Cure Study of an Acrylic Resin to Develop Natural Fiber Composites

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ABSTRACT: In the present study a new environmentally friendly acrylic resin was characterized to develop a high-performance biocomposite for future work. Differential scanning calorimetry measurements were used to determine onset of curing reaction as well as the degree of cure at a certain temperatures. Swelling equilibrium data for an acrylic resin were generally analyzed using the Flory–Rehner equation for a perfect network, to obtain a measurement of the molar mass between two crosslinks and the crosslink density of polymer, and to establish the effect of temperature and time on these parameters. The crosslink density of cured resin at 180°C and 10 min indicates the completion of a major part of the reaction under those conditions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 757–762, 2004

Key words: biopolymers; crosslinking; swelling; differential scanning calorimetry (DSC)

INTRODUCTION

Over the past few years the development of bio-based products has increased considerably because of growing environmental consciousness throughout the world, demands of governmental authorities, and removal of traditional structural composites. After decades of high-tech development of artificial fibers such as carbon, aramid, and glass, natural fibers like wood fiber, flax, hemp, and sisal have recently attracted the attention of scientists and technologists because of their advantages, such as low cost, low density, good strength properties, and biodegradability. There has been increasing interest in the commercialization of natural fiber composites and their use, especially for interior paneling in the automobile industry. A number of publications reported on natural fiber composites in automotive applications. Moreover, biopolymers, which are expected to be degradable, present an achievable solution to waste disposal problems connected with traditional petroleum-derived plastic.[1,2]

By embedding natural fibers into a biopolymeric matrix; new fiber reinforced materials called biocomposites or more specifically "green composites" can be formed and is still being developed. A survey of the literature reveals that little effort has been put toward such biocomposites.[3] Levit et al.[4] have manufactured biocomposites from poly (lactic acid) (PLA) and cellulosic fibrous materials by extrusion and compression molding and found the same or improved tensile strength compared to pure PLA. The mechanical properties of a biodegradable polyester composite reinforced with short abaca fibers were investigated.[5] Also, George et al.[6] were able to produce high-performance composite materials using natural fibers as reinforcement in a soy oil-based polymer matrix. The composites produced have properties that make them useful in different applications such as the automotive, vehicle, furniture, and construction industries.

The properties of natural fiber reinforced composites depend on a number of parameters. Both the matrix and the fiber play crucial roles in the performance of composites. The tensile strength is more sensitive to the matrix properties, whereas the modulus depends upon the fiber properties. For the thermoset composites, fibers are combined with phenolic, epoxy, acrylic, and polyester resin to form composite materials. Thermoset polymers have reactive groups, which assist interface development. These composite materials are chemically cured to a crosslinked, three-dimensional network. Because of the high degree of crosslinking, thermosets are infusible, insoluble, and dimensionally stable under loads. These properties make thermosets valuable as adhesives, for coatings, and in high-performance applications and matrices in advanced composites. Several works have been reported on the effect of process parameters such as curing schedule and various treatments on the properties of thermoset composites.[3,7]

Many researchers have reported on different methods for evaluating the degrees of conversion, reaction rates from isothermal experiments according to the reaction's experimental heat, and crosslink density of

thermoset resins.[8–11] In the present study, the cure behavior and degree of conversion, as well as the crosslink density of an acrylic resin, were evaluated to optimize the curing schedule of the reaction to develop a new high-performance biocomposite for automotive applications using resin transfer molding or the compression molding process to be described in future work.

EXPERIMENTAL

The acrylic resin, a modified polycarboxylic acid with a polyhydric alcohol as a crosslinking agent, was obtained from BASF, Canada, and used as it was.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) has been widely used to evaluate the kinetic behavior and reaction conversion of thermosetting resin.[8,9] In this technique it is assumed that the rate of exchanged heat is proportional to the rate of chemical reactions. It is possible to evaluate the reaction rate $d\alpha/dt$ at time t and the degree of conversion α reached in time t by means of the following expressions:

$$\alpha = \frac{\Delta H_t}{\Delta H_R} \tag{1}$$

$$\frac{d\alpha}{dt} = \frac{(dH/dt)_t}{\Delta H_R}, \tag{2}$$

where ΔH_t is the heat exchanged until time t and can be obtained directly by integration of the calorimetric signal dH/dt until time t. ΔH_R is the total reaction heat obtained with the complete conversion of all the reactive groups. $(dH/dt)_t$ is the heat exchanged by time unit.

To calculate the degree of conversion the variation of the isothermal and dynamic calorimetric signals according to the time or temperature is required. If the sum of the isothermal reaction heat and the residual heat is less than the dynamic heat, this can be due to that part of the heat that cannot be recorded isothermally by the calorimeter at the start and at the end of the reaction because of a lack of apparatus sensitivity. In this case the dynamic heat will be considered the total reaction heat:[9]

$$\alpha = \frac{\Delta H_t(\Delta H_{dyn} - \Delta H_{res})}{\Delta H_{iso}\Delta H_{dyn}} \tag{3}$$

$$\frac{d\alpha}{dt} = \frac{(dH/dt)_t(\Delta H_{dyn} - \Delta H_{res})}{\Delta H_{iso}\Delta H_{dyn}}. \tag{4}$$

When this method is applied to the calculation of the last degree of conversion reached isothermally, ΔH_t is equal to ΔH_{iso} and the degree of conversion is defined as

$$\alpha = 1 - \frac{\Delta H_{res}}{\Delta H_{dyn}} \tag{5}$$

In this work, the heat of curing reaction and degree of cure were evaluated using a thermoanalytical instrument DSC Q1000 apparatus following well-established procedures.[12] Nonisothermal experiments on uncured samples were carried out at 5, 10, and 15°C min^{-1}, from 30 to 300°C. The areas above the curves were quantified by drawing a straight line extension of both sides of each curve. The total heat of cure (ΔH_{dyn}) reaction was determined by calculating the area over the curve.

Then the isothermal scans were performed at 100, 130, and 160°C. After the isothermal scans, the samples were cooled to 25°C and dynamic scans of 30 to 250°C were done at 10°C/min to calculate the residual heat of reaction, ΔH_{res} The weight of samples was between 10 and 20 mg.

Crosslink density determination

A crosslinked polymer, when placed in a good solvent, rather than dissolving completely will absorb a portion of the solvent and subsequently swell. The swelling and elastic behavior of network was originally investigated by Huggins et al.[13] Network polymers are diluted by solvents when the polymer–solvent interactions lead to increased entropy of mixing.[14] The free energy of mixing will cause the solvent to penetrate and try to dilute the polymer solution. As the polymer chains in the crosslinked polymer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation. The equilibrium volumetric swelling is reached when the two forces balance each other.

Perfectly crosslinked networks swell in a good solvent uniformly. If the polymer is not crosslinked it is totally dissolved. The partially crosslinked sample shows an intermediate behavior.[15] Swelling is a simple and low-cost technique to characterize polymer networks. At the simplest level of analysis, swelling measurements can be used for quality control and serve as an indexing tool for polymer systems with different levels of crosslinking. The extent of swelling is inversely proportional to the density of crosslink in the network. The crosslink density is a quantitative measure of the number of crosslinks that exist in a given volume in the thermosetting polymer. The crosslink density defines the viscoelastic and mechan-

ical properties of the polymer.[7] A higher crosslink density means more dimensional stability and high mechanical strength. The crosslink density can be computed if the Flory interaction parameter for the polymer–solvent is known.

Another important structural parameter characterizing crosslinked polymer is the molecular weight per crosslink unit M_c, which is directly related to the crosslink density. The concept of M_c in terms of molar mass between crosslinks was introduced by Flory and Rehner.[11] It is defined as the weight of the cured sample in grams which has 1 mol of elastically effective network chains. The physical and mechanical properties of crosslinked polymer were affected significantly by molar mass between crosslinks. Usually, in the case of a loosely crosslinked network, M_c has high values, whereas highly crosslinked networks have low values of M_c.

In the present study, swelling equilibrium data for an acrylic resin were generally analyzed using the Flory–Rehner equation for a perfect network simply to obtain a measurement of the molar mass between two crosslinks, M_c, and crosslink density of polymer, v_x, and to determine the effect of temperature and time on these parameters.

According to the theory of Flory and Rehner, for a perfect network crosslink density v_x and the molecular weight per crosslink unit M_c are calculated using the equation[16]

$$\frac{1}{\bar{v} M_c} = v_x = -\frac{\ln(1 - v_2) + v_2 + \chi_1 v_2^2}{\varphi_1 (v_2^{1/3} - v_2/2)}, \quad (6)$$

where v_x is the number of moles of elastically effective network chains per cubic centimeter, M_c is the average molecular weight of the polymer between crosslinks, $[\bar{v}]$ is the specific volume of the polymer, v_2 is the volume fraction of the polymer in swollen matrix, ϕ_1 is the molar volume of the solvent, and χ_1 is the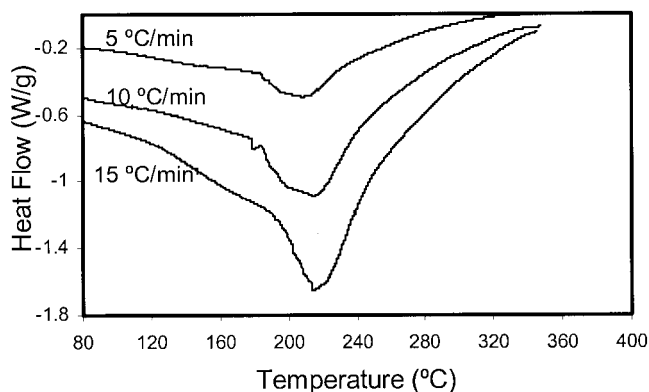 Flory–Huggins interaction parameter between solvent and polymer. Experimentally, by measuring the swell ratio, $q = V/V_0 = 1/v_2$, V_0 is the volume of the unswollen network, and V is the volume of the swollen network, and knowing the Flory interaction parameter, crosslink density and molecular weight between crosslinks can be computed.

In the gravimetric approach, a sample is weighed (W_d) and then immersed in a solvent at the required temperature for different times. At the end of each period, the sample is again weighed (W_g), the swell ratio is computed from these data, and the ratio of the densities of the solvent to the polymer, K, as

$$q = \frac{W_d + (W_g - W_d)K}{W_d}. \quad (7)$$

To determine the crosslink density, resin samples were cured over a wide range of temperatures from 140 to 200°C at different curing times from 5 to 20 min. To cure the resin a hot press was used and two spacers with 3 mm thickness were placed between the platens to obtain a certain specimen thickness. The cured samples were cut into approximately 2-cm squares, weighed using digital balance to the nearest 0.0001 g, and inserted in small beakers containing water as a solvent. Specimens were taken out at regular intervals, wiped free of solvent adhering to the surface, and weighed immediately at room temperature and then replaced. This procedure was continued till equilibrium swelling was achieved. This was repeated for at least two specimens from each network to ensure the accuracy of results.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Figure 1 shows dynamic DSC scans of the acrylic resin at different heating rates. The curing reaction takes place between carboxyl side groups of polyacrylic and hydroxyl groups of polyhydric alcohol. Table I shows the ultimate heat of reaction obtained by calculating the area over the dynamic curves. As mentioned before, ΔH_R reaction should ideally be constant for a given thermoset. However, at a slow heating rate some of the heat consumed at the beginning or at the end of the reaction is not recorded because of a lack of
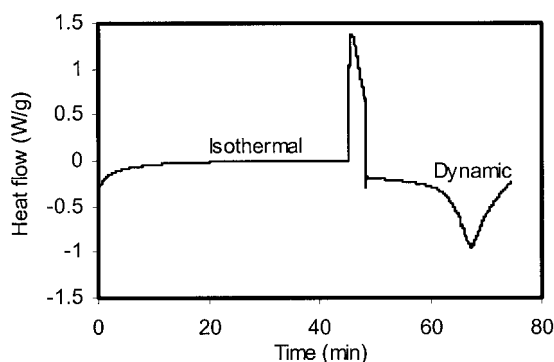
TABLE I
Results Obtained from Nonisothermal DSC Experiments

Scanning rate (°C min^{-1})	Peak temperature (°C)	Total heat of reaction (ΔH_R) (J/g)
5	208.69	−462.4
10	214.16	−504.1
15	215.58	−507.0

Figure 1 Dynamic scans of acrylic resin at different heating rates.

Figure 2 Isothermal scan of acrylic resin at 160°C and dynamic scan.

Figure 3 Percentage weight swelling versus time for samples cured at different temperatures. ●, $T=140°C$, $t=20$ min; ■, $T=160°C$, $t=10$ min; ▲, $T=180°C$, $t=10$ min; ◆, $T=190°C$, $t=10$ min; *, $T=200°C$, $t=10$ min.

calorimeter sensitivity. The average value of heat of reaction over the range of the experiments is 491 J/g.

The isothermal scans at 100 and 130°C showed that no curing reaction occurred because the scans did not give any curves and the amount of residual heat is almost equal to the total heat of reaction. Although the isothermal scan at 160°C did not demonstrate any curve due to a fast curing reaction (Fig. 2) but the residual heat is much less than the total heat of reaction ($\Delta H_{res} = 248.3$ J/g), which means that some curing reaction took place. Assuming the sum of the isothermal reaction heat and the residual heat is less than the dynamic heat; the maximum degree of cure for acrylic resin at 160°C, calculated by Eq. (5), is almost 50%.

Crosslink density measurement

The percentage increase in weight due to swelling in water is plotted against the time in hours at different curing temperatures as shown in Figure 3. It can be seen that almost all the swollen samples cured at different temperatures reach equilibrium after 24–30 h. The sample cured at 180°C for 10 min becomes rigid and swells relatively less compared to other cured samples and consequently the swelling ratio of this sample is of a lower order.

Using χ_1 equal to 0.498 from the literature,[17] data for the volume fraction of the swollen sample v, crosslink density v_e, and molar mass M_c at different curing temperatures from 140 to 200°C and different curing time from 3 to 20 min were calculated and are presented in Table II. The data reported in Table II indicate that the cure time and temperature have a significant effect on the crosslink density of the cured sample. The crosslink density of the acrylic resin increases from 1.76×10^{-4} to 3.54×10^{-4} mol mL^{-1} with increasing curing time from 10 to 20 min at 140°C. Consequently, the volume fraction of swollen samples (v), being inversely proportional to swelling ratio (q), increases with rigidity of the cured resin. The same
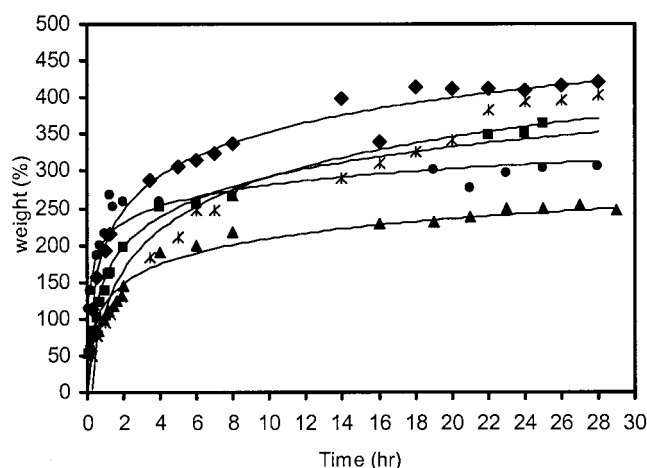
trend was observed at 160°C. By enhancing the cure time from 5 to 15 min the crosslink density increases from 1.28×10^{-4} to 2.42×10^{-4} mol mL^{-1}. Reduction of the crosslink density of the cured resin at 160°C for 15 min compared to that at 140°C for 15 min is probably due to the decomposition of the polymer network. Thus, a long curing time is not recommended for curing temperatures above 160°C. At 180°C a significant increase in crosslink density, from 1.54×10^{-2} to 5.6×10^{-4} mol ml^{-1}, at the curing time between 3 and 10 min can be observed. For the 3-min curing time, increasing the cure temperature above 180°C increases the crosslink density but further increase in the cure time to 6 min reduces the crosslink density.

TABLE II
Values of v, v_e, and M_c for Resins Cured at Different Temperatures and Times

Curing				
Temp (°C)	Time (min)	v	$v_e \times 10^4$ (mol ml^{-1})	M_c (g mol^{-1})
140	10	0.1552	1.76	4232.04
140	15	0.1825	2.822	2647.51
140	20	0.1973	3.54	2109.04
160	5	0.139	1.286	5801.50
160	10	0.162	1.996	3740.01
160	15	0.173	2.42	3084.64
180	3	0.148	1.54	4848.05
180	6	0.182	2.8	2667.04
180	10	0.23	5.6	1332.13
190	3	0.1605	1.94	3841.75
190	6	0.153	1.69	4409.19
190	10	0.152	1.66	4492.82
200	3	0.167	2.18	3425.23
200	6	0.16	1.925	3878.18
200	10	0.158	1.86	4015.55
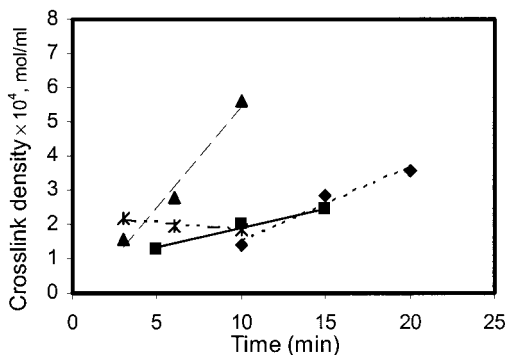
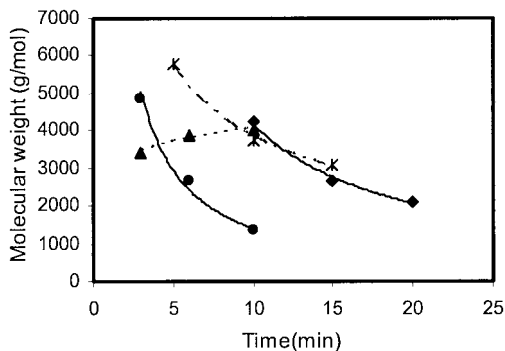**Figure 4** Crosslink density versus cure time for different cure temperatures. ♦, $T=140°C$; ■, $T=160°C$; ▲, $T=180°C$; *, $T=200°C$.

Figure 6 Molecular weight between crosslinks versus cure time for different cure temperatures. ♦, $T=140°C$; *, $T=160°C$; ●, $T=180°C$; ▲, $T=200°C$.

This can be attributed to enhanced degradation and damage of the network structure that occured during the curing reaction.

Figure 4 shows the variation of crosslink density versus time at different temperatures. The crosslink density is directly related to the degree of cure or conversion. The degree of cure represents a level of chemical crosslinking compared to the fully cured states. The slope of each linear regression gives the reaction rate during isothermal cure. The maximum conversion and reaction rates are much higher for 180°C. At 140 and 160°C the reaction rate increases gradually with time. The conversion rates for 190 (not shown) and 200°C are very similar and decrease slowly due to degradation of the network.

In Figure 5 the plot of crosslink density versus cure temperature at constant curing time (10 min) indicates completion of a major part of the reaction took place at 180°C. As the chains become denser, the ability of polymer chains to accommodate solvent molecules decreases. It was observed that the cured sample at 180°C swells relatively less at equilibrium compared to other samples.
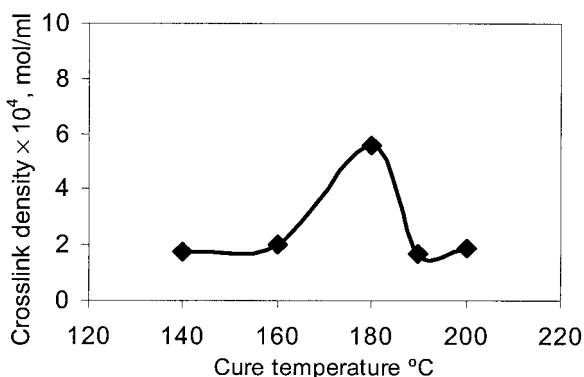
As mentioned earlier, the ultimate physical and mechanical properties of a network are highly affected by the molar mass between crosslinks. When the number of crosslink points increases, the system becomes more rigid in nature with low values of M_c. Figure 6 shows the change in molecular weight versus curing time at different curing temperatures. As the time increases, the molecular weight decreases because the curing reaction and consequently crosslink points intensify (except at 190 and 200°C). At temperatures of 190 and 200°C the decomposition reaction increases with time; therefore, the molecular weight increases. The lowest M_c (1332.13 g mol^{-1}) at 180°C reveals the highly three dimensional network at this temperature (Fig. 7). These cure parameters are now being used to manufacture biocomposites based on 30 to 70% of the resin content. Properties of these composites will be reported in future publications.

CONCLUSION

The curing reaction of an acrylic resin was determined by dynamic scanning calorimetry. Using isothermal and dynamic scans the maximum degree of cure was calculated at 160°C. The ultimate mechanical proper-
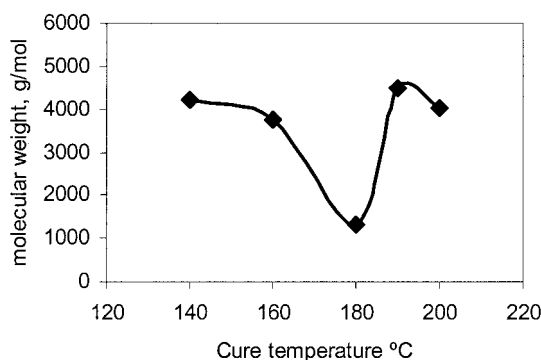

Figure 5 Crosslink density versus cure temperature at 10 min cure time.

Figure 7 Molecular weight between crosslinks versus cure temperature at 10 min cure time.

ties of cured resin depend on the structure of the network resulting from variation in curing schedules. Temperature and time are the most important parameters in a cure cycle. The effect of curing temperature and time on crosslink density and molecular weight between crosslinks was evaluated by equilibrium swelling measurements. Increasing the temperature and time over a limited range has a pronounced effect on the network crosslink density. The rate of curing reaction increases with increased cure time at specific temperatures. The optimum curing temperature and time was found to be 180°C for 10 min. Enhancing the cure temperature above 180°C causes some defects in the network structure.

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