

Self-toughening of epoxy resin through controlling topology of cross-linked networks



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ABSTRACT

A new strategy to toughen epoxy resins through control of topological structure of cross-linking network has been presented. With a tertiary amine initiator, the curing proceeded via chain-wise polymerization. The impact strength of epoxy resin increased to above 84 kJ/m² by only increasing the curing temperature, which is much higher than the reported value of 10–30 kJ/m² for pure epoxy resin. Meanwhile, yielding was found during uniaxial tensile and three-point bending measurements. At the molecular scale, the cross-linking density showed a bimodal distribution and decreased with increasing curing temperature. A mechanism based on controlled topology of cross-linking network has been proposed to explain these changes. The cross-linking of epoxy resins occurs via a continuous anionic ring-opening polymerization, resulting in well interpenetrated chains. The chain transfer converts active alkoxide anions into inactive hydroxyls, limiting the linear growth and cross-linking. The resultant branching structures display lower cross-linking density, serving as native tougheners at the segment scale. Chain transfer accelerates with temperature, thus the ductility increases monotonically with curing temperature. This mechanism was confirmed by deliberately introducing branching chains through a short time of high-temperature reaction at the first stage of curing. The impact strength was enhanced by 2.5 times in comparison to the samples without the initial high-temperature curing. This unique and facile strategy shows potential in directly obtaining more ductile epoxy resins materials by controlling the topology of cross-linked networks.

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1. Introduction

Epoxy resins are widely used thermosets due to their good mechanical properties, high thermal and chemical stability [1–3]. These properties originate from their highly cross-linked network structures. On the other hand, the cross-linked network also makes epoxy resins intrinsically brittle materials. For example, the high cross-linking density leads to a short chain length between the cross-linking points, such as 200–400 g/mol [4–6]. When subjected to deformation, the available strain becomes low and this poor toughness greatly restricts the application of epoxy resins.

It is a long-time pending question that whether the toughness of epoxy can be improved by controlling the topology of the cross-linking network. The most straightforward way to improve the toughness of epoxy resin is through reduction of the cross-linking

density. In early work, amine-cured epoxies were frequently used as model systems. Reduction of the cross-linking density have been attempted through adding nonstoichiometric hardener [7], using epoxy resins or hardeners with different molecular weight [8,9] and incomplete curing [10,11]. However, through these approaches, only minor or moderate improvement in toughness could be achieved with significant sacrifice of other properties, e.g. tensile strength and flexural strength. These failures stimulated investigations of second-phase toughening methods. Rubber particles serving as the second phase are the most successful tougheners [12–16]. The toughness could be increased by even one order of magnitude; however, the modulus and strength decreased significantly. Later, it was found that rigid particles can simultaneously improve both toughness and modulus, while the efficiency was modest [17–20]. Other second-phase components, such as thermoplastic polymers [21–24], liquid crystal polymers [25–27], micelle forming block copolymers [28–30] had also been explored and the toughness could be improved. Though great successes have been achieved in second-phase toughened systems, the general

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disadvantages such as high viscosity and complexity in the control of phase separation, make pure epoxy more suitable in practical use.

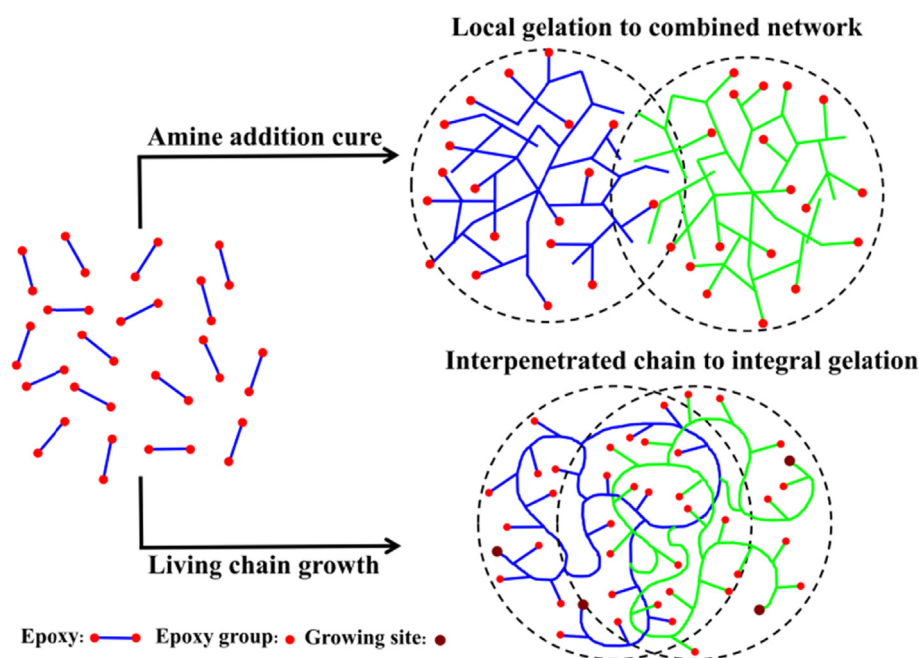
The variety in cross-linking pathways provides the possibility of toughening epoxy via controlling the topology of the cross-linking network. The failure in amine-cured epoxy system roots in the cross-linking pathway that gelled clusters connect at the boundary to form the final network, as shown in Scheme 1. For the amine hardeners, the epoxy resin and amine molecules form branching clusters via continuous addition reaction. The high reactivity makes all the amine groups as growth sites. The reactivity of the two hydrogen atoms is almost similar, except for some aromatic amines [31,32] (e.g. diaminodiphenylsulphone) and amines with strong steric hindrance [33,34]. Thus, once these clusters are formed they commonly become highly branched. The macroscopic gelation occurs at high conversion around 0.6 [35]. After that, these partially cross-linked clusters and the residual branching chains gradually combine to form the final network. The combination is limited at the boundary because the high conversion leads to a highly cross-linked core region. Evidently, lower conversion will weaken the connections between the clusters, which leads to a significant decrease in mechanical properties. The gelation point is determined only by the functionality of the initial molecules [36]. A lot of work showed that the fully cured structure is not affected by the curing kinetics [7,37,38]. Thus, any improvement on toughness can only be achieved by lowering the conversion and sacrificing other properties.

In contrast to the amine-cured epoxy, cross-linking occurs among interpenetrating branching chains in kinetic gelation, which gives a better control of the topology of the network. The kinetic gelation has been extensively investigated in chain-wise cross-linking systems [39,40]. The active species (free radicals and oxygen anions) randomly walk in space, resulting in a linear chain first. The branching, intrachain cyclic and interchain cross-linking topologies gradually appear with increased conversion. The interpenetration of formed chains occurs more easily since the linear chain growth gives a relatively loose chain. Gelation starts at a much lower conversion [41,42] (e.g. 0.1–0.2) and interpenetrating molecules

gradually become attached to the loose networks (Scheme 1). The chain transfer plays an important role in the network formation through chain branching, which determines the occurrence of interpenetration and gelation [42]. Meanwhile, branching causes steric hindrance. The growing sites with limited number cannot reach some of the reactive groups [43]; thus, the final conversion is less than unity. Intuitively, the topological features of interpenetration during cross-linking and reduced cross-linking density after final curing are beneficial for improving the toughness of the cross-linked network.

Several recent reports have given a hint on toughening epoxy via modification of network topology. Topological polymers (TPs), e.g. dendrimers and hyperbranched polymers, are first used to overcome the problem of high viscosity in particle-toughened epoxy [44,45]. The phase separation and toughening mechanism are similar to those of rubber-toughened system [46,47]. There have been reports where the end groups of TPs have been changed into epoxy groups, so that these TPs can participate in network formation, probably at a single molecule level [48,49]. The native cavity and fewer epoxy groups in TPs lead to lower cross-linking density. Interestingly, significant enhancement in impact strength was achieved, whereas, decrease in tensile strength and modulus was hardly observed. Similar results were also obtained when a reactive toughening agent was used [50]. These results imply the possibility of controlling the mechanical property through network topology.

In the present work, attempts have been made to control the network topology and the corresponding mechanical properties of epoxy resin through chain-wise cross-linking. *N,N*-dimethyl benzyl amine was used as the initiator in the curing process, during which linear chain growth competed with chain branching induced by chain transfer. The topological structure and corresponding mechanical properties were tuned by the temperature-accelerated chain transfer. A significant enhancement of the ductility was achieved through increased temperature, and the network showed a reduced cross-linking density. Based on these positively correlated results, a self-toughening mechanism assuming existence of native tougheners with lower cross-linking density was proposed.



Scheme 1. Schematic illustration of cross-linking pathways of amine addition curing via microgel combination and kinetic gelation through cross-linking of interpenetrated chains.

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