin at the same time, the toughening segment and curing group was compounded into a hyperbranched polymer, i.e. the dendritic structural polymer, which played a crucial role for the curing and toughening of epoxy resin. At early stage of curing, the blocked isocyanate can be deblocked to release the dissociative imidazole and the isocyanate end group as temperature reached the deblocked temperature. The curing started once the deblock occurred and the curing process was very complicated due to the simultaneous multi-reactions. The bisphenol-A type epoxy molecule reacts as a long chain polyol with epoxy structures. The large number of secondary hydroxyl groups can react with —NCO groups in isocyanate to form dendritic epoxy as shown in Scheme 2(1). Meanwhile, the epoxy rings can be open by the secondary amine from the dissociative imidazole and formed the secondary hydroxyl groups as seen in the Scheme 2(2). The newly formed secondary hydroxyl groups from the ring-opening reaction can continually react with the —NCO groups from cross-linking structure, as shown in the Schemes 2(3) and 2(4). Thus, the three dimensional dendritic cross-linking structure was obtained by using p1000-Im-b-TDI with hyper-branched polyester polyol in p1000. Furthermore, the dendrimer would react with epoxy groups owing to the existence of —NH— in carbamate (Scheme 2(5)). Therefore, cured epoxy resin has three dimensional dendritic cross-linking structure with uniformly dispersedp1000 as the cross-linking point.

Introduction of the toughening segment of p1000 into the curing system improves the toughness of the final product. In addition, internal cavities introduced by dendritic p1000 units also had a certain degree of toughening effect for the cured epoxy resin. Therefore, the curing and toughening occurred simultaneously for the system cured byp1000-Im-b-TDI as the curing agent.

Conclusions

Functional toughening and curing agent (p-Im-b-TDI) was synthesized using dendritic p1000 as the toughening segment and imidazole blocked isocyanate as the functional group. During the epoxy curing process, p-Im-b-TDI releases the dissociative imidazole and isocyanate group, which introduces the toughening segment from p1000 into the curing system to effectively toughen the epoxy resin. The simultaneous toughening and multiple curing mechanism was proposed.

Dynamic mechanical tests indicated that the content of p1000 has significant effects on T_g of cured epoxy resin, the higher content of p1000 the lower T_g the cure product has. However the excessive content of p1000 does not benefit the impact and tensile shear strength of the cured system. There exists an optimal content of p1000 to achieve the maximum impact and tensile shear strength, which is 1% p1000.

Acknowledgements

This research was supported by the Heilongjiang Province Science and Technology Agency [grant number E201230].

References

[1] Emel Y, Özdemir Ö, Tülay Yİ, Abdülkadir K, Attila G. Toughening of Epoxy Resins by Amine Terminated Poly(arylene ether ketone)s having Pendant Tertiary Butyl Groups. Polym Bull 2007; 58: 503-512.

[2] Dhevi DM, Prabu AA, Heecheul K, Pathak M. Studies on the toughening of epoxy resin modified with varying hyperbranched polyester-toluene diisocyanate content. J Polym Res 2014; 21:503-511.

[3] Zhang Y, Shang CY, Yang X, Zhao XJ, Huang W. Morphology and properties of TGDDM/DDS epoxy systems toughened by amino-bearing phenyl silicone resins. J Mater Sci 2012; 47: 4415-4427.

[4] Blanco I, Oliveri L, Cicala G, Recca A. Effects of novel reactive toughening agent on thermal stabilityof epoxy resin. J Therm Anal Calorim 2012; 108: 685-693.

[5] Akbari R, Beheshty MH, Shervin M. Toughening of dicyandiamide-cured DGEBA-based epoxy resins by CTBN liquid rubber. Iran Polym J 2013; 22: 313-324.

[6] Brocks T, Ascione L, Ambrogi V, Cioffi MOH, Persico P. Efficiency comparison of hyperbranched polymers as toughening agents for a one-part epoxy resin. J Mater Res 2015; 30:869-878.

[7] Yang XT, Yi FP, Xin ZR, Zheng SX. Morphology and mechanical properties of nanostructured blends of epoxy resin with poly(1-caprolactone)-block-poly (butadiene-co-acrylonitrile)-block-poly (1-caprolactone) triblock copolymer. Polym 2009; 50 (16): 4089-4100.

[8] Samanta B, Maity T, Banthia AK. Modification of cured epoxy with amine functional chloroaniline formaldehyde condensate. Pigm Resin Technol 2009; 38(3): 143-152.

[9] Cengiz C, Guneri A, Cevdet K. Modification of epoxy by a liquid elastomer and solid rubber particles. Polym Bull 2004;51:429-435.

[10] Kong J, Ning RC, Tang YS. Study on modification of epoxy resins with acrylate liquid rubber containing pendant epoxy groups. J Mater Sci 2006;41:1639-1641.

[11] Kong J, Tang YS, Zhang XJ, Gu JW. Synergic effect of acrylate liquid rubber and bisphenol A on toughness of epoxy resins. Polym Bull 2008;60:229-236.

[12] Kinlooch AJ, Taylor AC. The mechanical properties and fracture behaviour of epoxy-inorganic micro- and nano-composites. J Mater Sci 2006;41:3271-3297.

[13] Wang MH, Yu YF, Li SJ. Polymerization-induced phase separation in polyether sulfone modified epoxy resin systems: effect of curing reaction mechanism. Sci China Ser B-Chem 2007;50(4):554-561,.

[14] Yan C, Xiao KQ, Ye L, Mai YW. Numerical and experimental studies on the fracture behavior of rubber-toughened epoxy in bulk specimen and laminated composites. J Mater Sci 2002;37:921-927.

[15] Becu L, Taha M, Maazouz A, Merle G. Dispersion state and mechanical properties of core-shell particle modified epoxy networks. J Mater Sci 2002;37:41-49.

[16] Ormaetxea M, Forcada J, Mugika F, Valea A, Martin MD, Marieta C, Goyanes S, Mondragon I. Ultimate properties of rubber and core-shell modified epoxy matrices with different chain flexibilities. J Mater Sci2001;36:845-852.

[17] Bray DJ, Dittanet P, Guild FJ, Kinloch AJ, Masania K, Pearson RA, Taylor AC. The modelling of the toughening of epoxy polymers via silica nanoparticles: The effects of volume fraction and particle size. Polym 2013;54:7022-7032.

[18] Huang Y, Kinlocht AJ. The sequence of initiation of the toughening micromechanisms in rubber-modified epoxy polymers. Polym 1992;33(24):5338-5340.

[19] Bagheri R , Marouf BT, PearsonRA. Rubber-Toughened Epoxies: A Critical Review. J Macromol Sci Part C: Polym Rev 2009;49:201-225.

[20] Pearson RA, Yee AF. Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide), Polym 1993; 34(17):3658-3670.

[21] Velthem PV, Ballout W, Horion J, Janssens YA, Destoop V, Pardoen T, Bailly C. Morphology and fracture properties of toughened highly cross-linked epoxy composites: A comparative study between high and low T_g tougheners. Compos Part B 2016;101:14-20.

[22] Sun Z, Shi SS, Hu XZ, Guo X, Chen JY, Chen HR. Short-aramid-fiber toughening of epoxy adhesive joint between carbon fiber composites and metal substrates with different surface morphology. Compos Part B 2015;77:38-45.

[23] Xu F, Du XS, Liu HY, Guo WG, Mai YW. Temperature effect on nano-rubber toughening in epoxy and epoxy/carbon fiber laminated composites. Compos Part B 2016;95: 423-432.

[24] Wan JT, Bu ZY, Xu CJ, Li BG, Fan H. Learning about novel amine-adduct curing agents for epoxy resins: Butyl-glycidylether-modified poly(propyleneimine) dendrimers. Thermochim Acta 2011; 519: 72-82.

[25] Nguyen FN, Berg JC. Novel core–shell (dendrimer) epoxy tougheners: Processing and hot-wet performance. Compos Part A 2008; 39: 1007-1011.

[26] Selin M, Peltonen L, Hirvonen J, Bimbo LM. Dendrimers and their supra molecular nanostructures for biomedical applications. J. Drug Delivery Sci Techn 2016;02.008: 1-11.

[27] Bosman AW, Janssen HM, Meijer EW. About Dendrimers: Structure, Physical Properties, and Applications. Chem Rev 1999; 99:1665-1688.

[28] Emrick T, Chang HT, Fréchet JMJ. An A2 + B3 approach to hyperbranched aliphatic polyethers containing chain end epoxy substituents. Macromolecules 1999;32:6380-6382.

[29] Emrick T, Chang HT, Fréchet JMJ, Woods J, Baccei L. Hyperbranched aromatic epoxies in the design of adhesive materials. Polym Bull 2000;45:1-7.

[30] Wan JT, Li C, Bu ZY, Fan H, Li BG. Acrylonitrile-capped poly(propyleneimine) dendrimer curing agent for epoxyresins: Model-free isoconversional curing kinetics, thermal decomposition andmechanical properties. Mater Chem Phys 2013;138:303-312.

[31] Wan JT, Bu ZY, Xu CJ, Li BG, Fan H. Preparation, curing kinetics, and properties of a novel low-volatile starlike aliphatic-polyamine curing agent for epoxy resins. Chem Eng J 2011;171:357-367.

[32] Wan JT, Fan H, Li BG, Xu CJ, Bu ZY. Synthesis and nonisothermal reaction of a novel acrylonitrile-capped poly(propyleneimine) dendrimer with epoxy resin. J Therm Anal Calorim 2011;103:685-692.

[33] Che JF, Yuan W, Jiang GH, Dai J, Lim SY, Chan-Park MB. Epoxy composite fibers reinforced with aligned single-walled carbon nanotubes functionalized with generation 0-2 dendritic poly(amidoamine). Chem Mater 2009;21:1471-1479.

[34] Cheng YY, Xu TW, He PS. Polyamidoamine dendrimers as curing agents: the optimum polyamidoamine concentration selected by dynamic torsional vibration method and thermogravimetric analyses. J Appl Polym Sci 2007;103:1430-1434.

[35] Liu HW, Wilén CE, Skrifvars M. Reaction of epoxy resin and hyperbranched polyacids. J Polym Sci: Part A: Polym Chem, 2000;38:4457-4465.

[36] Okazaki M, Murota M, Waguchi Y, Tsubokawa N. Curing of epoxy resin by ultrafine silica modified by grafting of hyperbranched polyamidoamine using dendrimer synthesis methodology. J Appl Polym Sci 2001;80:573-579.

[37] Sidorenko A, Zhai XW, Simon F, Pleul D, Tsukruk VV. Hyperbranched molecules with epoxy-functionalized terminal branches: grafting to a solid surface. Macromolecules 2002;35: 5131-5139.

[38] Sun LY, Warren GL, O'Reilly JY, Everett WN, Lee SM, Davis D, Lagoudas D, Sue HJ. Mechanical properties of surface-functionalized SWCNT/epoxy composites. Carbon 2008;46:320-328.

[39] Xu DM, Zhang KD, Zhu XL. Curing of DGEBA epoxy resin by low generation amino-group-terminated dendrimers. J Appl Polym Sci 2006;101:3902-3906.

[40] Cheng YY, Chen DZ, Fu RQ, He PS. Behavior of polyamidoamine dendrimers as curing agents in bis-phenol A epoxy resin systems. Polym Int 2005;54:495-499.

[41] Shiravand F, Ascione L, Persico P, Carfagna C, Brocks T, Cioffi MOH, Puglisi C, Samperi F, Ambrogi V. A novel hybrid linear–hyperbranched poly(butylene adipate) copolymer as an epoxy resin modifier with toughening effect. Polym Int 2016; 65: 308-319.

[42] Tang B, Liu XB, Zhao XL, Zhang JH. Highly efficient in situ toughening of epoxy thermosets with reactive hyperbranched polyurethane, J Appl Polym Sci 2014; DOI: 10.1002/APP.40614

[43] Xu G, Shi WF, Shen SJ. Curing kinetics of epoxy resins with hyperbranched polyesters as toughening agents. J Polym Sci: Part B: Polym Phys 2004;42:2649-2656.

[44] Lou CH, Kong XZ, Wang JX, Ma LQ. Toughening of epoxy resins by modified m-phenylene diamine having soft ether chain. J App Polym Sci 2012;125:578-583.

[45] Lou CH, Gu JY, Di MW, Ma LQ, Wang YZ, Liu XJ. Synthesis and characterization of trichlorophenol-blocked polyaryl polyisocyanate. Iran Polym J 2011;20(3):247-255.

[46] Sankar G, Nasar AS.Effect of isocyanate structure on deblocking and cure reaction of N-methylaniline-blocked diisocyanates and polyisocyanates. Eur Polym J 2009;45:911-922.

[47]Subramani S, Park YJ, Lee YS, Kim JH. New development of polyurethane dispersion derived from blocked aromatic diisocyanate. Prog Org Coat 2003;48:71-79.

[48]Gnanarajan TP, Iyer NP, Nasar AS, Radhakrishnan G. Preparation and properties of poly(urethane-imide)s derived from amine-blocked-polyurethane prepolymer and pyromellitic dianhydride. Eur Polym J 2002;38:487-495.

[49] Yin LG, Liu YL, Ke Z, Yin JH. Preparation of a blocked isocyanate compound and its grafting onto styrene-b-(ethylene-co-1-butene)-b-styrene triblock copolymer. Eur Polym J 2009;45:191-198.

[50] Naruhito H, Kentaro A, Akio T. Effect of the ethylene/vinyl acetate ratio of ethylene-vinyl acetate emulsion on the curing behavior of an emulsion polymer isocyanate adhesive for wood. J wood sci 2008;54:294-299.

[51] Ishizu K, Makino M, Hatoyama N, Uchida S. Emulsion-induced ordered microporous films using amphiphilic poly(ethylene oxide)-block-poly(n-butyl isocyanate) block copolymers. J Appl Polym Sci 2008;108:3753-3759.

[52] Misaki T, Hirohata T, Yoshii M, Hamasaki T. Properties of networks obtained by internal plasticization of epoxy resin with aromatic and aliphatic glycidyl compounds. J Appl Polym Sci 1989;37:2617-25.

[53] Lloyd DR. Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation, J Membr Sci 1990;52:239-261.

[54] Brocks T, Ascione L, Ambrogi V, Cioffi MOH, Persico P. Efficiency comparison of hyperbranched polymers as toughening agents for a one-part epoxy resin. J Mater Res 2015;30(6):869-878.

[55] Krevelen DV. Properties of polymers, Elsevier: New York, 1972.

[56] Menard KP. Dynamic mechanical analysis: A practical introduction, second edition. Taylor & Francis Group: New York, 2008.

Figures:

Scheme 1 Synthesis of functional curing agents

Scheme 2 Scheme of curing and toughening epoxy resin

Figure 1 FTIR spectra of blocked isocyanates with p1000 as soft segments

Figure 2 FTIR spectra of cured epoxy resin systems with different curing agents

Figure 3 SEM micrographs of epoxy resins cured by different curing agent

Note: Curing agent: a: MI; b: MI-b-TDI; c: p1000-MI-b-TDI (n_{-OH}:n_{-NCO} is 1:100); d: p1000-MI-b-TDI (n_{-OH}:n_{-NCO} is 13:100)

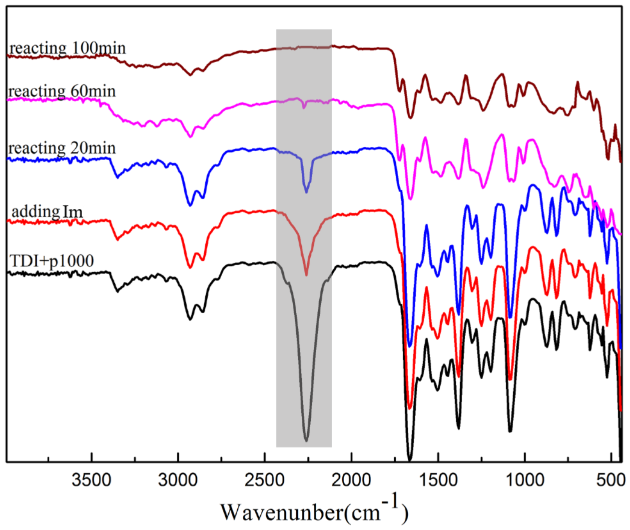
Figure 4 Effect of different curing agents on tan δ

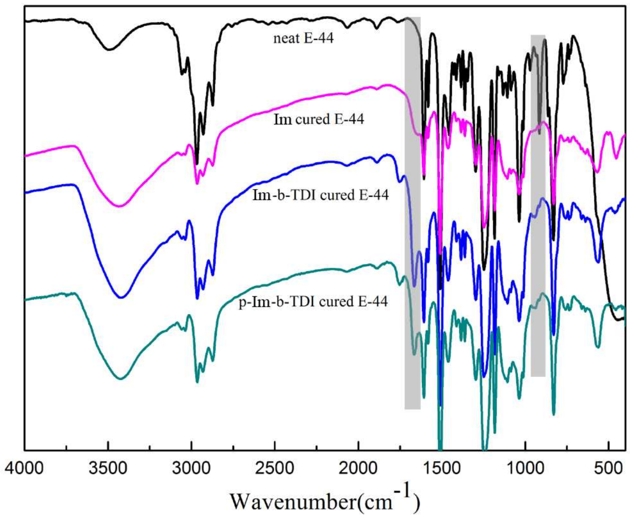
Figure 5 Effect of different curing agents on storage modulus

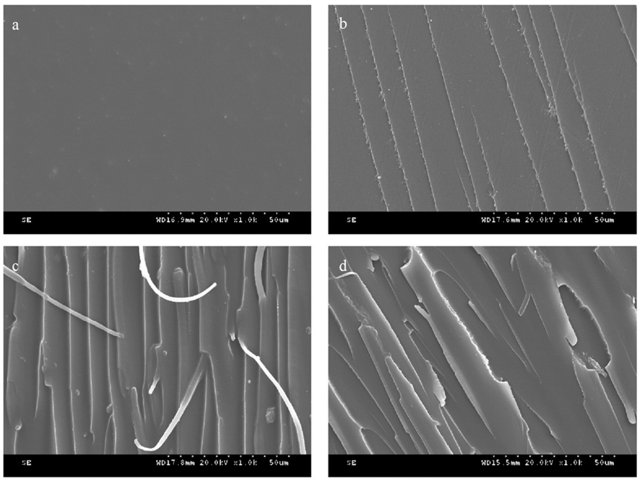
Figure 6 DSC curves of different curing agents cured epoxy resins

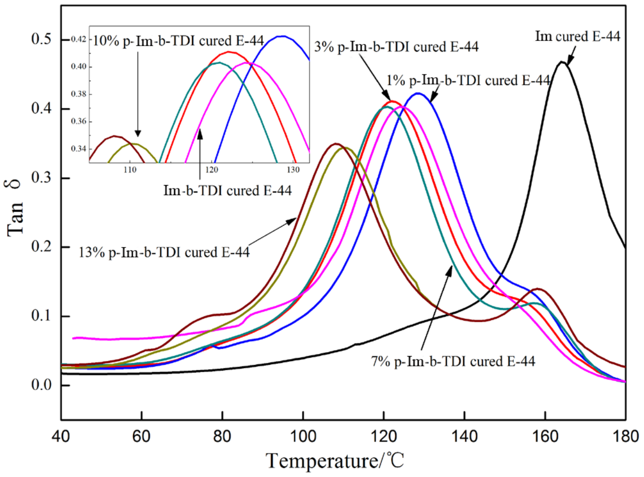
Figure 7 Impact strength of E-44 cured by different curing agents

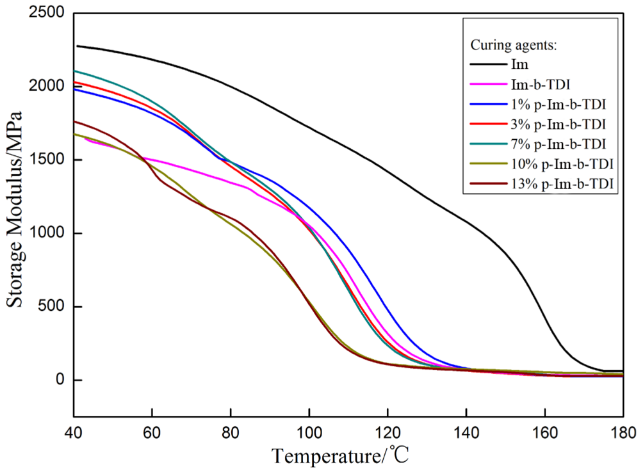
Figure 8 Tensile shear strength of E-44 cured by different curing agents

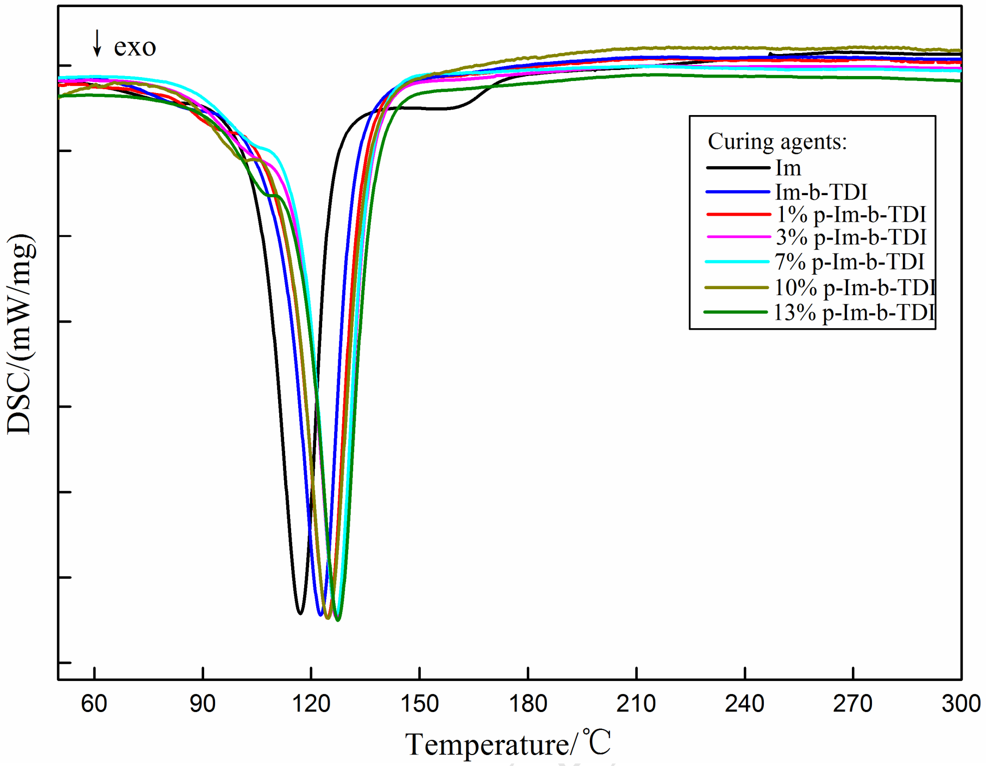

reacting 100min
reacting 60min
reacting 20min
adding Im
TDI+p1000
3500
3000
2500
2000
1500
1000
500
Wavenunber(cm^{-1})

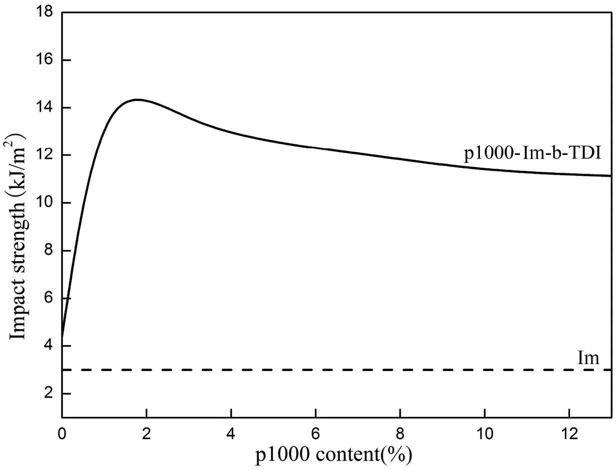

neat E-44
Im cured E-44
Im-b-TDI cured E-44
p-Im-b-TDI cured E-44
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm^{-1})

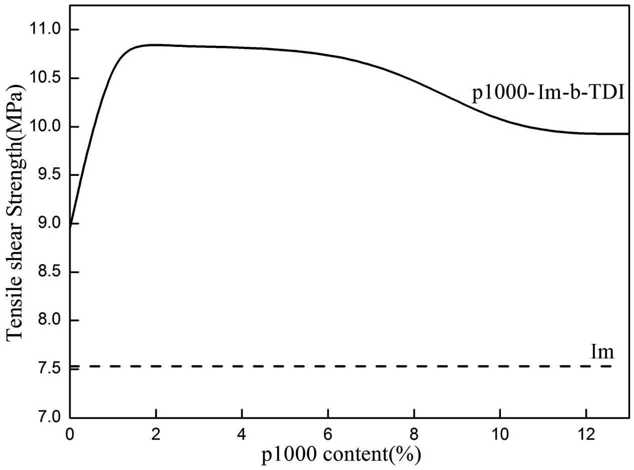

a
SE
WD16.9mm 20.0kV x1.0k 50um
b
SE
WD17.6mm 20.0kV x1.0k 50um
c
SE
WD17.8mm 20.0kV x1.0k 50um
d
SE
WD15.5mm 20.0kV x1.0k 50um

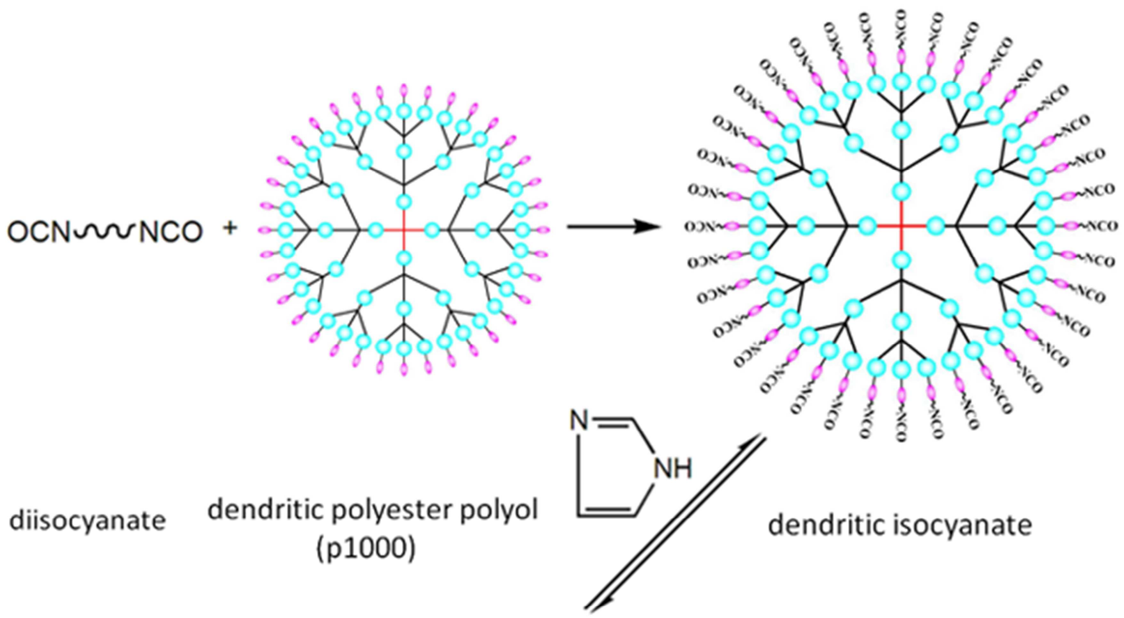

0.42
0.40
0.38
0.36
0.34
110
120
130
10% p-Im-b-TDI cured E-44
Im-b-TDI cured E-44
3% p-Im-b-TDI cured E-44
1% p-Im-b-TDI cured E-44
Im cured E-44
13% p-Im-b-TDI cured E-44
7% p-Im-b-TDI cured E-44
Tan δ
0.5
0.4
0.3
0.2
0.1
0.0
40
60
80
100
120
140
160
180
Temperature/℃


Storage Modulus/MPa
2500
2000
1500
1000
500
0
40
60
80
100
120
140
160
180
Temperature/℃
Curing agents:
Im
Im-b-TDI
1% p-Im-b-TDI
3% p-Im-b-TDI
7% p-Im-b-TDI
10% p-Im-b-TDI
13% p-Im-b-TDI

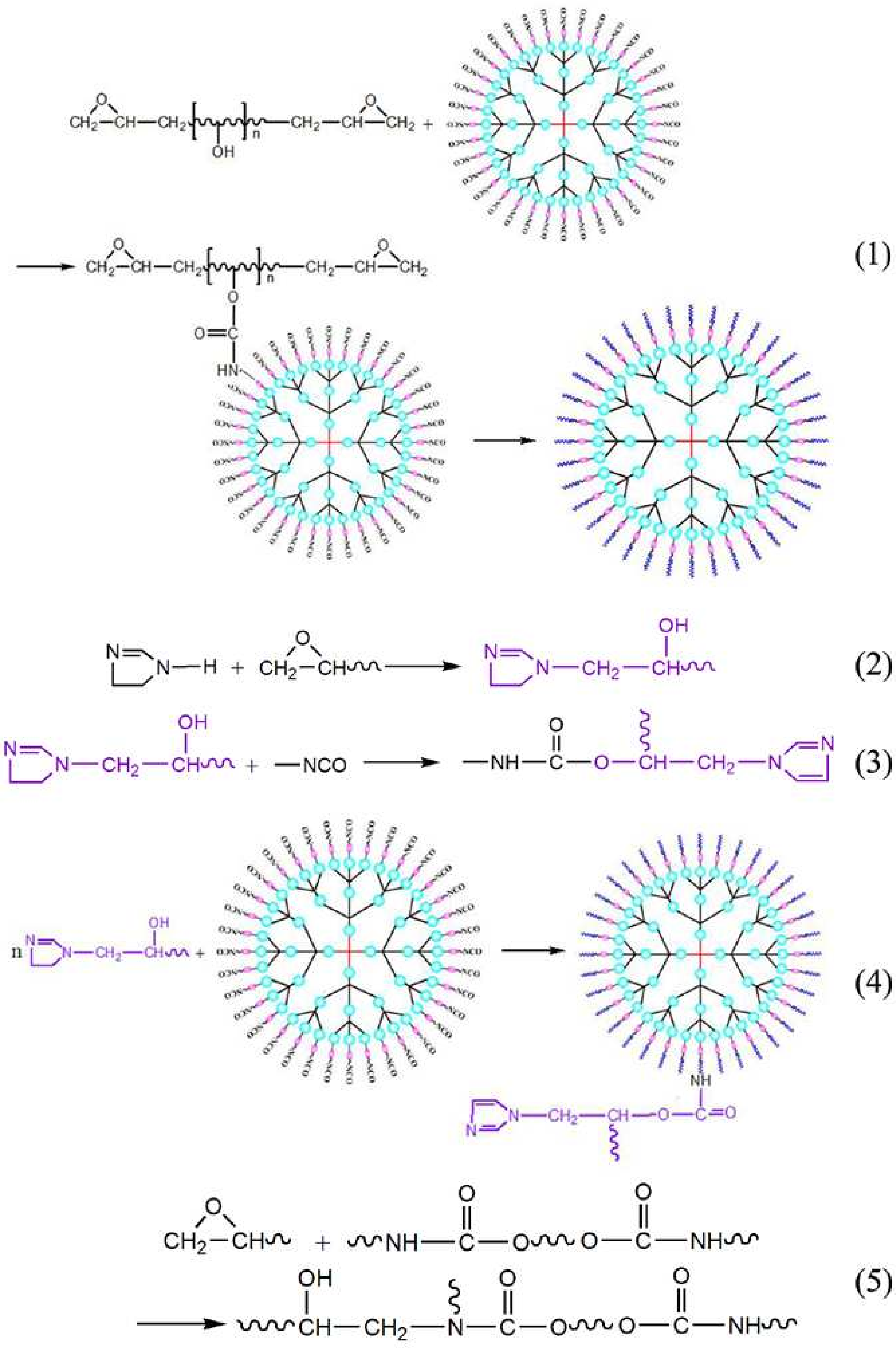

↓ exo
Curing agents:
Im
Im-b-TDI
1% p-Im-b-TDI
3% p-Im-b-TDI
7% p-Im-b-TDI
10% p-Im-b-TDI
13% p-Im-b-TDI
DSC/(mW/mg)
60
90
120
150
180
210
240
270
300
Temperature/℃


Impact strength (kJ/m^2)
p1000 content(%)
p1000-Im-b-TDI
Im
2
4
6
8
10
12
14
16
18
0
2
4
6
8
10
12


Tensile shear Strength(MPa)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
0
2
4
6
8
10
12
p1000 content(%)
p1000-Im-b-TDI
Im



blocked isocyanate
polyfunctional curing agent


CH2–CH–CH2 [ ]n –CH2–CH–CH2 +
OH
O
O=C
HN
NCO
(1)
N–H + CH2–CH → N–CH2–CH
(2)
–NCO → –NH–C–O–CH–CH2–N
(3)
n
(4)
NH
N–CH2–CH–O–C=O
CH2–CH + NH–C–O O–C–NH
→ CH–CH2–N–C–O O–C–NH
(5)