Characterization of Diene Monomers as Healing Agents for Autonomic Damage Repair

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Received 1 August 2005; accepted 20 September 2005
DOI 10.1002/app.23245
Published online 14 April 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: For effective autonomic healing of damaged polymers and composites, it is essential to understand how the encapsulated healing agent behaves during and after cure. In this study, two different diene monomers [dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB)] and their blends were investigated as candidate self-healing agents, using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DSC experiments for samples showed that DCPD has a melting transition while the blends and ENB have no melting in the temperature range measured. Samples for DMA were prepared and tested by two different methods in the presence of Grubbs catalyst. In the first case (method I), monomers were mixed with the catalyst directly. In the second case (method II), the catalyst was mixed with an epoxy/amine system and cured into a film that was polished to expose the catalyst. The cure behavior of monomer samples was examined on the epoxy/catalyst film. Method II is considered to be a simulative experiment, which can occur in a real situation for damaged epoxy matrix composite. It was found that acceleration of cure reaction and reduction of catalyst concentration is possible by blending DCPD with ENB from method I. Storage modulus (G′) value after cure in method II showed that a DCPD : ENB blend ratio of 1 : 3 reached the highest G′ value at shorter cure time and lower catalyst levels than other monomer combinations. DCPD and ENB are presumably responsible for increases in rigidity and reactivity, respectively. This may improve the healing efficiency in autonomic damage repairing applications. J Appl Polym Sci 101: 1266–1272, 2006

Key words: ROMP; rheology; curing of polymers; composites

INTRODUCTION

In polymer matrix composites, damage such as interfacial debonding and ply delamination is often initiated by matrix microcracks under load. Once this irreversible and normally invisible damage occurs within the composite, mechanical strength decreases and the structures lifetime is greatly shortened. An autonomic damage repairing technique in polymer matrix composites has generated significant attention, since the methodology for the repair was first reported in the literature.[1] The new repair concept involves recovery of mechanical strength by means of a liquid healing agent (monomer), which autonomically fills and vitrifies between crack planes. The healing agent is first microencapsuled in a polymer shell and then embedded in a host matrix with additional embedded catalyst. Upon damage-induced cracking, the healing agent is released into the cracks by capillary action when microcapsules are ruptured by the propagating crack fronts. The embedded catalyst in the matrix subsequently initiates polymerization of the released healing agent in the crack, preventing further crack development and healing the material.

In recent works,[1–8] dicyclopentadiene (DCPD) was used as a healing agent surrounded by a urea/formaldehyde (U/F) thermosetting resin thin wall to manufacture microcapsules for self-healing. Recovery in fracture toughness was observed in a fiber-reinforced polymer matrix composite[2,6] and a neat epoxy resin.[1,3,7,8] Average healing efficiency for a neat epoxy resin was 85% for specimens with a healing time (referred to as cure time in the remainder of the current work) of 48 h at RT with 2.5 wt % of Grubbs catalyst and 5 wt % of U/F microcapsules.[3] In the case of carbon fiber-reinforced epoxy composites with 5 wt % catalyst and 20 wt % U/F microcapsules, the maximum efficiency was 45% when cured at RT for 48 h and increased to 80% when heated at 80°C for 48 h.[6]

In the self-healing approach, there are several obstacles to be overcome for more effective healing. First

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Contract grant sponsor: Basic Research Program of the Korea Science and Engineering Foundation; contract grant number: R01–2002-000–00522–0.

of all, the rate of polymerization of the healing agent and the amount of catalyst required should be considered. Large amounts of catalyst and long periods of cure time are not desirable in practical applications. Therefore, it is essential to develop more reactive healing agents with lower catalyst loadings. Secondly, DCPD shows an endothermic peak beginning and extending from −5 to 15°C corresponding to the melting,[5] which means that the healing mechanism proposed may not work below this temperature. Development of healing agents with much lower freezing points is also an important requirement to the self-healing technique.

DCPD is capable of forming a crosslinked structure with high toughness and strength from a low molecular weight monomer through a ring opening metathesis polymerization (ROMP) mechanism[9–11] while 5-ethylidene-2-norbornene (ENB) polymerizes to a linear chain structure and may be inferior to DCPD in mechanical properties. However, ENB is known to be much faster in reaction.[12,13] Therefore, we may expect reduction of catalyst amount and effective healing within a short time period with higher mechanical properties by blending ENB with DCPD.

In this study, the thermal behavior using DSC and isothermal cure behavior at RT using DMA for DCPD, ENB, and their blends are investigated to develop more effective healing agents for the autonomic damage repairing technique.

EXPERIMENTAL

Two different diene monomers, dicyclopentadiene (DCPD, Acros Organics, Belgium), 5-ethylidene-2-norbornene (ENB, Aldrich Inc.), and their mixtures were characterized as candidate healing agents. Catalyst used was bis(tricyclohexylphosphine)benzyllidine ruthenium (IV) dichloride (Grubbs catalyst, Aldrich Inc.). The chemical structures of the monomers and the catalyst are represented in Figure 1. The compositions of the samples are shown in Table I.

Differential Scanning Calorimetry (Dupont 982, TA Instrument) was employed for all samples with no catalyst. About 5 mg of liquid sample was poured into a hermetic pan and tightly clamped with a cap on which four tiny holes were made to allow vaporization of the sample during testing. The temperature scans were made from −40 to 225°C at a heating rate of 10°C/min under a dry nitrogen atmosphere.

Dynamic mechanical analysis (DMA) is a versatile technique that may be used to simultaneously characterize both rheological and thermal/mechanical properties of a wide range of sample types.[14] Dynamic mechanical properties of the material are evaluated by either applying a small oscillating strain to the sample and measuring the resulting stress or by applying a periodic stress and measuring the strain. The quantitative properties measured under the controlled mechanical oscillation include storage modulus (G′) and loss modulus (G″). The storage modulus relates to the energy storing quality and is equivalent to the Young's modulus of an elastic solid, while the loss modulus relates to the dissipative and viscous component of the material. The ratio of loss (G″) to storage modulus (G′) is referred to as the mechanical damping (tan δ).

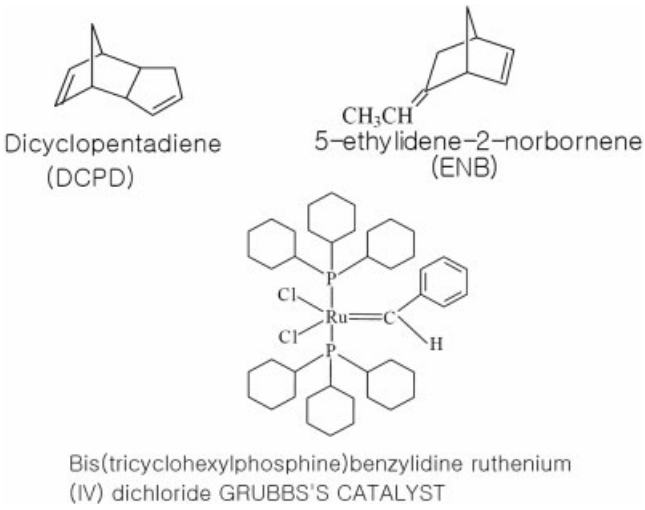


Figure 1 Chemical structures of two diene monomers and catalyst used in this study.

In the DMA experiment, two different methods for sample preparation were used to understand more clearly the cure of samples with catalyst for effective self-healing as shown in Figure 2: one (method I) was to mix the diene monomer directly with the catalyst, and the other (method II) was to mix the catalyst with an epoxy/amine system and then cure it in the form of film in which the cure behavior of the healing agent was to be examined. For method I, sample was vigorously mixed together with Grubbs catalyst for 10 s in a vial at room temperature. For method II, the catalyst was first mixed with epoxy (YD-115, Kukdo Chem., Korea) and hardener (KH-816, Kukdo Chem., Korea) at a stoichiometric ratio at room temperature for about 10 min to form a uniform mixture, coated on the aluminum plate, and cured in the oven at 40°C for 12 h. The uniform dispersion of the catalyst in the coating is very important in this experiment. The coating thickness was about 0.5 mm. The epoxy coating was polished with a sand paper (#2000) on the polisher at ~300 rpm, and then compressed air was used to clean the polished surface. The polishing is necessary to expose the catalyst covered by epoxy resin to the surface. Method II is especially designed to simulate the flowing of healing agent through a crack from fractured microcapsules and the subsequent in situ polymerization when the monomer contacts the catalyst in the matrix.

TABLE I
The Compositions of the Samples

	Sample				
	DCPD	D3E1	D1E1	D1E3	ENB
Monomer ratio by weight					
DCPD : ENB	1 : 0	3 : 1	1 : 1	1 : 3	0 : 1
Amount of catalyst (wt %)					
Method I catalyst in DCPD:					
ENB monomer	0.650	0.350	0.200		0.030
	1.000	0.500	0.350		0.050
	2.000	1.000	0.500	—	0.075
	5.000	2.000	0.750		0.100
Method II catalyst in epoxy	5.000		4.000	3.000	3.000
	7.000	—	5.000	4.000	4.000
	9.000		7.000	5.000	5.000
				7.000	7.000

DMA was performed using StressTech Rheometer (Reologica Instrument, Sweden) to investigate the isothermal cure behavior of samples reacting with catalyst in different weight percents. Two parallel plates, a stationary disc plate (ϕ = 30 mm) and an oscillatory upper plate (ϕ = 8 mm), accommodate approximately 50 mg of sample. Unreacted sample was injected into the gap between the plates in a sample holder. The epoxy resin/hardener system with catalyst was coated on a stationary plate for method II. The sample thickness was fixed to be 0.3 mm for method I and 0.15 mm for method II. Oscillation was imposed to the sample at a frequency of 1 Hz under an applied stress of 5 kPa for method I and 0.5 kPa for method II. The sample thickness and applied stress for both methods were determined from a series of preliminary tests.

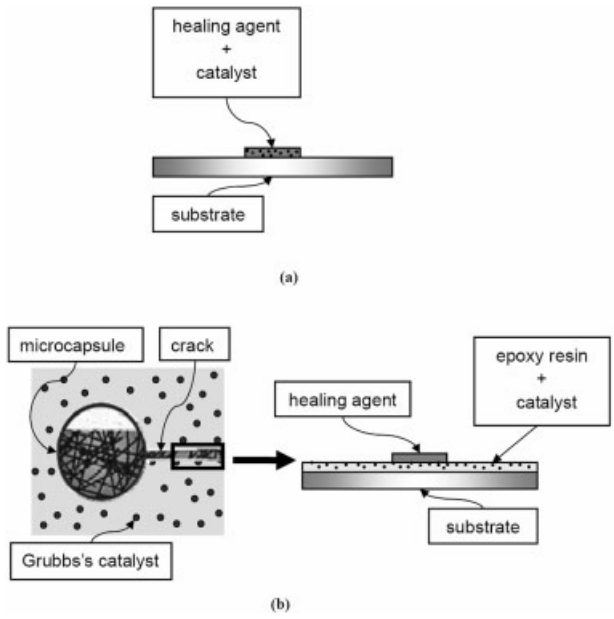


Figure 2 Samples preparation in two different methods: (a) method I and (b) method II.

All samples prepared by method I were cured at RT for 120 min and immersed into a good solvent (toluene in this experiment) up to 48 h. The weight of the samples was intermittently measured after complete drying for immersion times ranging from 0 to 48 h.

RESULTS AND DISCUSSION

Thermal behavior of samples with no catalyst

Figure 3 shows DSC thermograms for five samples (DCPD, D3E1, D1E1, D1E3, ENB) with no catalyst. DCPD showed two endothermic peaks: a small one at 15°C and a big one at 143°C, corresponding to melting transition and evaporation of the monomer, respectively. However, for either ENB or blends with DCPD, there was only one big endotherm due to evaporation with no melting point. The nonfreezing behavior is considered to be very important factor in real application of materials at low temperature for the self-healing technique. It has been visually observed that

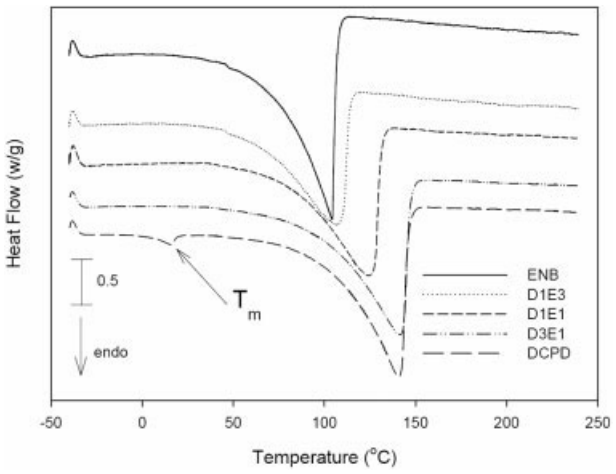


Figure 3 DSC thermograms of samples with no catalyst.

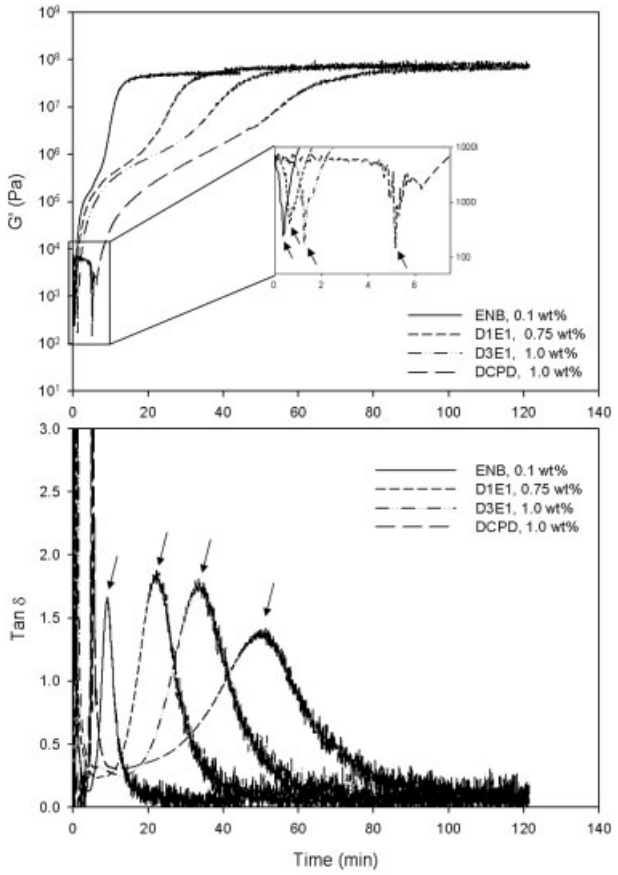


Figure 4 Typical G′ and tan δ versus time curves of samples with different amounts of catalyst for method I. (Gelation and vitrification time positions were marked by arrows).

ENB does not freeze in a freezer maintaining a constant −78°C. The endothermic peak position decreased with increase of ENB content. The continuous decrease of the endothermic peak from 143°C (DCPD) to 105°C (ENB) with increasing ENB indicates that DCPD and ENB are miscible in all proportions.

Isothermal cure behavior from method I

Understanding the cure process could be especially significant to improve performance qualities in network forming systems. During forming networks, extreme changes take place not only molecularly from monomers to highly crosslinked polymer, but also macroscopically (rheologically) from the fluid state prior to gelation to the glassy state after vitrification. In this study, dynamic mechanical properties, G′ and tan δ, were obtained for samples with various amounts of catalyst from method I during isothermal cure at RT. Typical G′ and tan δ versus time curves are shown for DCPD with 1.0 wt % of catalyst, D3E1 with 1.0 wt %, D1E1 with 0.75 wt %, and ENB with 0.1 wt % in Figure 4. There was substantial scattering in G′ and tan δ at the very beginning of cure time for all samples. The scattering may be due to the overly large oscillation of low viscous samples at the applied stress of 5 kPa. After that, G′ initially increased rapidly, and slowed down for a while, and then increased rapidly again, levelling off thereafter. Tan δ exhibited a clear and sharp peak in all cases. The whole G′ curve and tan δ peak shifted to a shorter time as ENB content increased even with lower amounts of catalyst for D1E1 and ENB. This means that ENB can accelerate the curing reaction for blends so that reduction of catalyst is also expected. Note that pure ENB showing the fastest reaction in the figure contains only 0.1 wt %, which is one tenth of the amount of catalyst used in DCPD. D1E3 was not tested in this case, but it is expected that the curve would be in between ENB and D1E1.

Gelation is defined by the incipient formation of branched molecule of mathematically infinite molecular weight on the molecular level. Macroscopically, there is a dramatic increase in viscosity. Beyond this point, processability decreases and resin flow is retarded greatly. During the process of vitrification, a stiff glassy solid is formed as a consequence of the network becoming tighter through further chemical reaction (crosslinking) and/or chain entanglement. Therefore, for the self-healing technique, it is helpful to estimate gelation time before which time the healing agent can flow into the crack planes, and vitrification time after which time the healing agent starts to reveal substantial stiffness for healing.

There are various ways to assign the location of gel point macroscopically. Dynamic parallel plate rheometry has been used to determine the macroscopic gel point at which viscosity increases abruptly.[15–17] Since the elasticity of the forming network begins to build at the gel point, the gelation has been taken as onset of the initial increase in modulus by DMA.[15,18] Vitrification is readily identified as a loss peak from DMA that accompanies a large increase in modulus during curing.[19] In this study, the times of the two rheological events, gelation and vitrification, were determined from onset of initial rise of the modulus (see the inset in the figure) and tan δ peak, respectively, as marked by arrows in Figure 4. Figure 5 shows the gelation and vitrification time as a function of catalyst amount for all samples. The times for the two events shorten with increase of catalyst amount in each sample and also with increase of ENB portion of the sample. However, the effect of catalyst and ENB was much greater in vitrification than gelation. Therefore, it is advantageous that, as ENB content increases, the time that the healing agent remains mobile (before gelation) does not shorten much, but stiffen rapidly thereafter (after vitrification). In the case of pure ENB, which does not form a chemically crosslinked structure, the gelation

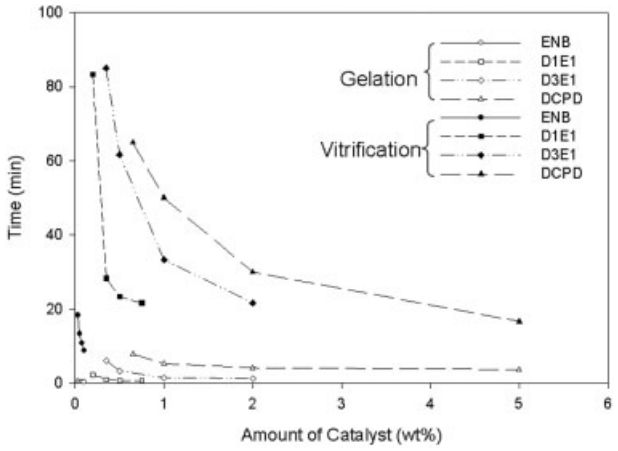


Figure 5 Gelation and vitrification time versus amount of catalyst for method I.

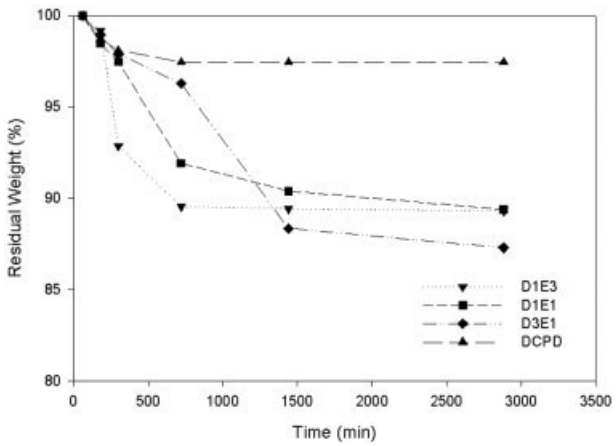
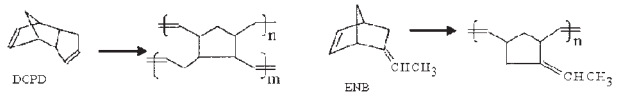


Figure 6 Weight loss versus immersion time in toluene for DCPD, D3E1, D1E1, and D1E3 cured for 120 min at RT.

may be due to physical crosslinking (i.e., entanglement) of chains.

DCPD forms a crosslinked structure so that the cured system will not dissolve, but swell in solvent; however, polymerized ENB with linear chains will dissolve. Reaction schemes for ROMP of DCPD and ENB are shown below:



In this study, samples were immersed in a good solvent and their weights were measured after drying to examine what chain structure can be formed in blends after curing. As expected, ENB cured for 40 min completely dissolved in the solvent, but loss of weight was observed for DCPD, D3E1, D1E1, and D1E3 after curing for 120 min. The cure times (40 min for ENB and 120 min for the rest of the samples) were the end of the test for each sample in Figure 4. Note that the times are after G′ levels off. Figure 6 shows the variation of weight faction (w_t/w_o where w_t and w_o are the dried weight after and before immersion, respectively) for the cured samples, which were immersed for different times up to 48 h. The weight fraction initially dropped and then maintained almost constant with time for all samples. The loss of weight was about 3% in DCPD, indicating an almost fully crosslinked structure. It is interesting that DCPD/ENB blends have about 10% weight loss regardless of blending ratios. This indicates that ENB can also be crosslinked by blending with DCPD, leading to a copolymerized network containing the same amount of soluble fraction.

Storage modulus (G′) during isothermal curing from method II

From method I, we realize that the reaction rate is increased by adding ENB to DCPD with even reduced amounts of catalyst. However, in self-healing applications, the healing agent is supposed to be cured by contacting catalyst particles embedded in a polymer matrix. Therefore, it is worthwhile to investigate the cure behavior of the healing agent in method II, which is a better simulation of the process occurring in microcracks of damaged polymer composite with autonomic healing functionality.

In Figure 7, G′ versus time curves are shown for samples reacting at RT with catalyst exposed on the epoxy resin coating of method II. In this experiment, data acquisition commenced after holding the sample for 5 min of time within the sample holder. The holding time was necessary for the prepolymer sample to become more viscous, since the sample viscosity was initially too low to maintain the sample geometry in the gap during oscillation. The ROMP reaction in method II was much slower than in method I, because the amount of contact with sur-

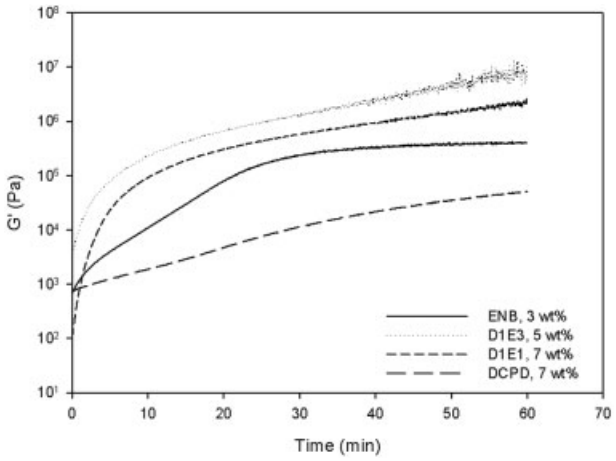


Figure 7 Typical G′ versus time curves of samples with different amounts of catalyst for method II.

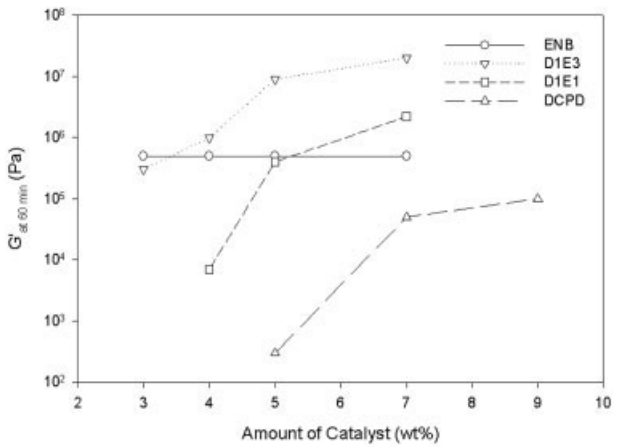


Figure 8 G′ after 60 min cure versus amount of catalyst for method II.

face of the solid catalyst particle with the monomers is limited to the exposed catalyst on the coating. Therefore, a much larger quantity of catalyst in epoxy is necessary for curing of samples than in method I. As shown in Figure 7, development of G′ with time was observed for DCPD, D1E1, D1E3, and ENB samples in the presence of 7, 7, 5, and 3 wt % catalyst embedded in epoxy, respectively. G′ values are relatively high at $t = 0$ because of initial reaction during the 5 min holding time. While G′ of DCPD increased gradually, that of ENB increased rapidly up to about 25 min and then became almost constant. G′ value of the blends maintains higher levels than DCPD or ENB during the testing time. This may be attributed to the combined effect of high rigidity from DCPD, high reactivity of ENB, and higher catalyst loadings compared with neat ENB.

For effective healing, it is also necessary for the cured healing agent to be rigid enough in the crack plane. The rigidity after cure can be estimated from the G′ value. In method I, G′ for DCPD, D3E1, and D1E1 after leveling off ($G'_{\text{level-off}}$) reached 8.0×10^7 Pa while that for ENB showed a relatively lower value of 5.5×10^7 Pa (see Fig. 4). Although the amount of catalyst in method I was much lower than that in method II, the reaction proceeded much faster in method I, since the effective contacting surface of catalyst particles with the monomers is much larger and leads to higher rigidity. Figure 8 shows storage modulus at the end of testing time ($G'_{\text{at 60 min}}$) for different samples in method II. For DCPD, $G'_{\text{at 60 min}}$ was only 1.0×10^5 Pa even at the highest amount of catalyst (i.e., 9 wt %) because of the slow reaction kinetics. Looking at ENB, $G'_{\text{at 60 min}}$ was 5.0×10^5 Pa for all catalyst amounts used (3–7 wt %). This indicates that the curing reaction proceeds very fast because that rigidity is already at a maximum level at a catalyst loading of 3 wt %. In the case of D1E3, $G'_{\text{at 60 min}}$ reached 2.0×10^7 Pa at 7 wt % ($G'_{\text{level-off}} = 8.0 \times 10^7$ Pa in method I). On the basis of the results in this study, D1E3 could satisfy the requirements for improving self-healing efficiency, higher rigidity, and higher reactivity with lower catalyst while improving low temperature capabilities because of the much lower freezing point. Note that the level of G′ or the degree of conversion can be affected by the uniformity and particle size of the solid Grubbs catalyst in this study. Also, the exothermic heat during ROMP may lead to further reaction when a sample size is large.

In method II, it should be noticed that the reaction starts by contacting the catalyst surface in epoxy coating and propagates through the thickness. Therefore, there may exist a gradient in properties (i.e., conversion, modulus, etc.). Since reaction activity of DCPD is so slow, D3E1 was not tested in this experiment.

Additional experiments are ongoing to manufacture microcapsules containing the blends as self-healing agents and examine the in situ healing efficiency for polymer matrix composites.

CONCLUSIONS

DCPD and ENB monomer and their blends were investigated as a healing agent candidate with no catalyst by DSC and with Grubbs catalyst by DMA. DSC results showed that ENB is miscible with DCPD at all proportions, and the melting point at 15°C for DCPD disappeared by blending with ENB. From DMA testing, it was found that the reaction becomes faster with increase of ENB content at lower catalyst loading. Rigidity after 120 min cure was the highest in a DCPD: ENB = 1 : 3 blend when it was cured on the epoxy resin coating. The faster reaction is the contribution of ENB during curing while high rigidity comes from DCPD after curing. Considering requirements for effective self-healing (i.e., fast reaction during cure, high rigidity after cure, reduction of catalyst amount, and lower temperature capabilities), DCPD/ENB blends are potential candidate for self-healing agents.

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