Cure Behavior of Epoxy Resin Containing Castor Oil and Cashew Nut Shell Liquid and Its Derivative

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Received 20 June 2005; accepted 9 April 2006
DOI 10.1002/app.24733
Published online 18 June 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The cure behavior of epoxy resin with a conventional amide-type hardener (HD) was investigated in the presence of castor oil (CO), cashew nut shell liquid (CNSL), and cashew nut shell liquid–formaldehyde resin (CFR) with dynamic differential scanning calorimetry (DSC). The activation energy of the curing reaction was also calculated on the basis of nonisothermal DSC thermograms at various heating rates. A one-stage curing was noted in the case of epoxy resin filled with CO, whereas the epoxy resin with CNSL and CFR showed a two-stage curing process. A competitive cure reaction was noted for the epoxy resin/CNSL(or CFR)/HD blends. In the absence of HD, CFR showed lower values of curing enthalpy than that of CNSL. The activation energy of epoxy resin curing increased with increasing CNSL and CFR loading. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 178–184, 2007

Key words: curing of polymers; kinetics; resins; crosslinking

INTRODUCTION

Among thermosetting polymers, epoxy resins have been extensively used as adhesives in the aerospace and surface coatings industries and as matrices in reinforced composites because of their high performance, including excellent thermal and mechanical properties.[1–3] The addition of a hardener (HD) and subsequent heating changes the material to a hard and brittle material with good thermal, electrical, and mechanical properties. However, their inherent brittle nature limits their many end-use applications to a great extent. To toughen the material, various types of rubbers and thermoplastics have been used so far.[4–7]

Recently, growing environmental concern has focused on the development of a biodegradable plastics matrix including thermosetting epoxy resins and environmentally friendly reinforcing materials, such as natural fibers.[8] The natural-fiber-reinforced echo-friendly composites, the so-called biocomposites, will get more attention in the future.[9] As a way of improving the degradability, several naturally occurring organic materials, such as soybean oil, castor oil (CO), and starch, have been blended into crosslinked polymer matrices such as epoxy resin.[1,2,10]

Cashew nut shell liquid (CNSL) is a phenol-based monomer isolated from cashew nut shells of the cashew tree (*Anacardium occidentale,* usually seen in the coastal areas of tropical and subtropical countries, e.g., Brazil, Mozambique, Tanzania).[11] The technical CNSL, which is processed by hot oil and roasting, is a mixture of cardanol, cardol, and anacardic acid, as shown in Figure 1.[12] The main component is cardanol.[13] The presence of multifunctionalities, such as OH, COOH, and aliphatic unsaturations, in the molecule offers the possibility for many chemical reactions with materials having similar functionality, including epoxy resins, and the long alkyl chains can provide some flexibility because of an internal plasticization effect, which leads to soft resins. Thus, CNSL is a good example of a natural plant-based resin precursor with the potential to crosslink with other functional resin systems.

Moreover, CNSL can be polymerized several ways.[14] It can be polymerized with active hydrogen-containing materials, such as formaldehyde at the ortho and para positions of the phenolic ring under acidic conditions, such as with sulfuric acid,[11] or alkaline conditions[15] to provide a more macromolecular nature. With the variation in the ratio of CNSL to formaldehyde, either novolac (1 : > 1) or resole (1 : < 1) type of resins can be prepared. Although CNSL has been studied as a biodegradable matrix or coating resin, relatively little work has been done on

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Contract grant sponsor: Ministry of Commerce, Industry and Energy of Korea.
Contract grant sponsor: Chonbuk National University of Korea (for a 2004 postdoc grant to G.M. and J.M.R.).

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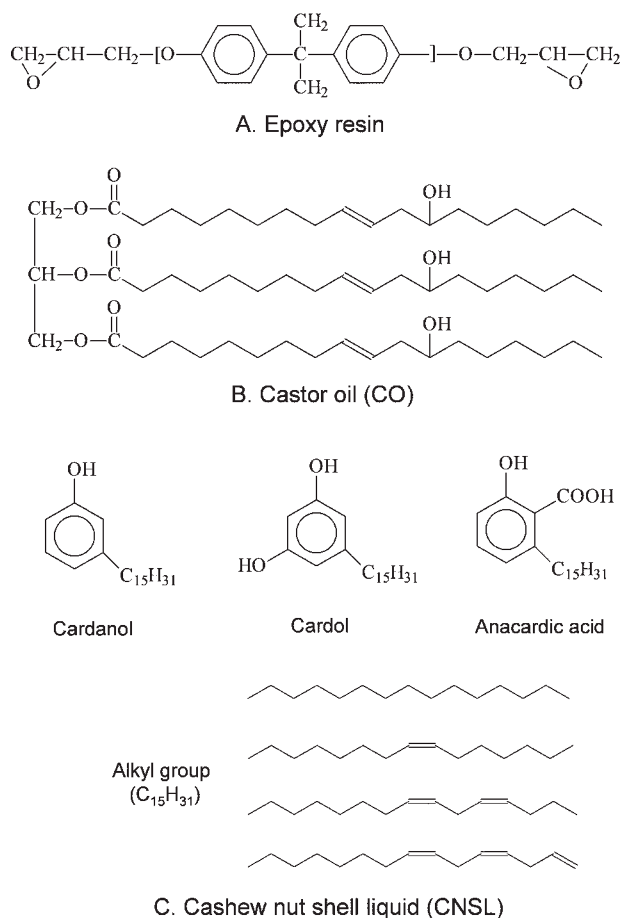


Figure 1 Chemical structure of epoxy resin, CO, and CNSL.

the behavior of curing with thermosetting resins such as epoxy resin.

The objective of this study was to examine the possibility of CNSL and its polymerized form, cashew nut shell liquid–formaldehyde resin (CFR), being used as a curing agent for epoxy resin. The curing behavior of epoxy resin/CO/HD and epoxy resin/CNSL (or CFR) blends in both the presence and absence of a conventional HD with differential scanning calorimetry (DSC). Thermal stability was compared among CO, CNSL, and CFR with thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials used

A diglycidyl ether of bisphenol A type of epoxy resin (YD-128, equivalent weight of epoxy group = 185–190 g/equiv, density = 1.16 g/cc at 25°C, Kukdo Chemicals, Seoul, South Korea) was dried at 80°C *in vacuo* for 2 h before use. The chemical structure is given in Figure 1. A polyamide type of epoxy HD (G-0240, Kukdo Chemicals) was selected to cure the epoxy resin. A triglyceride of ricinoleic acid type of CO (Showa Chemicals, Inc., Japan) was used to modify the properties of epoxy resin (Fig. 1). A technical grade of CNSL was supplied from Bola Raghavendra cashew nut oil industries (India). As shown in Figure 1, cardanol, cardol, and anacardic acid consist of mixtures of components with various degrees of unsaturation in the alkyl side chain, $C_{15}H_{31}$.[16] A formaldehyde solution of 38% was supplied from Showa Chemicals. CO and CNSL were used as received.

CFR was synthesized by condensation polymerization between CNSL and formaldehyde. The CNSL and formaldehyde in a molar ratio of 1 : 1.33 were mixed by stirring in the presence of the alkali catalyst sodium hydroxide at room temperature for 15 min. This mixture was kept undisturbed in a separating funnel for 24 h. The condensation reaction proceeded with the separation of a more distinct aqueous phase due to water from condensation as the bottom layer, as can be seen in Figure 2. The completely separated top layer could be obtained by the removal of the aqueous bottom layer. The obtained CFR could have been resole-type because the reaction was performed in conditions with a formaldehyde excess.[15] Because the main composition of the technical CNSL were cardanol and cardol, the final condensation product were also expected to be a mixture of them, as shown in Scheme 1. The mixtures of various compositions with epoxy resin, CO, CNSL, and CFR were prepared with a mechanical stirrer in an oil bath at 80°C for 30 min.

Characterization

The nonisothermal cure behavior was investigated with a differential scanning calorimeter (DSC 2910, TA Instruments) under a N_2 atmosphere at various heating rates (β's), including 5, 10, 15, and 20°C/min.

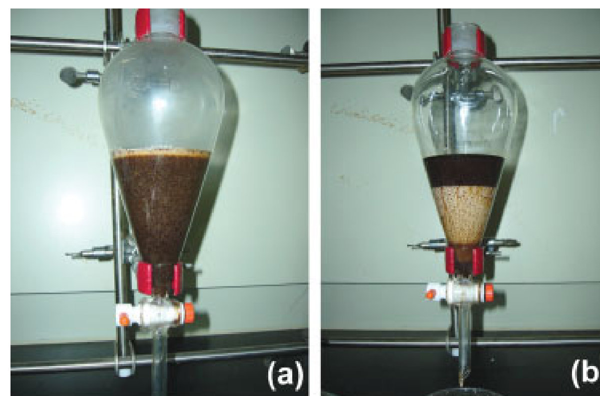
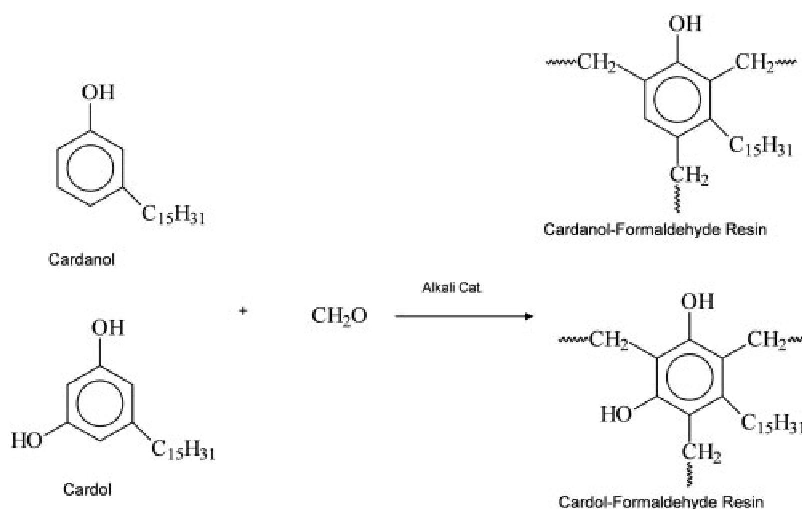


Figure 2 Photos of the condensation reaction between CNSL and formaldehyde (a) before and (b) after complete separation of the aqueous layer (24 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 1 Formation of CFR.

TGA was also carried out with a thermogravimetric analyzer (TGA-Q-50, TA Instruments) under a N_2 atmosphere at $\beta = 10°C/min$ to determine the thermal stability of the additives.

Determination of the activation energy (E_a) of the cure reaction

E_a of the nonisothermal cure reaction was calculated on the basis of two analysis methods, the Kissinger[17] and Ozawa[18] methods, as in our previous studies on the cure kinetics of fluoroelastomer[19] and acrylonitrile–butadiene rubber/clay nanocomposites.[20] With the Kissinger method, E_a can be given by

$$E_a = -R[d \ln(\beta/T_{mc}^2)/d(1/T_{mc})] \quad (1)$$

where E_a can be obtained from the slope of a plot of $\ln(\beta/T_{mc}^2)$ versus $1/T_{mc}$ and R is the gas constant. In the Ozawa method, it can be given by

$$E_a = -R[d \ln \beta/d(1/T_{mc})] \quad (2)$$

where E_a can be calculated from the slope of a plot of ln β versus $1/T_{mc}$. Here, β is the heating rate, and T_{mc} is the temperature at the maximum rate of cure conversion or peak temperature.

RESULTS AND DISCUSSION

Epoxy resin/CO blends were subjected to dynamic DSC evaluation to investigate their curing behavior. Figure 3 represents the typical nonisothermal DSC cure curves of the blends in the presence of 20 phr HD at $\beta = 5°C/min$. The cure reaction generally occurred in the temperature range 40–160°C. As the amount of CO was increased, the enthalpy of the cure reaction (ΔH_c) decreased, whereas T_{mc} shifted slightly to higher temperature ranges. The observed cure behav-

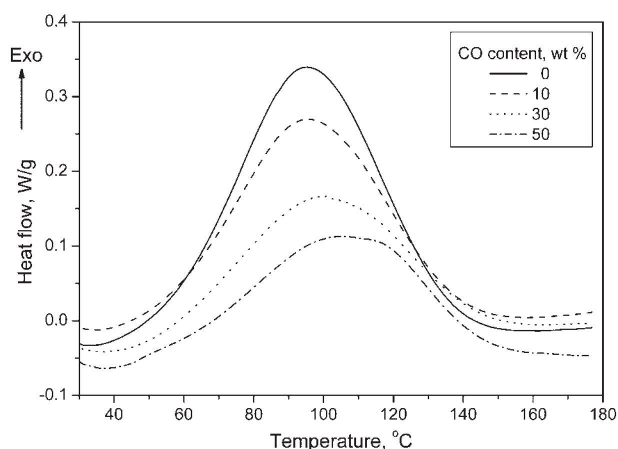


Figure 3 DSC thermograms of epoxy resin/CO in the presence of HD (β: 5°C/min).

TABLE I
ΔH_c and T_{mc} for Epoxy Resin/CO Blends

β (°C/min)	CO content (wt %)	ΔH_c (J/g)	T_{mc} (°C)
5	0	213	94
	10	165	95
	30	124	100
	50	114	104
10	0	194	109
	10	171	111
	30	150	115
	50	108	122
15	0	204	118
	10	167	120
	30	133	125
	50	94	131
20	0	205	126
	10	176	127
	30	139	133
	50	102	140

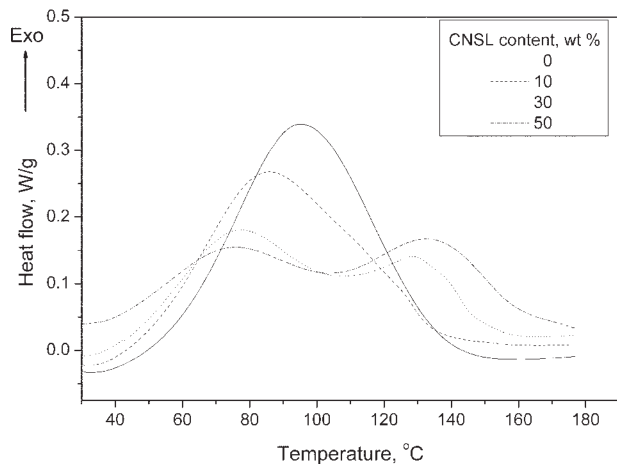


Figure 4 DSC thermograms of epoxy resin/CNSL in the presence of HD (β: 5°C/min).

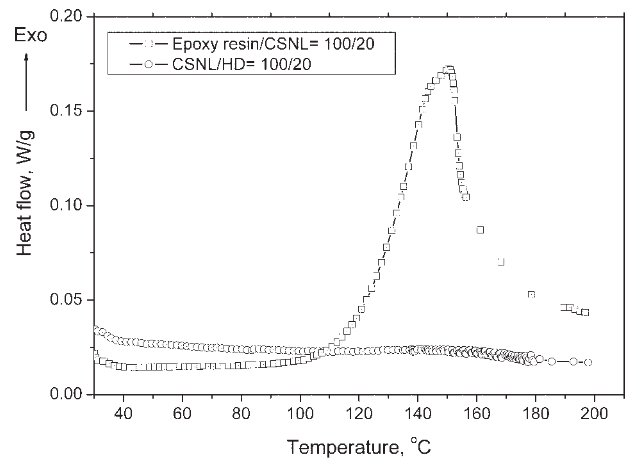
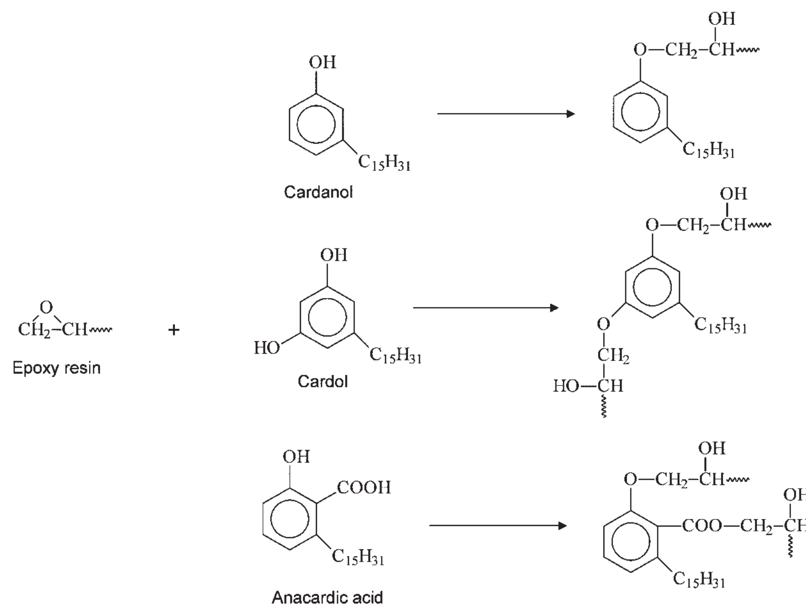


Figure 5 DSC thermograms of CNSL/HD (100/20) and epoxy resin/CNSL (100/20) mixtures (β: 5°C/min).

ior indicates that the addition of CO into epoxy resin retarded the curing reactions because of the reduction in the amount of HD proportional to epoxy resin. The lower ΔH_c, indicating a lower crosslink density in the blends, can improve the ease of degradation during and after the service span, although a slight decrease in mechanical strength might be expected, as reported earlier.[10] For a fuller analysis of the cure kinetics, β was also varied. ΔH_c and T_{mc} are summarized in Table I. As expected, T_{mc} shifted to higher temperatures because of a well-known superheating effect at elevated β's in DSC analysis.

To figure out the effect of CNSL, epoxy resin/CNSL blends were also subjected to dynamic DSC analysis. Figure 4 represents the nonisothermal curing behavior of the blends with 20 phr HD at β = 5°C/min. It is very interesting to see that two peaks were found with the addition of CNSL, and the peaks become more distinct with increased CNSL loading. The first peak was roughly in the temperature range 40–100°C, and the second peak was in the range 100–160°C. The observed two peaks strongly indicate that the curing of epoxy resin proceeded in a two-stage process. The first curing peak seemed to be related to the curing of epoxy resin with HD because the first curing curve closely overlapped with that of the epoxy resin/HD blend. So, what caused the second peak? Could the CNSL react with HD or epoxy resin? To answer that question, two different systematic blends (100/20 wt % CNSL/HD and 100/20 wt % epoxy resin/HD) were subjected to DSC analysis. The results are shown in Figure 5. No curing peak was detected for the CNSL/HD blend, whereas a distinct cure peak was observed in



Scheme 2 Cure reaction of epoxy resin with CNSL.

TABLE II
ΔH_c and T_{mc} for Epoxy Resin/CNSL Blends

β (°C/min)	CNSL content (wt %)	No HD		20 phr HD	
		ΔH_c (J/g)	T_{mc} (°C)	ΔH_c (J/g)	T_{mc} (°C)
5	0	—	—	213	94
	10	18	140	175	85
	30	61	150	48 (17)	77 (128)
	50	123	154	28 (33)	75 (132)
10	0	—	—	194	109
	10	27	156	186	98
	30	69	164	48 (10)	89 (141)
	50	122	169	28 (26)	88 (145)

The numbers in parentheses represents the values for the second peak when two peaks were observed.

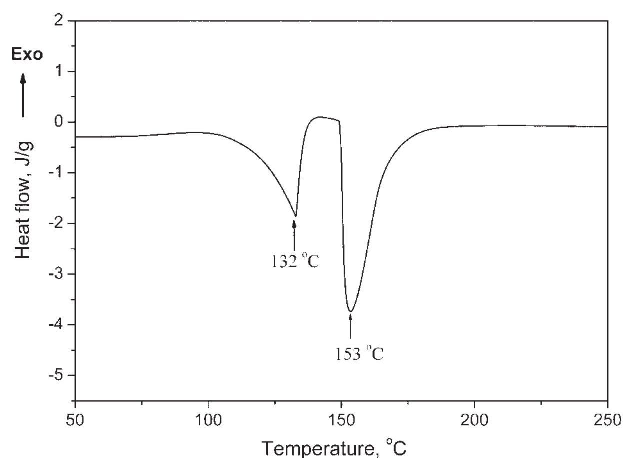
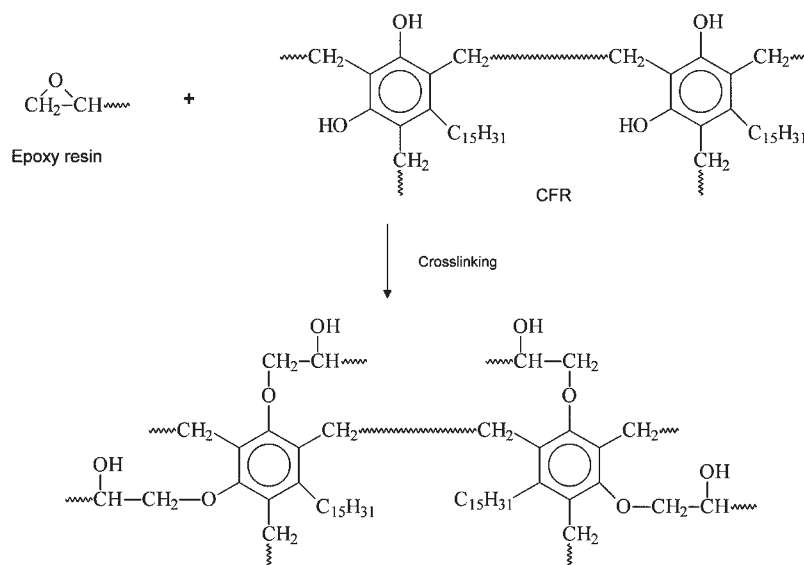


Figure 6 DSC thermograms of CFR at β = 10°C/min.

the temperature range 100–180°C for the epoxy resin/CNSL blend. The observed temperature range was similar to that of the second peak shown in Figure 4. This strongly suggests that the second peak in Figure 4 was due to the curing of epoxy resin by CNSL. A possible reaction between epoxy resin and CNSL is explained in Scheme 2. A similar reaction was also reported between epoxy resin and phenolic materials.[21] Thus, the naturally occurring CNSL could be considered a curing agent for epoxy resin.

For more detailed understanding of the cure behavior, the cure behavior of epoxy resin/CNSL without HD was also investigated and are compared with those of the blends with HD in Table II. In the absence of HD, ΔH_c and T_{mc} increased with increasing CNSL loading. A similar trend was also observed at higher β's. This again supported the conclusion that the CNSL could act as a HD. In the presence of HD, the cure reaction proceeded by a two-stage process, as described previously. As in the case of epoxy resin/CNSL without HD, the addition of CNSL showed an increasing trend with ΔH_c and T_{mc} of second-stage curing at relatively higher loading levels, above 30 wt %. On the other hand, the addition of CNSL caused both a reduction in magnitude of ΔH_c and a considerable shift in T_{mc} to lower temperatures for the first-stage curing. The reduction in ΔH_c could also be explained by a proportional reduction of HD along with epoxy resin with the increased CNSL level by weight because the amount of HD was based on parts per hundred resin. However, the decrease in the first T_{mc} is not clear at this moment. The CNSL seemed to affect the reactivity between epoxy resin and HD. A more detailed mechanism is under investigation.

The curing ability of CNSL against epoxy resin led us to synthesize another type of curing agent, CFR. Before examining the cure behavior of CFR, we performed DSC analysis. Figure 6 shows the DSC trace of CFR. Two endotherms were observed at 132 and 153°C. This was assigned to the loss of moisture or



Scheme 3 Cure reaction of epoxy resin with CFR.

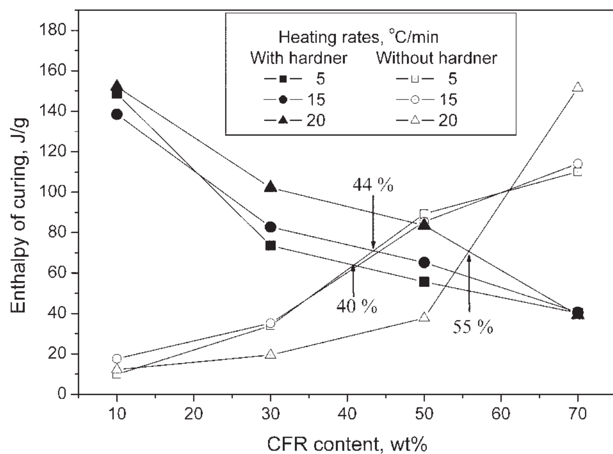


Figure 7 Variation of ΔH_c for epoxy resin/CFR/HD and epoxy resin/CFR systems.

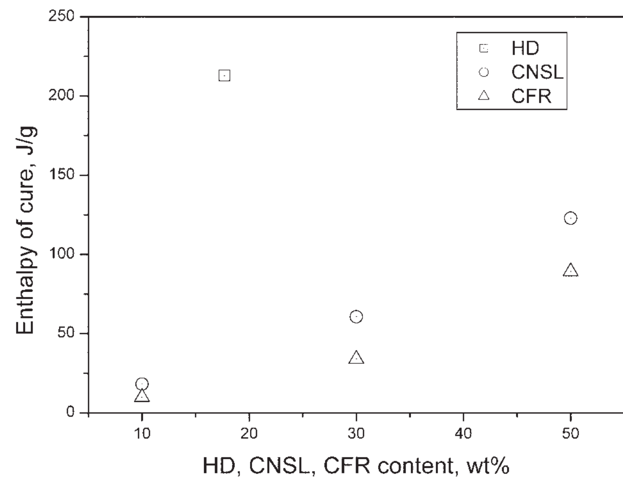


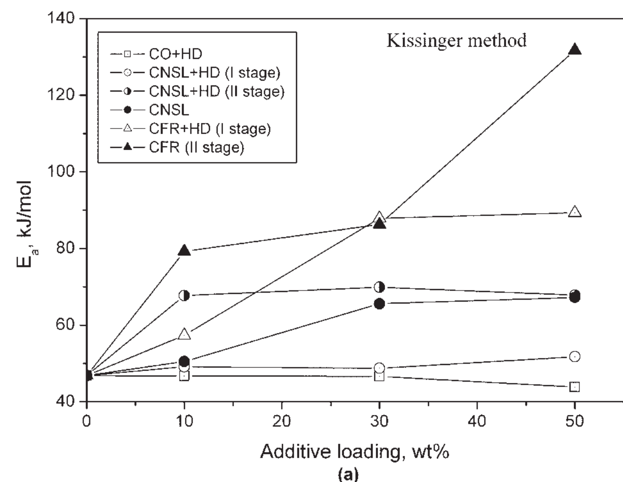
Figure 8 Comparison of ΔH_c for epoxy resin/CFR and epoxy resin/CNSL systems with and without HD.

byproducts during the condensation reaction, as reported in the literature for a similar system.[15]

As in the case of CNSL, epoxy resin could also react with CFR, as shown in Scheme 3. Figure 7 compares ΔH_c of epoxy resin/CFR blends with and without HD as a function of CFR content. As with CNSL, the addition of CFR gave rise to a reduction of ΔH_c in the presence of HD and an increase of ΔH_c without HD. This trend was similar at all of the β's tried in this study. A comparison was made to determine the CFR loading at which ΔH_c with and without HD matched. At β = 5°C/min, the matching occurred around 40 wt % CFR. This means that at a concentration of 40 wt % CFR, ΔH_c of epoxy resin in the presence of HD matched with that of the epoxy resin curing in the absence of HD. This matching concentration value increased somewhat with increased β.

Because CNSL and CFR were considered curing agents in this study, it is worth it to compare their ΔH_c values with that of HD (Fig. 8). At the same loading level, the ΔH_c values showed a decreasing order of HD ≪ CNSL < CFR. The CNSL and CFR showed much lower values compared with a conventional amide-type curing agent because of lower reactivity with epoxy resin. This could lead to a lower degree of curing, which could result in a decrease in the mechanical properties. Although CNSL and CFR showed a slight defect in curing efficiency, they still were promising candidates to meet the stronger industrial demands for future materials of low cost, including their ability to be recycled, echo friendliness due to their natural occurrence, and thermal stability during service because of higher curing temperatures above 140°C.

E_a of epoxy resin curing under nonisothermal condition was calculated by the Kissinger and Ozawa methods as shown in eqs. (1) and (2). They are plotted in Figure 9 as a function of the loading levels of CO, CNSL, and CFR. A similar trend was observed between the two methods. There was no considerable change in E_a for the first curing stage between epoxy resin with HD with the addition of CO and



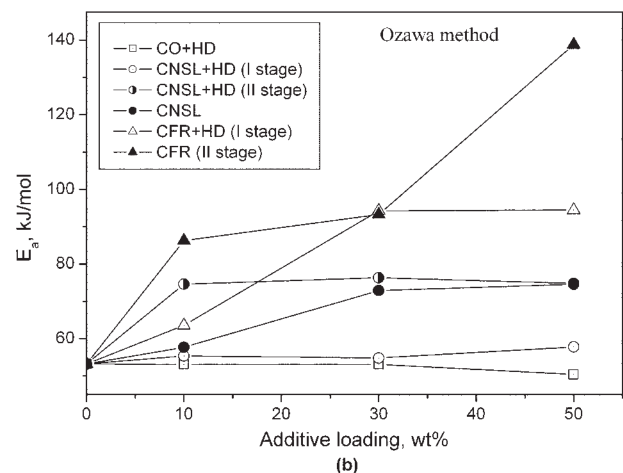


Figure 9 Effects of type and loading of cure additives on E_a of cure by the (a) Kissinger and (b) Ozawa methods.

CNSL, whereas the addition of CFR resulted in an increase in E_a. In the second curing stage between epoxy resin with CNSL or CFR, much higher increases in E_a were found regardless of the presence of HD. This again supported the lower reactivity of CNSL and CFR compared to HD.

To figure out the thermal stability, TGA was carried out for CO, CNSL, and CFR. The results are given in Figure 10. The thermal degradation of CO proceeded in a single-step process (initiation and maximum temperatures = 360 and 375°C, respectively). However, the degradation of CNSL and CFR proceeded in a two-step process if the moisture loss step at 120°C was ignored for CFR. The first degradation step at 277°C in the case of CNSL was assigned to the degradation of cardanol, and the second one at 441°C was assigned to the cardol because the higher thermal stability of cardol compared to cardanol was already reported.[12] A similar degradation process was expected for CFR because it came from CNSL. However, a considerably higher degradation temperature was observed for CFR at 343°C for cardanol and at 466°C for cardol, which indicated improved thermal stability.

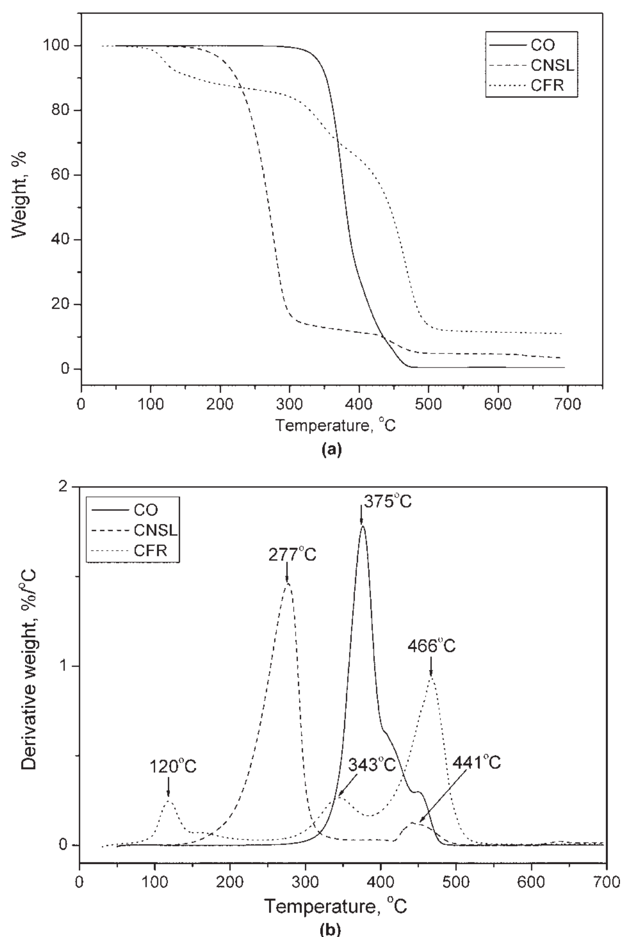


Figure 10 (a) TGA thermograms and (b) their derivatives for CO, CNSL, and CFR.

CONCLUSIONS

The cure behavior of epoxy resin with an amide-type typical HD in the presence of CO, CNSL, and CFR was investigated with dynamic DSC. The curing of epoxy resin containing CO was made by a single-stage process, whereas it was made by a two-stage process for epoxy resin containing CNSL and CFR. The first stage was attributed to the curing reaction between epoxy resin and HD, whereas the second one to the reaction between epoxy resin with CNSL and CFR. A competitive curing reaction was noted in the case of epoxy resin containing CNSL and CFR in the presence of HD. The curing of epoxy resin by CNSL and CFR occurred at much higher temperatures than that by the conventional HD system. It was possible to cure the epoxy resin with CNSL and CFR only, although ΔH_c and the reactivity were lower compared with that of the conventional HD. Because CNSL is a naturally occurring biodegradable material and has a higher thermal stability, it may be a promising candidate to meet the stronger industrial demands for future materials of low cost, including its ability to recycle, echo friendliness, and thermal stability.

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