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Influence of cross-link density on the properties of ROMP thermosets

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ABSTRACT

A norbornene-based cross-linker was synthesized and mixed at different loadings with two separate monomers for self-healing polymer applications: 5-ethylidene-2-norbornene (ENB) and *endo*-dicyclopentadiene (*endo*-DCPD). The monomer/cross-linker systems were polymerized by ring-opening metathesis polymerization (ROMP) with Grubbs' catalyst. The thermal–mechanical properties of the polymerized networks were evaluated by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) and the curing process was monitored by parallel plate oscillatory rheometry. The viscosities of the pre-polymer blends are shown to be adequately low for self-healing, and exhibit a high ROMP reactivity to form cross-linked networks with enhanced thermal–mechanical properties. The addition of cross-linker increases the glass transition temperature (T_g) and the storage modulus both above and below T_g. The storage modulus increase above T_g is used to estimate the molecular weight (M_c) between entanglements or cross-link sites for both ENB and *endo*-DCPD-based networks. The cross-linker also greatly accelerates network formation as defined by the gelation time.

1. Introduction

Self-healing polymer composites represent a new paradigm in materials design [1,2]. In these materials, which are inspired by biological systems where damage triggers an autonomic healing response, self-healing is accomplished by embedding liquid healing agent filled microcapsules within a polymer matrix. When damage occurs, matrix microcracks develop and coalesce to rupture the embedded capsules, releasing healing agent into the crack plane. There the released healing agent contacts an embedded chemical trigger (catalyst) and polymerizes, bonding the crack faces back together. Because of its mild reaction conditions and ability to be triggered at room or even lower temperatures without external heating, ring-opening metathesis polymerization (ROMP) has proven to be an excellent polymerization technique for the *in situ* cure of cyclic olefin healing agents and resulting repair of damage in these self-healing material systems. Specifically, norbornene-based monomer, *endo*-dicyclopentadiene (*endo*-DCPD), has been used extensively as the healing agent in self-healing composites with good results [3–10]. In these works, ROMP of DCPD healing agent was initiated by embedded 1st generation Grubbs' ruthenium catalyst. The catalyst shows high reactivity, functional group tolerance, and air/moisture insensitivity [11–13]; however, usage of catalyst in self-healing materials is restricted because of its high cost. In order for the self-healing strategy to be successfully realized, the encapsulated healing agent should meet several special requirements: 1) the healing agent should polymerize at room temperature to produce a very strong thermoset with good thermomechanical properties and adhesive strength; 2) the catalyst loading should be as low as possible to eliminate its deleterious effect on the virgin mechanical properties of the polymer matrix and to reduce overall cost; 3) the self-healing agent should have a very low viscosity and low surface energy to completely fill the microcracks before polymerization occurs.

While the previously used *endo*-DCPD healing agent is capable of forming a cross-linked structure with high toughness and strength, it has a relatively slow *in situ* polymerization rate and requires high loadings of catalyst, which is undesirable for self-healing applications. Low temperature self-healing applications are also limited because pure *endo*-DCPD has a melting point (33 °C) just above room temperature.

Another norbornene-based monomer (Fig. 1), 5-ethylidene-2-norbornene (ENB) has a very low melting point of −80 °C, and much higher ROMP reactivity than DCPD [14,15]. However, ENB forms a linear polymer through ROMP. Also, the strength and glass transition temperature (T_g) for poly-ENB are both lower than the cross-linked poly-DCPD. ENB can be blended with *endo*-DCPD or with other cross-linking agents (or cross-linkers) to form a

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Fig. 1. Chemical structures of *endo*-DCPD and ENB monomers.

cross-linked network and improve its thermal–mechanical properties. Liu et al. [16] reported that blends of ENB and DCPD polymerize much faster than neat DCPD, even at lower catalyst loadings, with increasing ENB content. The ENB/DCPD also shows increased rigidity after cure compared to pure ENB. In our previous work [17], norbornene-based cross-linkers (CL-2 and CL-3) with varying degrees of complexity were synthesized from norbornadiene (CL-1) (Fig. 2). By adding the cross-linker at varying concentrations to the ROMP monomers, the properties of the resulting polymers can be tailored. With addition of CL-2 and CL-3, the glass transition temperature (T_g) of both ENB and *endo*-DCPD systems increases, while the addition of CL-1 decreases T_g for both systems. In addition, the cross-linkers were shown to decrease the melting point of DCDP-based healing agents and expand their applications to lower temperature ranges.

In this study, we first investigate the influence of CL-2 and CL-3 on the viscosity of the DCPD and ENB healing agents. Based on these results we then select the most promising cross-linker as CL-2 (hence forth referred to as CL) and investigate its effect on gelation kinetics by parallel plate oscillatory rheometry. The thermal–mechanical properties of cured ENB/CL and DCPD/CL systems are characterized by using dynamic mechanical analysis (DMA) and dynamic scanning calorimetry (DSC).

2. Experimental

Dicyclopentadiene (*endo*-DCPD, 95%, Acros Organics, Belgium), 5-ethylidene-2-norbornene (ENB, 99%, Sigma–Aldrich Inc., St. Louis, MO) were used as received without further purification. Grubbs' 1st generation catalyst, bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Sigma–Aldrich Inc.) was first dissolved in methylene chloride and then recrystallized under dry nitrogen flow to form much smaller, more soluble crystals than the as received powder [18]. Synthesis of CL (CL-2) and CL-3 was reported in our previous work [17], CL is a mixture of *exo*, *endo*-isomer (83 mol%) and *exo*, *exo*-isomer (17 mol%).

Mixtures of cross-linker/monomer were prepared at different cross-linker loadings, ranging from 2.6 to 20.3 wt.%. The catalyst concentration was 1.0 mg/mL and 2.0 mg/mL for ENB and *endo*-DCPD systems, respectively, unless otherwise stated. To make fully cured samples, recrystallized catalyst was added to the cross-linker/monomer mixtures and stirred for 10 s in a vial at room temperature for the DCPD systems and at 0 °C for the ENB samples. Next, the catalyzed mixture was poured into glass molds (1 × 10 × 80 mm). The DCPD-based samples were cured isothermally in a programmable oven at 70 °C for 2 h, followed by a post-cure at 170 °C for 1.5 h. For the ENB-based systems, the samples were polymerized with the following cure schedule: 5 °C for 5 h, then 30 °C for 1 h, 70 °C for 1 h, and finally 170 °C for 1 h. After the sample was slowly cooled down to room temperature in the oven, it was removed from the glass mold for subsequent DMA and DSC testing.

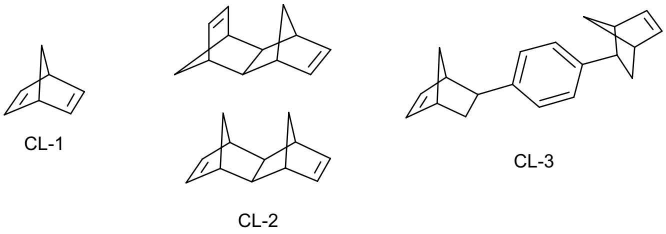

Fig. 2. Chemical structures of cross-linking agents. CL-2 (CL) is a mixture of *exo*-, *endo*-isomer and *exo*-, *exo*-isomer.

The viscosity of an uncatalyzed mixture of ENB/CL and *endo*-DCPD/CL was measured with a cone (0.45°, 15.11 mm radius) and plate viscometer (High Shear CAP-2000+, Brookfield Engineering, Inc., Middleboro, MA). The experiment was conducted at 20 °C with shear rate of 13,333 s^{-1} (1000 rpm).

Isothermal cure characterization of catalyzed ENB/CL and *endo*-DCPD/CL systems was monitored with a parallel plate rheometer (ARES parallel plate rheometer, Rheometric Scientific Inc., USA) by applying a small oscillating strain to the sample and measuring the response stress. All experiments were performed at 23 °C, using stress control mode at an amplitude of 6% strain and 1 Hz, with the 25-mm diameter disposable parallel plates and 0.6 mm gap.

Differential scanning calorimetry (DSC Q20, TA instruments, Inc., New Castle, DE) was used to measure the glass transition temperature (T_g) of fully cured samples. Tests were performed at a heating rate of 10 °C/min from 40 to 200 °C under dry nitrogen purge at 50 mL/min.

The thermal–mechanical properties of ENB/CL and DCPD/CL were evaluated by dynamic mechanical analysis (DMA Q800, TA instruments). All samples were tested in the thin film tension mode at an oscillating strain of 5 μm and frequency of 1 Hz, using a sample size of 1 × 5 × 35 mm. The experiments were performed at a heating rate of 3 °C/min from 30 °C to 230 °C under a nitrogen atmosphere.

3. Results and discussion

In functional self-healing materials, the healing agent must have a low viscosity and low surface energy to wick into matrix microcracks before it polymerizes. The viscosity of *endo*-DCPD with various loadings of CL and CL-3 is shown in Fig. 3. The viscosity of ENB is too low to measure with our experimental set-up and is not reported here. While both CL and CL-3 increase the viscosity of *endo*-DCPD systems, the addition of CL-3 increases the viscosity more than CL at the same loading levels. A simple rule of mixtures was used to fit the experimental data:

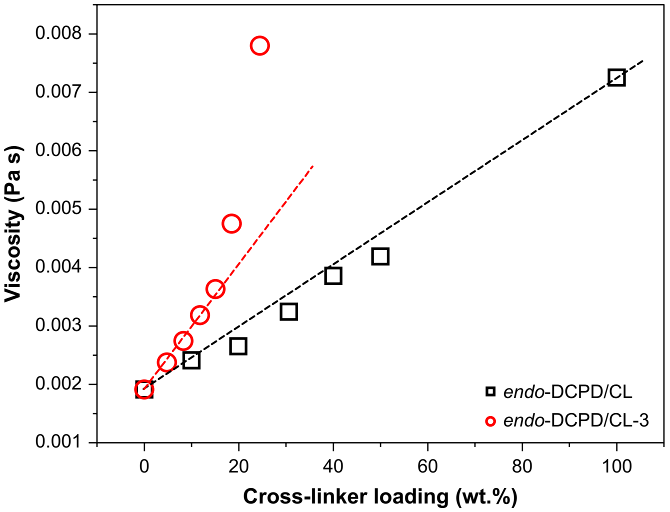

Fig. 3. Viscosity of *endo*-DCPD with different loadings of cross-linking agents.

$$\eta_{\mathrm{m}} = \eta_1 w_1 + \eta_2 w_2 \tag{1}$$

where η_{m}, η_1, and η_2 are the viscosities of the mixture, component 1, and component 2, respectively, and w_1 and w_2 are the weight fractions of the components.

Viscosities of pure *endo*-DCPD and pure CL are measured as 1.91×10^{-3} Pa s and 7.25×10^{-3} Pa s, respectively, at a shear rate of 13,333 s^{-1}. The fitting results are shown in Fig. 3 as dashed lines. At low loadings, the simple rule of mixtures fits the measured data well for both *endo*-DCPD/CL and *endo*-DCPD/CL-3, while at high loadings, the *endo*-DCPD/CL-3 blend deviates from linearity. CL-3 is solid at room temperature, so its viscosity cannot be measured directly. From the simple rule of mixtures for low loadings of CL-3, the effective viscosity of CL-3 at room temperature is estimated as 0.4 Pa s, which is much higher than CL. For self-healing applications, the low viscosity system is more favorable. Hence, the most promising cross-linker, CL, was selected and the *endo*-DCPD/CL blend was further characterized.

ENB monomer can be polymerized in a linear structure through ROMP. With addition of the cross-linker, the ENB/CL blend is expected to form a random cross-linked network (Fig. 4, top). For *endo*-DCPD monomer, which itself polymerizes into a cross-linked network through the additional ring-opening metathesis of the less reactive cyclopentenyl double bond (Fig. 4, bottom), additional cross-linker is expected to increase the overall cross-linking density of the resulting thermoset. A swelling test was performed to qualitatively evaluate the cross-link density. Fully cured ENB/CL and *endo*-DCPD/CL samples were cut into small rectangular pieces (1 × 10 × 20 mm) with initial weights of W_{initial}. Next, the weighed samples were soaked in toluene at room temperature for 72 h. Finally, the samples were taken out and weigh to determine the weight of the sample, W_{final}, which includes the mass of the solvent absorbed. Swelling percentage is calculated by Eq. (2) below and plotted versus cross-linker loading in Fig. 5:

$$\text{Swelling}\,(\%) = \frac{W_{\mathrm{final}} - W_{\mathrm{initial}}}{W_{\mathrm{initial}}} \times 100\% \tag{2}$$

Because ENB (0 wt.% CL) is polymerized into a linear polymer, poly-ENB can dissolve in toluene completely so that W_{final} is undefined. With increasing loadings of CL, the swelling decreases substantially for both ENB and DCPD-based systems, indicating the formation of more highly cross-linked networks. Compared to the ENB/CL system, the *endo*-DCPD/CL polymer swells less in toluene at the same CL loading due to its higher cross-linking density resulting from the additional ROMP active cyclopentenyl ring in the DCPD monomer.

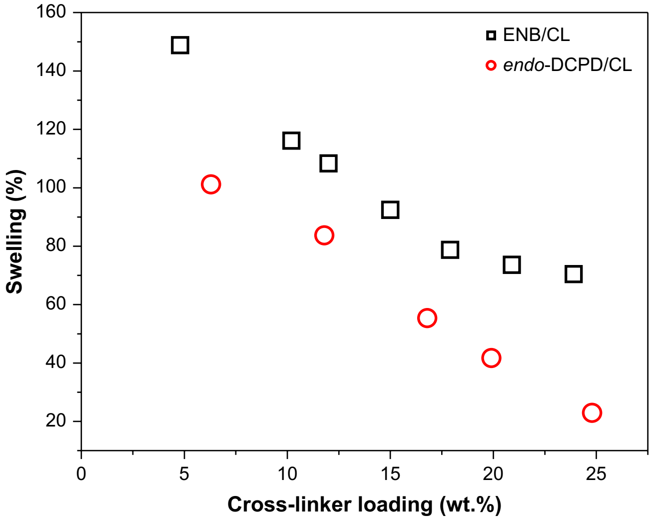

Fig. 5. Swelling test results of fully cured samples.

In addition to the swelling test, Soxhlet extraction was performed to measure the gel content of the samples. After refluxing for 24 h in THF, the extracted content was isolated from solution by rotary evaporation and further dried along with sample residues at 110 °C in a convection oven. Since DCPD polymerizes into a cross-linked network without adding cross-linker, the DCPD/CL system was completely cross-linked and did not have any extract removed during the Soxhlet extraction. In contrast, the ENB/CL system had an extract percentage of 12 wt.% with 5 wt.% CL loading and decreases to 6 wt.% extract when the CL loading exceeds 15 wt.%. The decreased extract is consistent with a higher cross-link density caused by the addition of CL.

The thermal–mechanical properties, as well as the cross-linking densities, of the copolymers were investigated by dynamic mechanical analysis (DMA). Storage modulus (E') and loss modulus (E'') are determined from the in phase and out of phase response of the materials to an applied oscillating strain. The storage modulus relates to the ability of materials to store energy, while the loss modulus is attributed to dissipative and viscous losses in the materials. The ratio of E'' to E' is the mechanical damping (tan δ). In

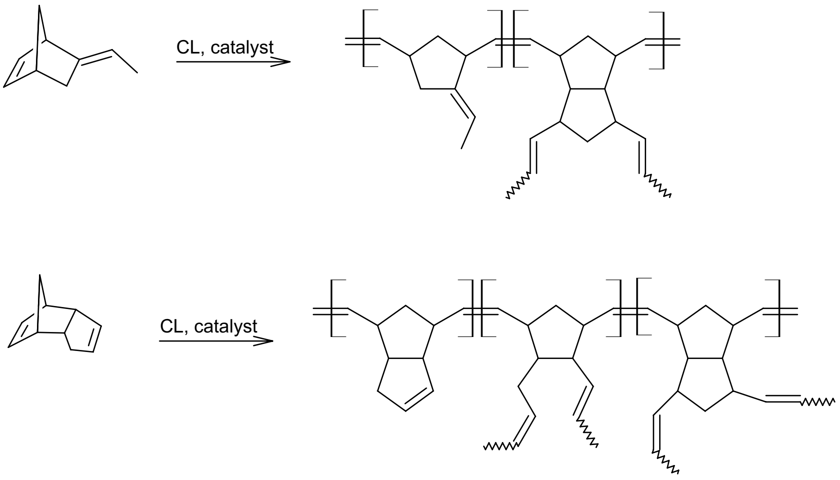

Fig. 4. Reaction scheme for ENB/CL and *endo*-DCPD/CL polymerized through ROMP to form cross-linked structures.

this work, both onset of storage modulus E' drop and peak of loss modulus E'' are used to mark the glass transition temperature (T_g) of the networks. The T_g was also measured by DSC as determined from the step change in the heat capacity (midpoint calculation method). The DMA curves for ENB/CL and *endo*-DCPD/CL are shown in Fig. 6(a–d).

The cross-linking density can be described by M_c, the molecular weight between entanglements or cross-link sites [19]. The value of the storage modulus in the rubbery plateau region is inversely proportional to the chain length between entanglements, M_c, and is given by [20]:

$$M_c = \frac{3qdRT}{E'_{T_g+50\ \mathrm{K}}} \tag{3}$$

where, q is the front factor, usually equal to 1; d, the density of the material (0.93 g/cm^3 and 1.0 g/cm^3 for polymerized ENB and *endo*-DCPD systems, respectively.); R, the universal gas constant (8.314 J K^{-1} mol^{-1}); T is equal to $T_g + 50$ K; $E'_{T_g+50\ \mathrm{K}}$ is the storage modulus at temperature of $T_g + 50$ K. The values of M_c obtained from Eq. (3) can be used for comparing the cross-linking density of all the samples investigated in this study. Table 1 lists the results obtained from both DMA and DSC experiments.

As shown in Table 1, increasing CL loading slightly increases storage modulus, E', in the glassy region (below T_g). The storage modulus increases about 12% for both ENB/CL and *endo*-DCPD/CL systems with CL loading increasing from 0 to 20 wt.%. For thermosetting networks, the glassy state storage modulus has been shown to be a function of the packing density of the glassy state [21]. The appearance of chemical cross-links introduced by additional CL provides a better packing of all chain fragments and contributes to the slight increase of glassy storage modulus. This phenomenon is related to the free volume of chain segments, which decreases with increasing cross-link density, thereby decreasing the polymer's ability to move in various directions [22]. This decreased mobility in either side chains or small groups of adjacent backbone atoms results in a lower compliance of the molecule, and greater storage modulus of the network.

The T_g determined by the peak in the loss modulus also increases with the addition of CL, in agreement with our previous DSC results [17]. For the *endo*-DCPD, the efficiency of the cross-linker decreased above 10 wt.% CL (with M_c dropping only 18% from 10 to 20 wt.% CL versus a 37% reduction from 0 to 10 wt.%). This is presumably because of the already high cross-link density in the DCPD system caused by the additional strained cyclic olefin in the monomer. As a result of the higher cross-link density, T_g increases with increasing CL. This effect is more pronounced at low loadings of CL. For example, there is a 7.1 °C increase in T_g with the addition of 5 wt.% CL, while the T_g only increases by 1.1 °C when the CL loading increases from 15 to 20 wt.%. One possible reason is that CL has a higher ROMP reactivity than *endo*-DCPD (*endo*-DCPD has been shown to be significantly less reactive for ROMP than its *exo*-isomer, primarily for steric reasons [23]). At high loadings, the CL molecules tend to react first, forming a microphase heterogeneity and property gradients throughout the network structure as the

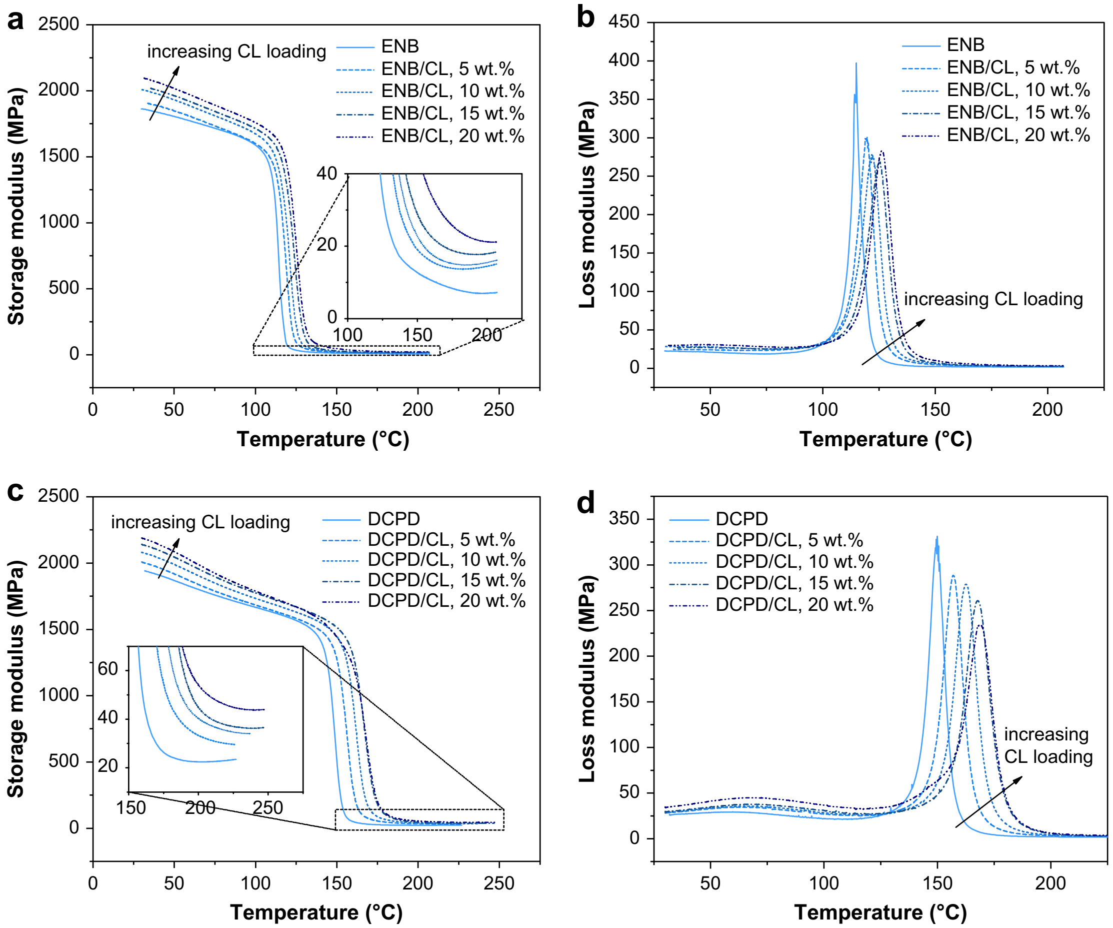

Fig. 6. Temperature dependence of viscoelastic properties from DMA experiments: (a) storage modulus for ENB/CL system; (b) loss modulus for ENB/CL system; (c) storage modulus for *endo*-DCPD/CL system; (d) loss modulus for *endo*-DCPD/CL system.

Table 1
Experimental data obtained from DMA and DSC tests.

	CL loading (wt.%)	T_g (DSC) (°C)	T_g (E'' peak) (°C)	E' at 35 °C (MPa)	E' at $T_g + 50$ °C (MPa)	M_c (g/mol)
ENB/CL	0	111.4	114.9	1852	10.5	954
	5.7	115.6	119.7	1903	15.2	665
	10.3	117.3	121.9	1993	16.6	614
	14.8	121.1	125.1	2020	20.4	501
	19.6	122.3	126.4	2083	28.3	362
DCPD/CL	0	140.0	150.0	1930	22.5	469
	5.2	151.7	157.1	1989	31.7	338
	9.9	157.4	162.7	2063	37.0	294
	15.1	162.2	167.8	2121	37.9	290
	20.3	164.4	168.8	2167	46.0	240

DCPD monomer is consumed later. This hypothesis is supported by the broader glass transition region on the DSC curves for *endo*-DCPD samples containing the higher loadings of CL. Our recent research on the ROMP of modified linseed oil (modified with norbornene functionality) copolymerized with CL shows similar phase-separation phenomena: cured samples changed from transparent to cloudy with increasing CL loading [24]. This lack of homogenous copolymerization with increasing CL loading, reduces the overall cross-linking efficiency.

While ENB monomer polymerizes into a linear polymer, physical entanglements still contribute to a rubber plateau above T_g and an apparent M_c of 954 g/mol. With addition of CL, a chemically cross-linked network is formed and M_c decreases. The decrease of M_c indicates a reduction of chain mobility due to the increasing number of chemical cross-links provided by the additional cross-linker. The formation of the more highly cross-linked networks is also apparent by the temperature dependence of tan δ. The tan δ curve for poly-ENB shows a small peak around 200 °C in the rubbery region above T_g (Fig. 7a). This transition is attributed to movement of coordinated segments in the amorphous polymer that relate to viscous flow [25]. With addition of cross-linker, the cross-linked network prevents the chains from slipping past each other (viscous flow) and this secondary peak in the tan δ curve is eliminated.

While addition of CL increases the glass transition temperature and cross-link density for both ENB and *endo*-DCPD systems, it also affects the cure behavior of the blends. Gelation time is an important parameter for processing of thermosetting resins in general and for the healing agents in self-healing polymers. For self-healing applications, the gelation time of the healing agent is a lower bound for the healing time, the period when the monomer is able to wick into the damage zone before polymerizing after contacting the embedded catalyst. Generally, gelation is associated with a dramatic increase in viscosity. Gelation time can be determined rheologically by measuring the time between the beginning of the reaction and the attainment of an asymptotic viscosity increase or when the storage shear modulus, G', exceeds the loss shear modulus, G''. Parallel plate oscillatory rheometer was used to measure the time dependence of G' and G'' for the ENB/CL and *endo*-DCPD/CL systems. During the polymerization, both G' and G'' increased with reaction time. The crossover of G' and G'', where tan δ equals 1, is recorded to determine the gel point of the blend. The beginning of the reaction is defined as the moment when the catalyst is added and mixed with the blends, so the gel point includes the time used to load the sample into the parallel plate apparatus.

Fig. 8 shows the rheological results of the *endo*-DCPD system containing 25.1 wt.% CL. The gelation time of *endo*-DCPD/CL (25.1 wt.%) is measured as 219 s at these experimental conditions. Since ENB has a much higher ROMP reactivity than the *endo*-DCPD, a low catalyst concentration of 0.2 mg/mL is used (versus the 2.0 mg/mL for *endo*-DCPD). The gelation times from the rheology experiments for catalyzed ENB/CL and *endo*-DCPD/CL samples are shown in Fig. 9.

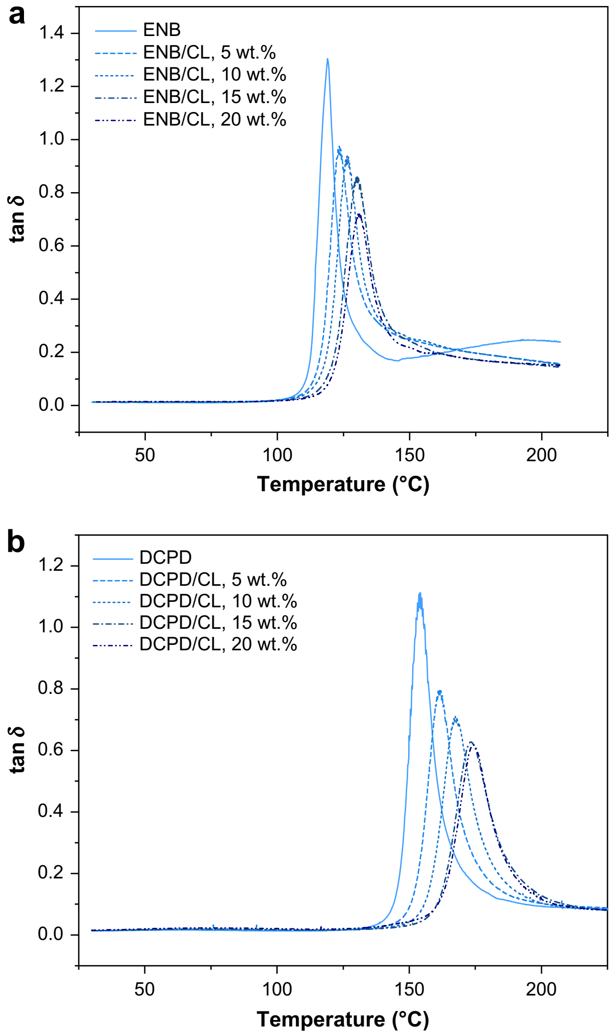

Fig. 7. Tan δ curves for (a) ENB/CL and (b) *endo*-DCPD/CL systems.

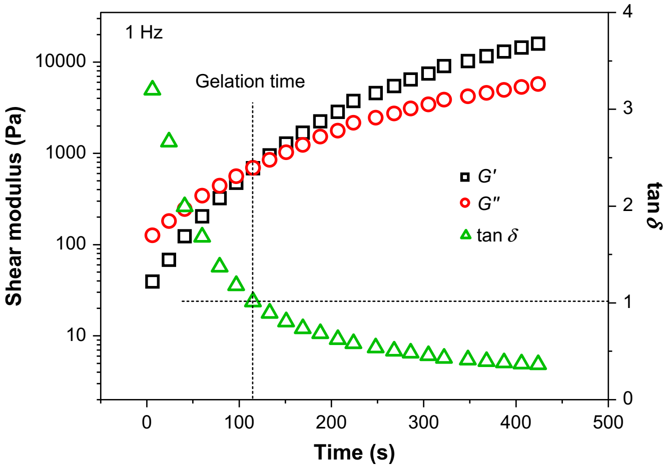

Fig. 8. Evolution of storage modulus, loss modulus, and tan δ during the reaction of the co-monomer blend. Shown here is *endo*-DCPD/CL (25.1 wt.%) curing at room temperature.

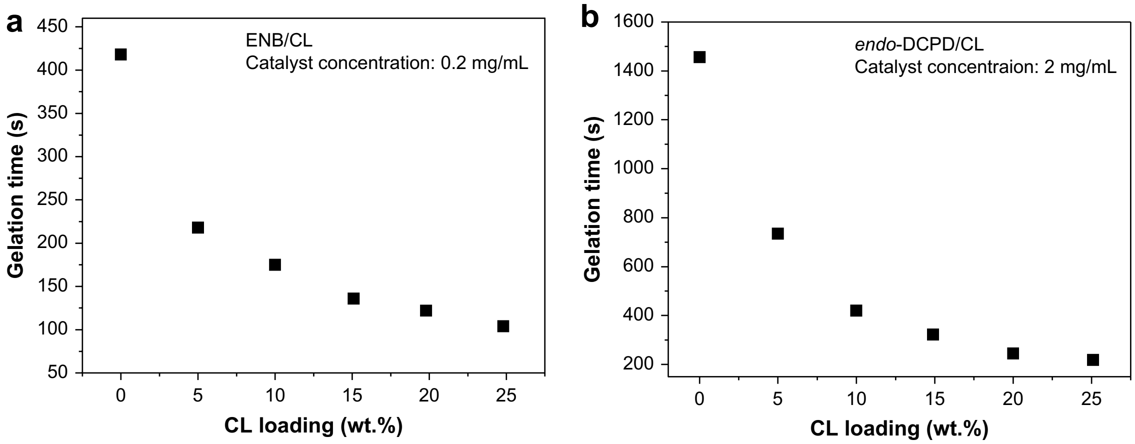

Fig. 9. Effect of CL loading on gel times for (a) ENB and (b) *endo*-DCPD.

The addition of CL reduces the gelation time for both the ENB and *endo*-DCPD systems. The addition of CL is so effective that 5 wt.% loading of CL decreases the gelation time of ENB and *endo*-DCPD by half, from 418 to 218 s and from 1456 to 735 s, respectively. For the ENB/CL system, the highest cross-linker loading (24.8 wt.%) reduces the gelation time to 104 s, which is 4 times shorter than pure ENB without any cross-linker. For the *endo*-DCPD/CL system, the effect of cross-linker on gelation time is even more remarkable: at a CL loading of 25.1 wt.% the gelation time decreased 7 fold to 219 s. The CL provides additional cross-linking sites for ENB and *endo*-DCPD. The gelation time is the time when a cross-linked network is first formed to develop a percolating giant macromolecule throughout the system; and the extra cross-linking sites lower the conversion necessary to form the percolating network structure. As a result, addition of CL makes the whole monomer/cross-linker system reach the gel point more quickly. In addition, since the CL is more reactive toward ROMP than *endo*-DCPD, the gel point is further reduced by the increasing cure rate of the CL blended systems. This increase in the effective cure kinetics for the *endo*-DCPD is responsible for the greater reduction in gelation time in the DCPD/CL systems than in the ENB/CL systems. The ability of self-healing agents to gel rapidly at room and/or sub ambient temperatures are favorable for reducing the required healing times in self-healing polymer composites.

4. Conclusions

CL can be used to modify the properties of norbornene-based monomers, ENB and *endo*-DCPD, with application for self-healing polymers. Samples of ENB and *endo*-DCPD containing different loadings of CL were prepared through ROMP. Addition of CL did not significantly increase the low viscosity of the monomer, facilitating the complete filling of microcracks in self-healing applications. Swelling tests revealed that addition of CL contributes to the formation of a more highly cross-linked network structure. Quantitative characterization was performed by both DMA and DSC. DMA results showed that the storage modulus below the glass transition temperature increases with increasing CL loading. The increased T_g and modulus allow for use of these materials in applications with higher temperature requirements. The storage modulus in the rubbery plateau region was used to evaluate the molecular weight between cross-links, M_c. The decreasing trend of M_c with CL loading confirms the formation of highly cross-linked networks for both ENB and *endo*-DCPD systems. Rheological results of catalyzed ENB/CL and *endo*-DCPD/CL showed that CL greatly decreases the gelation time. The ENB/CL system is more reactive toward ROMP than the *endo*-DCPD/CL system and reaches gelation quickly at low catalyst concentrations. Importantly, lower catalyst requirements are of great benefit to reduce the overall cost of self-healing materials. Future work is aimed at demonstrating improved healing efficiencies with these ENB/CL based healing agents.

Acknowledgements

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