

Ultraviolet-Curable Liquid Natural Rubber

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ABSTRACT: Preparation of ultraviolet (UV)-curable liquid natural rubber was achieved by fixation of photosensitive molecule onto liquid natural rubber. The liquid natural rubber (LNR) was prepared by oxidative degradation of natural rubber latex, using the phenylhydrazine/O₂ system. The LNR was further treated with *in situ* performic acid, which leads to epoxidized liquid natural rubber (ELNR). The progress of the addition reaction of photosensitive acrylic acid onto epoxide ring of the ELNR was followed by infrared spectroscopy. It was found that at 80°C reaction temperature, epoxide ring opening reaction of ELNR came to completion within 2 h, which is faster than the reaction at 60°C. The photocrosslinking reaction of the acrylated ELNR was studied by monitoring the exothermic heat of photocuring of acrylate double bond using a double beam photocalorimeter (DPA7). It was found that the fast crosslinking-polymerization occurred when the rubber was exposed to UV irradiation in the presence of photocleavage initiator (Irgacure 184 and Darocur 1173) and liquid diacrylate monomer (1,6 hexanediol diacrylate and tripropylene glycol diacrylate). The cure kinetics of the elastomers were also investigated, and it was found that the diacrylate monomer, photoinitiator concentration play an important role on the rate and extent of the reaction. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1478–1485, 2000

Key words: UV curing; natural rubber; acrylate; epoxidized liquid natural rubber; photocalorimeter

INTRODUCTION

Ultraviolet (UV) radiation curing is a widely established area of industrial importance and academic interest, due to the combined attributes of rapid, energy efficient curing at ambient temperature on exposure to radiation and the possibility of achieving formulations free of volatile organic components. Because of its distinct advantages, the photocuring technology has found a growing number of applications, mainly in coating industry, graphic arts, microelectronics, wood finishes, photoresists, electronics/electrical, decorative ap-

plications, converting/packaging, dental restorations, flooring, and adhesives.¹ Applications continue to grow as new initiators, monomers, and prepolymers are being developed. Among the different types of photopolymers developed so far, those based on photosensitive acrylic moieties appear particularly promising because of their high reactivity under irradiation, moderate cost, and low volatility. Although methacrylate, cinnamate, vinyl, and allyl functionalities are seen in some applications, the base material of the photocurable polymer is generally derived from the synthetic polymers, which can be a thermoplastic or an elastomer. The principle method to prepare a UV-curable elastomer is to introduce a UV-curable or photosensitive molecule into an elastomeric chain. Azuma et al.² introduced cin-

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amic acid moieties into synthetic polyisoprene while D. Derouet et al.³ followed similar procedure for maleinized liquid natural rubber.

Natural rubber, a native produce of Thailand that is cultivated densely in the southern part of the country, is an interesting raw material to develop a new photo-oligomeric material as the presence of unsaturation in the polyisoprene unit of the natural rubber, technically paves the way for the production of acrylated resins. The acrylated natural rubber can be synthesized through acrylation of the natural rubber previously epoxidized. If the low molecular weight rubber is used as a starting material, then epoxidized liquid natural rubber or ELNR is obtained. Addition of acrylic acid onto ELNR, which gives acrylated epoxidized liquid natural rubber (AELNR), were studied by several scientists.^{4–6}

Generally, the method of investigation of UV-curable material is carried out by UV and infrared (IR) spectroscopic methods. In the case of photocurable elastomers, it also was found that most of the scientists explored the photocrosslinking reaction by using these two techniques.^{2–6} In general, polymerization reaction or formation of the carbon–carbon linkage system is an exothermic reaction and the heat released can be measured by a calorimeter. On irradiating photosensitive materials, the photopolymerization or photocrosslinking reaction that occurs will also lead to the evolution of heat. It has been reported that the kinetic and extent of photoreaction can be investigated with the aid of a photocalorimetric system such as a modified differential scanning calorimeter with an irradiation unit.^{7–9} In spite of many published papers on photocrosslinking of cinnamated or acrylated natural rubber, up to now there has been no report dealing with the study of photoreaction by measuring the heat released from the reaction. In this study, the preparation of the UV-curable liquid natural rubber was carried out by focusing on the photosensitive acrylate moieties. The preparation and characterization of ELNR are first presented. Then the study of the addition reaction of acrylic acid onto the ELNR is reported. Photocrosslinking of the prepared acrylated rubber was then carried out in the presence of a photoinitiator (Irgacure 184 and Darocure 1173) and diacrylate diluents (1,6 hexanediol diacrylate and tripropylene glycol diacrylate) in a photocalorimeter.

EXPERIMENTAL

Materials

Natural rubber latex (dry rubber content, DRC = 60%) was supplied by Bangkok Rubber Company, Thailand. Phenylhydrazine (synthesis grade) was used as purchased from Fluka. Acrylic acid (synthesis grade) was used as purchased from Merck. Vulcastab LW, a latex stabilizer, was supplied by Bulnax International Limited. Formic acid (98–100% analytical grade) was used as purchased from Merck. Hydrogen peroxide (50% standard grade) was supplied by Thai Peroxide Co., Ltd. HDDA (1,6 hexanediol diacrylate) and TPGDA (tripropylene glycol diacrylate) were supplied by Sartomer Co., Ltd. and used without further purification. Irgacure 184 and Darocur 1173 (photoinitiators) were supplied by Ciba-Geigy (Thailand) Co., Ltd.

Preparation of ELNR

Three hundred milliliters of natural rubber latex (30% DRC) stabilized with Vulcastab LW (3% by weight of DRC of natural rubber latex) was poured into a 1-L glass reactor, equipped with a mechanical stirrer, a condenser, a dropping funnel, and an air inlet tube. After heating the latex up to 60°C, a desired amount of phenylhydrazine (15 or 20 mL) was slowly added and the air was flowed at the rate of 2–3 Ls/min into the latex. The reaction mixture was stirred for 24 h. During this period, depolymerization or degradation of natural rubber latex, giving low molecular weight polymer or liquid natural rubber (LNR), took place. About 10 mL of the latex was taken for chemical structure analysis and molecular weight determination by viscosimetric method. The liquid rubber latex was then diluted with 150 mL distilled water and the temperature was reduced to 50°C. Neutralization of the latex was then carried out by adding formic acid. Then 9.5 mL of formic acid was added dropwise. After stirring the latex for 15 min, 61 mL of 50% H₂O₂ was added. The epoxidation reaction was allowed to take place for 48 h. At the end of the reaction, 30% aqueous NaOH was added in order to neutralize the latex. ELNR was recovered by precipitation in methanol. The obtained ELNR was dried under vacuum at 40°C.

The NR, LNR, and ELNR were analyzed by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy (Bruker AM 400 spectrometer, 300 MHz)

and Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, PE 2000). The epoxidation level was determined from area of proton peaks obtained from $^1\text{H-NMR}$ spectrum as shown in the following relationship:

$$\% \text{ mole epoxidation} = 100 \times [A_{2.70}/(A_{5.14} + A_{2.70})] \quad (1)$$

$A_{2.70}$ = integrated area of proton adjacent to

epoxide ring at 2.70 ppm

$A_{5.14}$ = integrated area of olefinic

proton at 5.14 ppm

$A_{2.70}$ is the integrated area of proton adjacent to epoxide ring at 2.70 ppm and $A_{5.14}$ the integrated area of olefinic proton at 5.14 ppm.

Addition Reaction of Acrylic Acid to ELNR

Five grams of ELNR was dissolved in 5 g of toluene in a round-bottom flask equipped with a condenser. The reaction flask was put into a thermostatically controlled bath, at the desired temperature (60 and 80°C). After the solution was stirred for 15 min, 10 g of acrylic acid was added. The solution was taken at different time to follow the progress of the addition reaction by using FTIR spectroscopy. The product so-called acrylated liquid natural rubber (AELNR) was obtained at the end of the reaction.

The evolution of acrylation reaction was investigated by following the decrease of epoxy group at 870 cm^{-1} . Therefore, the percentage of acrylation can be calculated from the decrease of infrared absorption band ratio of epoxy at 870 cm^{-1} and methyl group of the isoprene unit at 1357 cm^{-1} , which was taken as the reference peak. % Acrylation reaction was obtained from equation stated below:

$$\% \text{ Acrylation} = 100 \times [1 - (E_t)/(E_0)] \quad (2)$$

(E_0) : The peak area ratio of epoxy and methyl group at the beginning $t = 0$

(E_t) : The peak area ratio of epoxy and methyl group at time t

(E_0) is the peak area ratio of epoxy and methyl group at the beginning $t = 0$ and (E_t) the peak area ratio of epoxy and methyl group at time t .

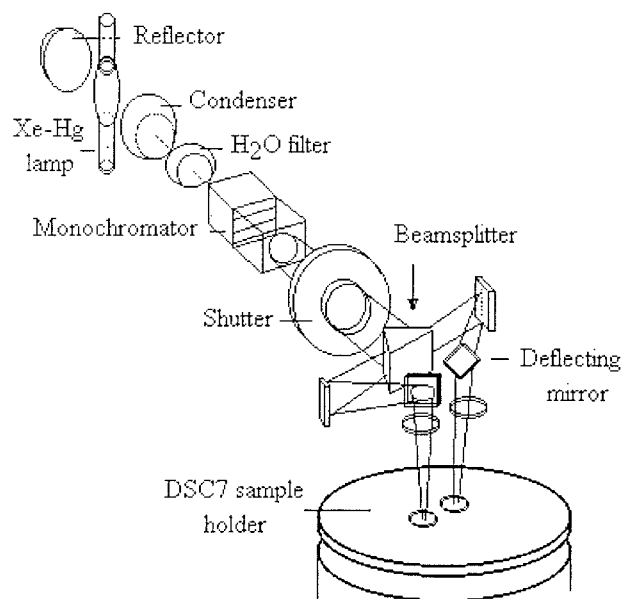


Figure 1 DPA 7 light path.

Study of Photocrosslinking Reaction

The study of photocrosslinking of AELNR was performed by using a Double Beam Photocalorimeter Accessory (DPA7, Perkin-Elmer) connected to Differential Scanning Calorimeter (DSC7, Perkin-Elmer). The DPA 7 light path was adjusted to focus on sample holder cells, as shown in Figure 1.

AELNR, HDDA or TPGDA, and a photoinitiator (Irgacure 184 or Darocur 1173) were mixed in various compositions by simple mixing in a small bottle before curing. About 1 mg of the sample was placed in an aluminum DSC pan covered with quartz window, using a calibrated weighing, and purged with high purity nitrogen gas for 10 min before irradiation. Polymerization was carried out at 60°C. Light from a 200 W medium pressure Xenon Mercury lamp (Hanovia 901-B0011) was filtered through a monochromator to obtain radiation of 314 nm wavelength before reaching the sample and the reference cells. The light intensity was calibrated by placing a black DSC graphite pan in the sample cell and incident intensity at the sample position was measured to be $320 \mu\text{W}/\text{cm}^2$ by placing a UV black meter above the sample cell.

RESULTS AND DISCUSSION

Epoxidation of LNR

Epoxidation of LNR was carried out by using performic acid *in situ* generated from formic acid and

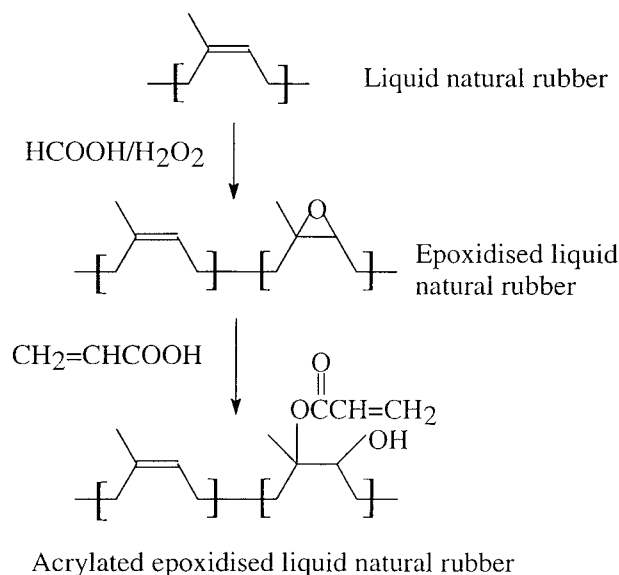


Figure 2 Schematic diagram of acrylation reaction of liquid natural rubber.

hydrogen peroxide. The schematic diagram of the reaction is shown in Figure 2. The LNR was previously prepared by oxidative degradation of NR in latex phase using phenylhydrazine and oxygen following Pautrat's method.¹⁰ Different molecular weights of LNR were obtained by varying the amount of phenylhydrazine, and it was evaluated in terms of viscosity average molecular weight. The molecular weight of ELNR is considered to be the same as the corresponding LNR, as it has been reported that no degradation reaction occurs during epoxidation reaction.¹¹ Three types of ELNR were prepared and their characteristics are shown in Table I.


¹H-NMR spectroscopic analysis shown in Table II revealed that LNR has significant characteristic signals similar to NR. For ELNR, the signal of proton adjacent to epoxide ring at 2.7 ppm confirmed that epoxidation did occur. Side reactions such as opening of epoxide ring and cyclic ether formation did not occur, as typical peaks for hydroxyl or diol protons and cyclic ether at 3.4 and

Table I Characteristics of Prepared ELNR

Properties	ELNR1	ELNR2	ELNR3
\bar{M}_v	5100	4700	7000
% Epoxidation ^a	25	22	25

^a Determined by ¹H-NMR spectroscopy.

Table II ¹H-NMR Characteristic Peaks of NR, LNR, and ELNR

Proton Resonance	Chemical Shift (ppm)		
	NR	LNR	ELNR
—CH ₂ , —CH ₃	1–2.5	1–2.5	1–2.5
—C=CH— O H	5.14	5.14	5.14
	—	—	2.70


3.9 ppm were not detected. ¹³C-NMR spectrum confirmed that the formation of tetrahydrofuran on polymeric chains did not occur because of the absence of furanized carbon resonances at chemical shifts of 75–80 ppm. IR spectroscopic results shown in Table III also confirmed similar result of the formation of epoxide ring by signals at 870 cm⁻¹ and unreacted double bond at 1660 cm⁻¹. Epoxidation level of the prepared ELNR was evaluated from the characteristic peaks at 2.70 and 5.14 ppm in the ¹H-NMR spectrum¹² by eq. (1). As shown in Table I, about 22–25% epoxidation of the liquid rubber were achieved. These epoxide moieties were then used as reactive sites for fixation of photosensitive molecules onto the rubber chains.

Acrylated Epoxidized Liquid Natural Rubber

Incorporation of photosensitive group such as acrylic function onto LNR was carried out by addition of acrylic acid onto reactive epoxide function of LNR, as shown in Figure 2. The reaction was carried out by mixing acrylic acid and ELNR at 2:1 weight ratio in toluene. The progress of acrylation reaction was monitored by following the changes in the infrared absorption bands of the epoxide function. The degree of acrylation of the rubber was calculated from eq. (2) by assuming that no secondary reactions occur, and that all the epoxy groups consumed were converted into acrylate and hydroxyl groups.

By using ELNR1 as the starting material, it was found from the results given in Figure 3 that the completion of the addition reaction was attained within 2 h at the reaction temperature of 80°C, which was faster than the reaction at 60°C. Thus, increasing reaction temperature resulted in considerable reduction in reaction time. This is thought to be due to enhancement of probability

Table III Major Characteristics of IR Absorption Bands of NR, LNR, and ELNR

Functional Groups	Wavenumber (cm ⁻¹)		
	NR	LNR	ELNR
=CH stretching	3028	3028	3028
C—H stretching of CH ₃	2960, 2870	2960, 2870	2960, 2870
C—H stretching of CH ₂	2925, 2850	2925, 2850	2925, 2850
C—H bending of CH ₃	1375	1375	1375
C—H bending of CH ₂	1465	1465	1465
C=C stretching	1660	1660	1660
	—	—	1250, 870
C—H wagging	835	835	835

of molecular collisions. The reaction temperature of 80°C was selected for further fixation of acrylic acid onto other types of ELNR for the preparation of acrylated elastomers for studying the photocrosslinking reaction. Similar results were obtained in the case of ELNR2 as it has similar molecular weight and % epoxidation. However, in the case of ELNR3, the FTIR spectrum of the addition product showed unreacted epoxide at the reaction time of 2 h, while ELNR1 and ELNR2 showed completion of epoxide ring opening. This may be due to the higher molecular weight of ELNR3 than ELNR1 and ELNR2, which retarded the movement of the chain, resulting in a decrease of molecular collision between the epoxide ring and acrylic acid. This result is in accordance

with the report of C. Deeprasertkul⁶ that higher molecular weight resulted in lower rate of addition reaction.

Study of Photocrosslinking Reaction by Photocalorimeter

Photoreaction of the prepared AELNR was studied by exposing AELNR to UV irradiation in the presence or absence of 5 phr photoinitiator (Irgacure 184 or Darocur 1173), using a DPA 7 photocalorimeter. It was found that no significant exotherm could be detected after 30 min of UV exposure. These results showed that the reactivity of the acrylated rubber under UV irradiation was poor. This might be due to the long pendent isoprenic chain lengths that limit the overlap of the excited acrylate function. Scranton et al.¹³ also reported that the reactivity of photosensitive monomer decreases as the pendent chain is increased.

Table IV shows various formulations of UV curable AELNR used for further study of photocrosslinking reaction. Liquid diacrylate monomers such as HDDA and TPGDA were added into AELNR as reactive plasticizers or diluents. Figure 4 illustrates a typical thermogram obtained from UV irradiation of AELNR2 in the presence of HDDA and Iragacure 184 where the rate of heat released by the sample (dH/dt) is plotted vs elapsed time of reaction. It can be seen that dH/dt rapidly increases to a maximum and then asymptotically decreases to zero value. This result shows that the reactivity of photocurable AELNR could be enhanced by the addition of liquid difunctional monomers which act as a reactive plas-

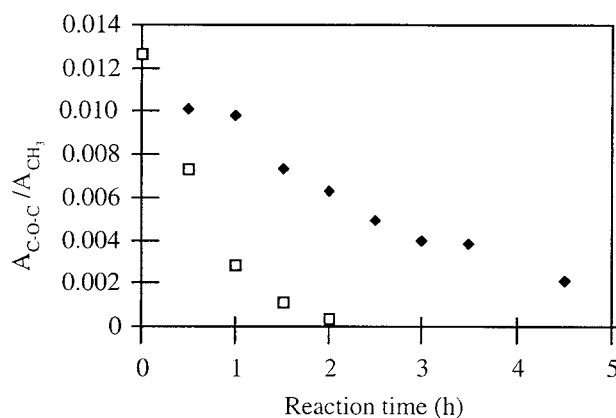


Figure 3 Plots of peak area ratio of epoxide to methyl group (A_{C-O-C} / A_{CH_3}) vs reaction time of the addition reaction of acrylic acid onto ELNR1 carried out at (◆) 60 and (□) 80°C.

Table IV Composition of AELNR Containing Diacrylate Monomers and Photoinitiators

Codes	AELNR (g)	HDDA (g)	TPGDA (g)	Irgacure 184 (g)	Darocur 1173 (g)
A2H30I20	100	30	—	20	—
A2H45I20	100	45	—	20	—
A2H60I20	100	60	—	20	—
A1H30T20I05	100	30	20	5	—
A1H20T20I10	100	20	20	10	—
A1H20T30D05	100	20	30	—	5
A1H20T20D15	100	20	20	—	15

ticizer,¹⁴ as well as contributing to production of the tridimensional network.⁹ From the reaction curve, it suggests that upon irradiation of AELNR in the presence of photoinitiator, a radical forms and initiates polymerization, and then a photocrosslinking reaction involving acrylate functional groups rapidly occurred. If the rubber chains took part in the crosslinking with the acrylate monomer, it should not have much difference of reactivity; otherwise two separate reaction curves should be observed.¹⁵

The photo-DSC thermogram also indicates a high initial rate of reaction that quickly slows due to exhaustion of acrylate reactive group available for further polymerization. This behavior has been noted by Tryson and Shultz,⁸ and has been interpreted as evidence of rate acceleration due to the gel effect. As shown by the thermogram, as light was switched on the reaction starts imme-

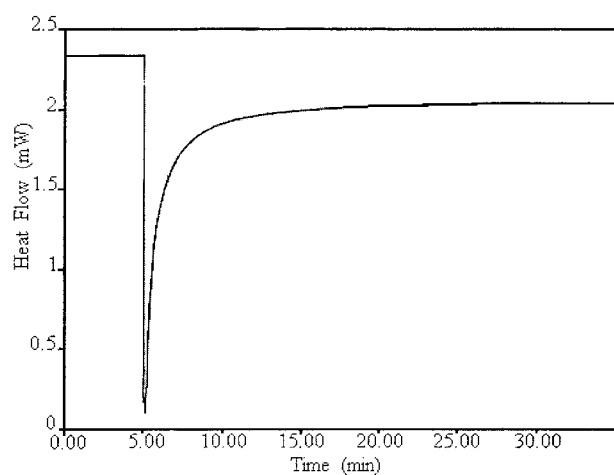


Figure 4 Typical thermogram obtained from photocuring by using a photocalorimeter (DPA7) of AELNR2 with HDDA in presence of the Irgacure photoinitiator.

diately, then high molecular weight macroradicals are rapidly produced as the result of propagation in the absence of termination. It takes less than 30 s to achieve maximum polymerization. This autoacceleration, called the Trommsdorff effect or gel effect, causes the formation of unusually high molecular weight polymer. In the network forming system, the cause of the gel effect is chemical crosslinking rather than physical entanglement, which produces an enhanced gel effect due to reduced mobility of the gel-bound radicals. Upon further irradiation, the reaction slowed down, due to both the depletion of acrylate double bonds and mobility restrictions of the reactive sites trapped in the highly crosslinked network. After 30 min, essentially no more reaction could occur. Also, generation of branching led to formation of insoluble polymer. A schematic representation of the tridimensional network generated in the case of AELNR and HDDA mixture is proposed in Figure 5. The rubber chains are connected either directly through the acrylate poly-

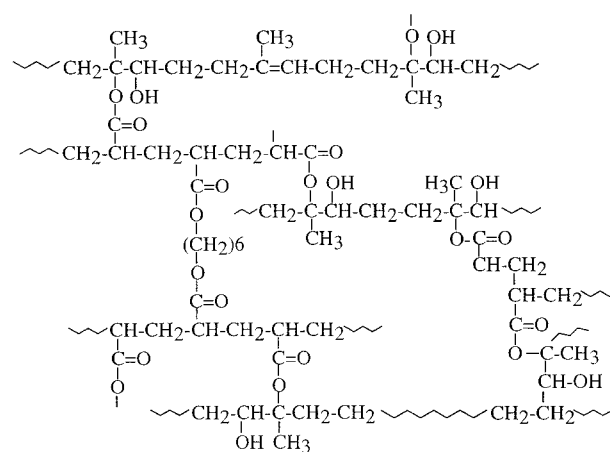


Figure 5 Proposed chemical structure of the polymer network that occurred from UV-cured AELNR-HDDA.

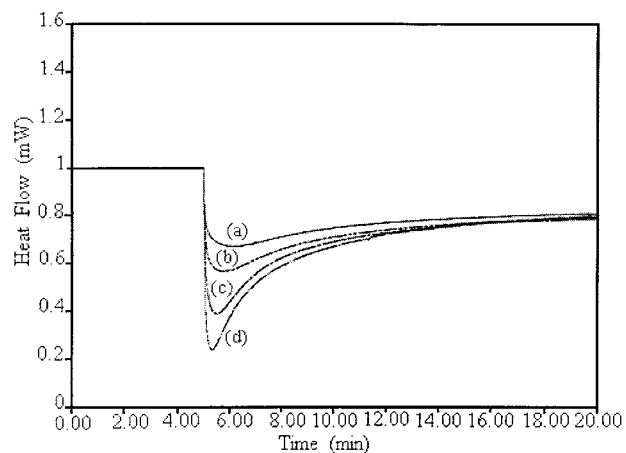


Figure 6 Photocrosslinking exothermic traces of various formulations of AELNR1 with diacrylate monomers in the presence of the photoinitiator. (a) A1H30T20I05, (b) A1H20T30D05, (c) A1H20T20I10, and (d) A1H20T20D15.

mer chains or through the polymerized HDDA. In addition, some loops are likely to arise through intramolecular polymerization of the pendent acrylate double bonds located on the rubber chains.

Figure 6 shows series of thermogram of AELNR1 in the presence of two types of diacrylate and photoinitiators. Under UV irradiation, it can be seen that each mixture presents its distinct profile of heat of polymerization. The thermograms show the effect of initiator concentration on the reaction rate. Here, comparing between the profiles of (a) A1H30T20I05 and (c) A1H20T20I10 and those of (b) A1H20T30D05 and (d) A1H20T20D15, it was found that the time of the onset of autoacceleration decreased as the initiator concentration was increased. The highest rate of photoreaction occurred when the highest amount of photoinitiator was used. For example, the reaction of A1H20T20D15 containing 15% Darocur photoinitiator was faster than that of A1H20T30D05 containing 5% Darocur photoinitiator. The results obtained revealed that the efficiency of photocrosslinking reaction or the maximum reaction rate increased when photoinitiator concentration was increased. It is also seen that broader exotherm thermograms were obtained comparing to the thermogram in Figure 4. This may be due to the presence of diluent such as TPGDA, which possesses a longer pendent chain between acrylate functions than the HDDA. As a result, mobility of the growing chains would increase, and, therefore the probability of collision between the reactive radicals and the unreacted

acrylate would decrease, thereby reducing the magnitude of the gel effect.

Heat of Photocrosslinking Reaction

Generally, upon irradiation of photoreactive monomer in the presence of photoinitiator, the radical polymerization process rapidly results in heat released. The extent of photopolymerization or photocrosslinking reaction is proportional to the heat of reaction ΔH , represented by the total area of the thermogram. The heats of reaction determined from exotherm thermogram of AELNR2 formulated with HDDA and Irgacure 184 are shown in Table V. All the samples of AELNR2 were heated from 60 to 300°C at scanning rate of 20°C/min. ΔH calculated theoretically of acrylate function present in the formulation also was derived by using the value of 77.9 kJ/mol for the heat of polymerization of the acrylate double bond and assuming that all acrylate functional groups were consumed. It can be seen from Table V that the heats of polymerization of each AELNR sample obtained from photoreaction were lower than those obtained by thermally induced reaction and were lower than the theoretical values. The results obtained are in accordance with the work of Abadie and Appelt,⁹ who showed that multifunctional acrylate resins undergo more extensive conversion when the sample is thermally polymerized than when using light-induced reaction. This is largely due to the difference in polymerization temperatures. The properties of the resulting networked polymers may also be different. The heats of polymerization occurred by both photo and thermal methods were well below the theoretical values. This suggests that some reactive sites may still remain in the system.

Table V The Heat of Polymerization Obtained from Photoreaction, Thermal Reaction, and Theoretical Calculation of AELNR2 Containing HDDA and Irgacure 184 at Various Compositions

Codes	ΔH_{photo} (J/g)	$\Delta H_{\text{thermal}}$ (J/g)	ΔH_{theory} (J/g)
A2H30I20	-119.22	-166.42	-267.71
A2H45I20	-157.19	-168.86	-302.85
A2H60I20	-192.53	-191.22	-337.99

CONCLUSIONS

Preparation of UV-curable liquid natural rubber could be carried out by fixing a photosensitive function, i.e., acrylic acid, onto liquid natural rubber, which was previously transformed into epoxidized liquid natural rubber.

It was found that temperature affected the addition reaction of acrylic acid onto ELNR and the evolution of peak area ratio of epoxide to methyl groups studied by FTIR technique could be used to evaluate the progress of the reaction.

Photocalorimetry is an efficient technique for a study of photocrosslinking of UV-curable materials. It was shown in the present study that the reactivity of photocurable epoxidized liquid natural rubber could be substantially enhanced by the addition of a liquid diacrylate monomer such as HDDA or TPGDA, which acts as a reactive plasticizer, and the rate and extent of polymerization depend primarily on concentration of these diacrylate monomers and photoinitiator employed. The photocalorimetric method can also provide information concerning relative crosslink density of the UV-curable materials.

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