Environmentally Friendly Radiation Hard *d*-Limonene and Laccol Copolymers Synthesized via Cationic Copolymerization

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In the modern world, petroleum-based synthetic polymers have a great number of applications in fields ranging from food packaging to space travel. However, the processing of petroleum products and the resulting depletion of fossil fuels are major environmental concerns in today's society. As a result, the development of sustainable polymers which are made up of renewable resources and waste products is an immerging area of research. Considering the world food production, citrus fruit is most abundant and its contribution to waste generation is immense. Therefore, this study focuses on offering an alternative to the use of petroleum-based polymers and also providing a regulatory pathway to manage citrus waste by developing novel copolymers of laccol and limonene. Two environmentally friendly compounds, laccol, derived from the sap of *Toxicodendron succedaneum* tree and limonene, extracted from orange peels, were copolymerized via cationic polymerization to generate *d*-limonene:laccol copolymers with radiation hardening capabilities which is relevant in fields such as nuclear energy generation, medicinal sterilization, commercial irradiation, and space exploration. Formation of these copolymers was verified with infrared and nuclear magnetic resonance analysis. The synthesized copolymers were characterized using different methods and exposed to Co-60 gamma radiation to identify alterations to their properties. POLYM. ENG. SCI., 60:607–618, 2020. © 2019 Society of Plastics Engineers

INTRODUCTION

Polymers play an essential role in modern society and currently the main source for the components of synthetic polymers is fossil fuels. Monomers derived from petroleum products can be used to synthesize polymers with extraordinary properties including remarkable durability, conductive properties, and radiation resistance, all at a very low cost. However, the environmental impact caused by depletion of these fossil fuels and the environmental damage that accompanies processing petroleum products are rapidly becoming major issues with the use of petroleum-based polymers. Therefore, in search of alternative measures, many scientists have focused on producing environmentally friendly and sustainable polymers from renewable sources and waste products [1, 2]. In particular, the incorporation of citrus waste into the next generation of renewable polymers has recently gained considerable attention due to its appreciable metabolites.

Out of the worldwide fruit and vegetable production, most abundant crop is citrus and one-third of the crop is processed [3]. In the entire industrialized crop, approximately 98% contains oranges, lemons, grapefruits, and mandarins which oranges are the most relevant with 82% of total. Citrus fruits are processed mainly to obtain juice. They are also used in the canning industry to produce marmalade, segments of mandarin, and in chemical industry to extract flavonoids and essential oils. From the whole fruit mass 50% of residual obtained as waste and it consists of peels, seeds and fruit pulp remaining after juice and essential oil extraction [4]. When considered on the industrial scale, this becomes a huge environmental concern. Therefore, utilizing these waste products to develop useful chemical resources has recently become an important topic of investigation. The citrus peel is a good source of a plethora of possibly useful compounds, including molasses, pectin, and limonene [5].

In this study, limonene extracted from citrus peels is utilized as one of two monomers used to develop copolymers with laccol, a compound that is extracted from Vietnamese lacquer sap. The major constituent of essential oil resulting from the citrus fruit skin is limonene and 90% of it contains *d*-limonene isomer [6]. This belongs to the family of terpenes [7]. Terpenes are secondary metabolites synthesized mainly by plants, but also by a limited number of insects, marine microorganisms, and fungi. Although these terpenes were initially considered as "waste," later, their involvement in biosynthetic processes and ecological important role was discovered [8]. Limonene is used in cosmetic production, foods, and beverages as well as a green solvent [2, 7]. This contains double bonds that provide the necessary bifunctionality for polymerization (Scheme 1-limonene). Limonene is also an allylic monomer (CH_2═CH─CH_2R; R is the rest of the molecule) which is hard to homopolymerize via free-radical polymerization due to stable radical formation and steric hindrance compared to vinyl radicals [9]. Therefore, copolymerization of *d*-limonene using $AlCl_3$.EtOAc cationic coinitiator with laccol monomer is investigated herein as a novel approach.

Laccol monomer is extracted from *Toxicodendron succedaneum* tree lacquer sap which grows mainly in Vietnam. Lacquer saps are popular since ancient time periods because of its excellent toughness, high solvent resistivity, and high durability [10–13]. It contains two reactive hydroxyl groups in the phenyl ring and a C-17 unsaturated side chain at third position of the phenyl ring (Scheme 1-laccol). Due to the unsaturation of this C-17 side chain, it is a potent candidate for cationic polymerization process. As described in our previously published article [14], laccol was successfully polymerized via cationic polymerization using $AlCl_3$.EtOAc coinitiator. Further broadening the applicability of laccol in industrial environment, copolymerization of laccol with limonene via cationic polymerization was studied herein to develop radiation hard copolymers. Copolymerization process involved two or more monomers during chain growth polymerization which can balance the properties of commercial polymers [15]. Laccol and *d*-limonene was copolymerized with $AlCl_3$.EtOAc coinitiator. Conjugated double bonds (trans) in unsaturated side chain of laccol and terminal double bond in limonene was

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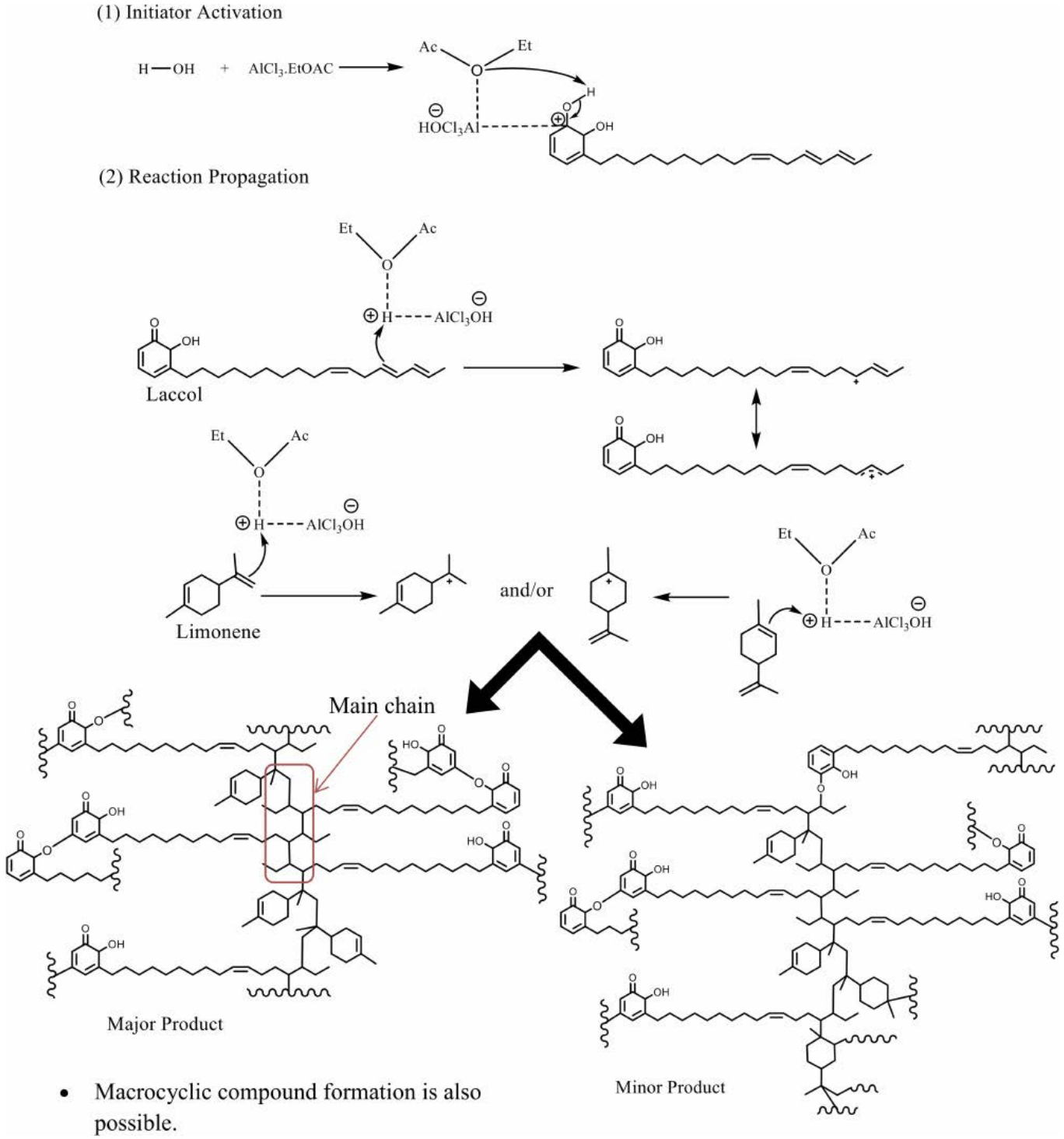

SCH 1. The proposed mechanism for limonene:laccol copolymer formation. [Color figure can be viewed at wileyonlinelibrary.com]

involved prominently during the chain growth polymerization. Additionally, as explained by Rozentsvet et al. [16] macrocyclic compound formation is also possible due to the phenate ions and cis/trans double bonds (unsaturated groups) in the laccol side chain. These phenomena were clearly observed in the infrared and nuclear magnetic resonance (NMR) data obtained for the synthesized copolymers. During this cationic polymerization process, 70% of limonene by weight was able to copolymerize with laccol is a promising outcome compared to the reported literature regarding limonene copolymers [17, 18]. Synthesized copolymers irradiated with gamma rays and alterations to the properties of materials were investigated.

The overall hypothesis for this work is to develop environmentally friendly sustainable copolymers of limonene and laccol from citrus waste and lacquer sap via cationic polymerization which possess potent radiation resistivity. These synthesized copolymers will be an alternative to petroleum-based synthetic polymers with appreciable properties and also a promising pathway to regulate

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citrus waste. In laccol, there are hydroxyl groups which can behave as radical scavengers. These hydroxyl groups can convert excitation energy into nonchemistry inducing energy to enhance the radiation resistivity of lacquer [19, 20]. In addition, enhancement of radiation hardness in nanotubes of organic polymer matrices [21–23] and laccol polymer [14] after gamma irradiation has shown by Harmon's group. Further, this is the first article documenting the synthesis of laccol:limonene copolymers which possess radiation hardening.

Irradiation can cause many different alterations to the polymer matrix forming radicals, anions, cations, gases, and other different species. Curing of the polymer matrixes could be achieved by the radiation exposure due to physical and chemical crosslinks formation. Physical crosslinks can be formed because of secondary interactions such as ionic and/or hydrophobic interactions, hydrogen bonding, and chain entanglements [24] whereas chemical crosslinks occur through two adjacent molecules forming a new bond. Formation of three-dimensional networks due to crosslinks could lower the solubility of polymer matrix and make the material harder. Chain scissions also possible due to radiation exposure which make lesser hardened and solubilize polymers [25]. These properties make the materials as ideal candidates to be used in radiation hard environments in industrial setup such as nuclear reactors, medicinal sterilization plants, commercial irradiators, and space operations [26]. Limonene:laccol copolymers synthesized herein was analyzed as cured copolymers and irradiated copolymers with the help of IR, NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), shore hardness, and swelling analysis.

EXPERIMENTAL

Materials

High purity food grade *d*-limonene was provided by Blubonic Industries and Viet Lacquer Interior Co., Ltd. in Vietnam provided the raw lacquer sap. Acetone and dichloromethane (CH_2Cl_2) were used as reagent grade solvents. Magnesium sulfate anhydrous, granulated anhydrous calcium chloride, HPLC grade (99.9%) tetrahydrofuran, and sodium hydroxide were purchased from Fischer Scientific. Aluminum chloride ($AlCl_3$) reagent plus grade 99%, toluene (C_7H_8) assay 99.8% and HPLC grade ethyl acetate (EtOAc) assay 99.9% were purchased from Sigma Aldrich.

Preparation Procedures

Laccol extraction, laccol polymer preparation, and initiator preparation were carried out according to the procedures published in our previous article [14]. High pure food grade *d*-limonene was used as received without further purification.

Copolymers of Limonene and Laccol. According to the monomer ratios illustrated in Table 1, copolymers of limonene and laccol were synthesized. L-10, L-30, L-50, and L-70 sample names corresponded to 10%, 30%, 50%, and 70% (vol/wt) limonene in laccol, respectively. Typical preparation procedure for L-10 copolymer is as follows. A 36.0 g of laccol extract was measured to a flask containing 3.70 mL of CH_2Cl_2. While stirring the reaction mixture in an ice bath, 4.70 mL of *d*-limonene was added and also 11.6 mL of initiator complex (~1 M) was added dropwise afterward. With time (15–30 min), the reaction mixture became more viscous. The vacuum oven was used to dry the samples for at 60°C for 4 days and another 4 days in hot air oven at ~100°C. Scheme 1 illustrated the proposed mechanism for limonene–laccol copolymer formation [27, 28].

TABLE 1. Limonene and laccol contents in synthesized materials.

Sample name	Laccol extract (g)	Limonene (ml)	Initiator complex (ml)	CH_2Cl_2 solvent (ml)	Total volume (ml)
L-10	36.0	4.70	11.60	3.70	20.0
L-30	28.0	14.20	10.80	5.00	30.0
L-50	20.0	24.00	10.00	6.00	40.0
L-70	12.0	33.30	9.20	7.50	50.0

Characterization Methods

Identification of polymer formation and its thermal, physical, and chemical characteristics were studied using various characterization methods. Additionally, the effects resulted due to gamma irradiation was also examined to identify the proper polymer matrices for applications.

Fourier Transform IR Analysis. Solid films prepared from polymer materials were used with UATR Two spectrometer (Perkin Elmer) to conduct Fourier transform IR (FTIR) study. Parameters were maintained as follows: resolution set at 4 cm^{-1}; 400–4,000 cm^{-1} scan range; and 16 average scans for each experiment.

NMR Spectroscopy. Limonene:laccol copolymers dissolved in chloroform-*d* was used for NMR analysis with Varian INOVA 400 spectrometer having the following instrument parameters. The temperatures was maintained at 298 K, spin set and maintained at 20 Hz, 16 transients used in block sizes of 8 and d1 relaxation time 2.000 s.

Differential Scanning Calorimetry. The DSC from TA Instruments (model 2920) was used to identify the glass transition temperature (T_g) of synthesized copolymers. Dry nitrogen gas with a flow rate of 70 mL/min was purged through the sample cell. Cooling was accomplished with the liquid nitrogen cooling accessory. For the temperature calibration, indium was used and three different ramp rates were maintained (10, 20, and 30°C/min) for proper identification of T_g range. Samples were first cooled to −50°C, heated to +150°C, cooled again to −50°C and heated again for second time to +150°C (two heating and cooling cycles).

Dynamic Mechanical Analysis. The rectangular bars were molded with length 50 mm, width 10.5 mm, and thickness 2 mm using heated Carver hydraulic press with slow cooling to room temperature under pressure. The linear viscoelastic region (LVR) was identified through isothermal strain sweep test at −100° C using rheometer (TA Instruments, AR 2000). The 0.3% strain was selected within the measured LVR region to characterize the samples with a temperature ramp in oscillation mode to identify the glass transition temperature (T_g). Conditions were maintained for temperature ramp experiment as −60°C to 200°C at 10°C/min for copolymers while cooling with liquid nitrogen.

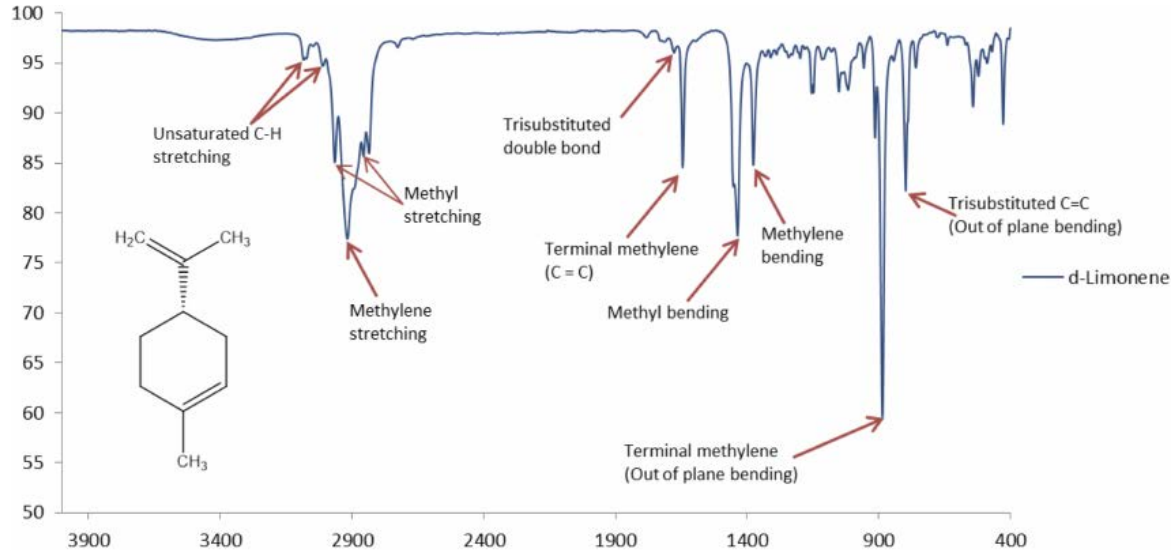

FIG. 1. IR spectrum of *d*-limonene with important functional groups. [Color figure can be viewed at wileyonlinelibrary.com]

In addition, rectangular bars were utilized to conduct frequency sweep experiment for limonene:laccol copolymers. The parameters were adjusted for the experiment as follows: 0.300% strain, frequency range from 0.1 to 10.0 Hz, starting temperature of −15°C with 5°C increments each time until the sample collapse. Activation energy associated in the glass transition region was calculated for each sample using the frequency sweep experimental data.

Thermogravimetric Analysis. A 10 mg sample of each copolymer formulations was analyzed using TA Q50 (TGA model). Weight loss versus temperature scans were recorded at a ramp rate of 10°C/min in air from room temperature (~22°C) to 700°C.

Shore Hardness. The hardness of polymerized samples was measured incorporating ASTM D2240 Shore A durometer. Discs with diameter 2.54 cm and thickness 0.25 cm were punched from sheets that were compression molded using a Carver laboratory press (model C) equipped with heating elements. Hardness of the samples was measured before and after the γ-radiation treatment averaging eight indentations per sample.

Radiation Studies. The radiation studies were conducted using Co-60 Gamma Irradiator at University of Florida, Gainesville. The utilized gamma ray source (1.25 MeV) was delivered about 200–250 krad/h (~30 Gy/min) to six to eight adjacently placed samples (discs with diameter 2.54 cm and thickness 0.25 cm) per each exposure. Samples were exposed to 10.0 Mega Rad in air with the required exposure time of 336 h.

Swelling Analysis. The sample flasks were prepared with ~30 mL toluene in each and limonene:laccol copolymer specimens were placed at room temperature (~22° C) for 72 h. The exact weight (M_I) of those specimens was determined using a precision balance. After 72 h, the solvent was decanted and liquid solvent adhering to the sample's surface removed by short contact with filter paper. The weight of the swollen polymer (M_{II}) was determined immediately afterward. Percent weight gain was calculated as follows incorporating [29, 30] *Eq 1*.

$$\text{Weight gain}\,(\%) = \left(\frac{M_{II}}{M_I} - 1\right) 100, M_{II} \geq M_I \qquad (1)$$

RESULTS AND DISCUSSION

Limonene and laccol copolymerized via cationic polymerization with $AlCl_3$.EtOAc coinitiator to produce environmentally friendly sustainable copolymers which possess radiation hard ability. Characterization of these copolymers was carried out using IR, NMR, DSC, rheology, TGA, and various other methods. Samples were reinvestigated after the gamma radiation treatment to identify the alterations occurred and L-10, L-30 samples illustrated the promising results. All the samples were further cured due to crosslinks (physical and chemical) after gamma irradiation and materials were not deteriorated. Obtained results analyzed with further details here after.

FTIR Analysis

Identification of important functional groups was acquired using FTIR for *d*-limonene and resulted graph is illustrated in Fig. 1. Peaks observed in the region of 3,080–3,020 cm^{-1} are for stretching of unsaturated C—H group, 2,925–2,855 cm^{-1} for stretching of methylene group, 2,970 and 2,870 cm^{-1} for stretching of methyl, 1,680 cm^{-1} for trisubstituted double bond, 1,646 cm^{-1} for terminal methylene (—C═C—), 1,438 and 1,380 cm^{-1} for methyl and methylene bending, 888 cm^{-1} for out of plane bending of terminal methylene and 802 (840–800) cm^{-1} for out of plane bending of tri substituted double bond [31].

Peaks at 1,644 cm^{-1} and 887 cm^{-1} which are relevant to terminal C═C bond were completely utilized and peak at 802 cm^{-1} for out of plane bending of internal C═C bond was also involved in the copolymerization process with laccol. A new peak at 1,712 cm^{-1} was appeared which could attribute as laccol quinones. In laccol monomer, peaks around 987 and 968 cm^{-1} were consumed during the reaction and this is a clear evident of

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polymerization which was occurred in the side chain of laccol monomer. Obtained results are illustrated in Fig. 2a. The peaks related to phenyl ring vibrations were observed at 1,621; 1,596; and 1,470 cm^{-1} region. The peaks at 988 cm^{-1} (trans) and 966 cm^{-1} (trans) were shown the bending vibrations of conjugated alkene. Also cis alkene could observe in the region 732 cm^{-1} [13, 32, 33]. These observed peaks were altered and/or completely disappeared during the copolymerization process. According to the results maximum content of limonene in laccol was obtained as 70 weight percentage (L-70 sample) and this is a promising outcome of the process compared to the reported literature [17, 18].

Samples were reinvestigated after the gamma radiation treatment. The peaks relevant to phenyl ring —C=C— vibrations (1,621; 1,596; and 1,470 cm^{-1}) were mainly altered after the gamma radiation treatment as illustrated in Fig. 2b and c due to the formation of dimers and polymers [13, 33]. The peak at 1,640 cm^{-1} shifted to 1,710 cm^{-1} and broadened after gamma irradiation due to the formation of laccol quinones [13, 33].

Peaks at 987 and 968 cm^{-1} were reappeared after radiation treatment. Because of the gamma radiation feasibility of forming radicals is increased and it could favor the reactions occurring through phenyl ring of laccol with limonene terminal double bond [13, 33] compared to laccol side chain reactions. According to the obtained results, all the samples were cured further because of radiation. Also physical and small amount of chemical crosslinks involved in the curing process. Materials were not deteriorated after expose to gamma radiation and promising results were observed for L-10 and L-30 copolymers.

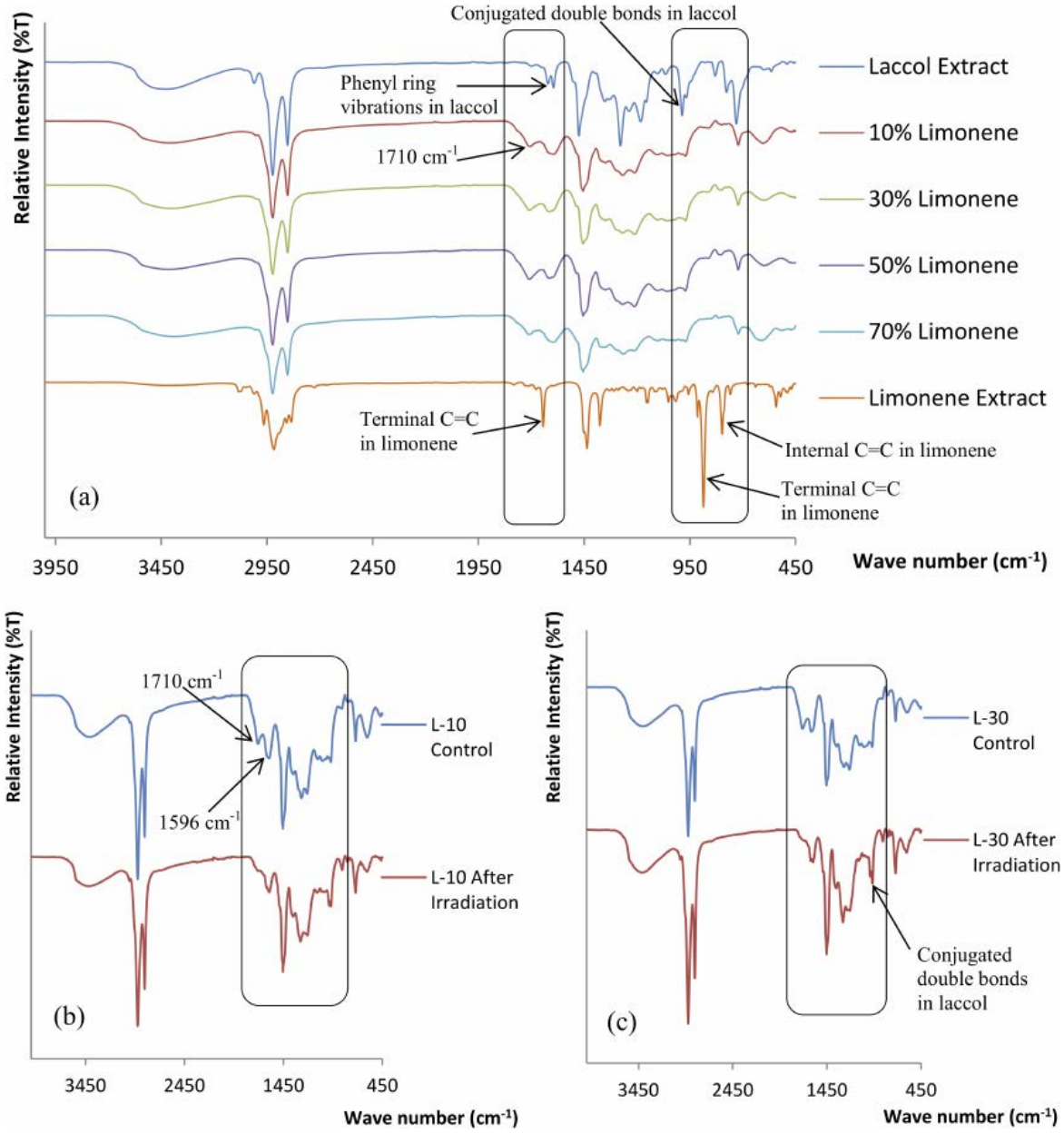

FIG. 2. IR spectra of (a) *d*-limonene:laccol copolymers, (b) L-10 (10% limonene in laccol) before and after irradiation, and (c) L-30 (30% limonene in laccol) before and after irradiation. [Color figure can be viewed at wileyonlinelibrary.com]

NMR Analysis

Copolymer formation between *d*-limonene and laccol via cationic polymerization was further confirmed using ^{1}H NMR analysis. Cured polymers were hard to dissolve in any organic solvent, therefore partially solubilize samples in deuterated chloroform were analyzed herein. The NMR spectrum of laccol extract (Fig. 3a) was used to identify the involvement of functional groups in the reaction with *d*-limonene. Peaks appeared in the region of 5.5–6.0 ppm denote the conjugated double bonds (13′—16′) in the laccol side chain. In the region of 5.0–5.5 ppm denotes the cis double bond (10′, 11′) of the side chain and hydroxyl groups (a) in the phenyl ring. For *d*-limonene, peaks in the region 4.1 to 5.0 ppm denote the terminal C═C bond and region 5.0–5.5 ppm denotes the internal C═C bond [34].

During the copolymerization process the peaks at 4.1–5.0 ppm region (Fig. 3b) which represent the terminal C═C bond of *d*-limonene [34] and peaks at 5.5–6.0 ppm region which are relevant to conjugated double bonds in laccol side chain [35, 36] were disappeared. This provides the clear evidence of cationic polymerization which occurred through these double bonds of limonene and laccol. Further, the peaks relevant to laccol phenyl ring 4–6 were reduced and this could be due the crosslinking reactions occurred through phenyl ring. New peak appears in the region 4.0–4.3 ppm which is related to —C—O—C— bond formation during the process. The formation of new —C—O—C— bonds could observe through phenyl ring and also through the side chain [13] because of the cationic polymerization as illustrated in Scheme 1. Further, this could be due to the macrocyclic compound formation [16] as well during the copolymerization of *d*-limonene and laccol. After the gamma irradiation, test samples became harder and it was difficult to dissolve in any solvent to do the NMR analysis for data collection after radiation treatment.

DSC Analysis

Glass transition temperature (T_g) of the materials was analyzed using the DSC. T_g value is greatly influenced by the tacticity, molecular weight, sample weight, ramp rate, and laboratory processing conditions [37–40]. To identify the proper T_g region three different ramp rates (10, 20, and 30°C/min) were used in the analysis and results obtained for 30°C/min ramp rate was illustrated in Fig. 4. With increment of the ramp rate, the T_g values are also increased accordingly for each synthesized copolymer (Table 2). Neat laccol polymer (NLP) and *d*-limonene were used as control samples during the experiment. Data obtained for NLP is broad and rheology is a proper method to analyze T_g for NLP [14]. *d*-Limonene homopolymer was very brittle and could not use to develop rectangular bars for rheology analysis. Therefore, DSC was utilized to analyze T_g and obtained value was 72.5°C at 30°C/min ramp rate (Table 2). L-10, L-30, and L-70 samples were illustrated significant change in the heat flow inside the temperature region of 5°C–55°C which is a broad T_g range. To further confirm the T_g values of each copolymer and their activation energies; rheology was used and results were analyzed in detail in the following section.

Dynamic Mechanical Analysis

Rheometer was utilized for this analysis to identify the glass transition temperature (T_g) where long chain segments slip at specific temperature region. Tan δ curve obtained from the experiment of temperature ramp was used to identify the T_g values for each limonene:laccol copolymer, as illustrated in Table 2. T_g values obtained for copolymers were reside in the temperature region of 17.0°C–24.0°C with the increasing order of L-30 < L-10 < L-70 < L-50. According to the results, more ordered packing was observed for L-50 with higher T_g value. This copolymer contains 1:1 monomer ratio from both laccol and limonene. When deviating from the 1:1 monomer ratio, it could possibly effects the physical crosslinking of the materials hence disturbs the proper packing of the molecules in temporary network.

The observed plateau in the rubbery region specifically for L-10, L-50, and L-70 tan δ curves, as shown in Fig. 5 was a consequence of long molecules entanglement which led to physical crosslinks that restrict molecular flow through the formation of temporary networks [41]. At higher temperatures, tan δ curve shows increment, possibly due to the reactions occurring inside the materials which influenced further curing [11]. After the gamma irradiation, the test samples could not use for dynamic mechanical analysis (DMA) due to the fact of the sample shapes. For the radiation studies, disc shaped was utilized per the requirement and for DMA; rectangular bar shaped was required for better analysis of T_g and activation energy. If the samples were remolded after the gamma radiation studies, it could cause a different effect due to temperature increment and this will alter the data. Therefore, alternative test methods were utilized to support the crosslinking process after gamma radiation as described in the Fourier Transform IR Analysis, TGA Analysis, Shore Hardness Analysis, and Swelling Analysis sections.

Frequency sweep experiment was conducted to calculate the activation energy in the region of glass transition temperature (Table 2). Resulting graphs from this experiment were analyzed via time–temperature superposition software with shift factor versus temperature and obtained results were followed WLF behavior. Accordingly, activation energies were calculated using the *Eq. 2* where R is universal gas constant (8.314 J mol^{-1} K^{-1}), C_1 and C_2 are material constants, T is temperature given in Kelvin (K), and E_a is the activation energy [42, 43]. L-50 sample was shown the highest activation energy and the least was observed for L-30 sample. For the L-50 sample, higher T_g was observed hence more ordered packing and therefore required high activation energy to move long chain segments in the glass transition region. As the control sample, NLP was shown 244 kJ mol^{-1} value as the activation energy in the T_g region. Obtained WLF graphs for L-30 and L-50 are illustrated in Fig. 6.

$$\Delta E_a = (2.303)\left(\frac{C_1}{C_2}\right)\mathrm{RT}^2 \tag{2}$$

TGA Analysis

Weight loss of the materials was identified incorporating dynamic thermogravimetric method where the sample is heated at a linear rate in predetermined temperature changing environment [44]. Promising results were obtained for L-10 and L-30 copolymers which were used as examples to describe the results herein. Figure 7 illustrates the TG curves of L-10 and L-30, before and after the gamma radiation treatment. In the temperature region from 50.00°C to 200.0°C the weight loss of copolymers L-10 and

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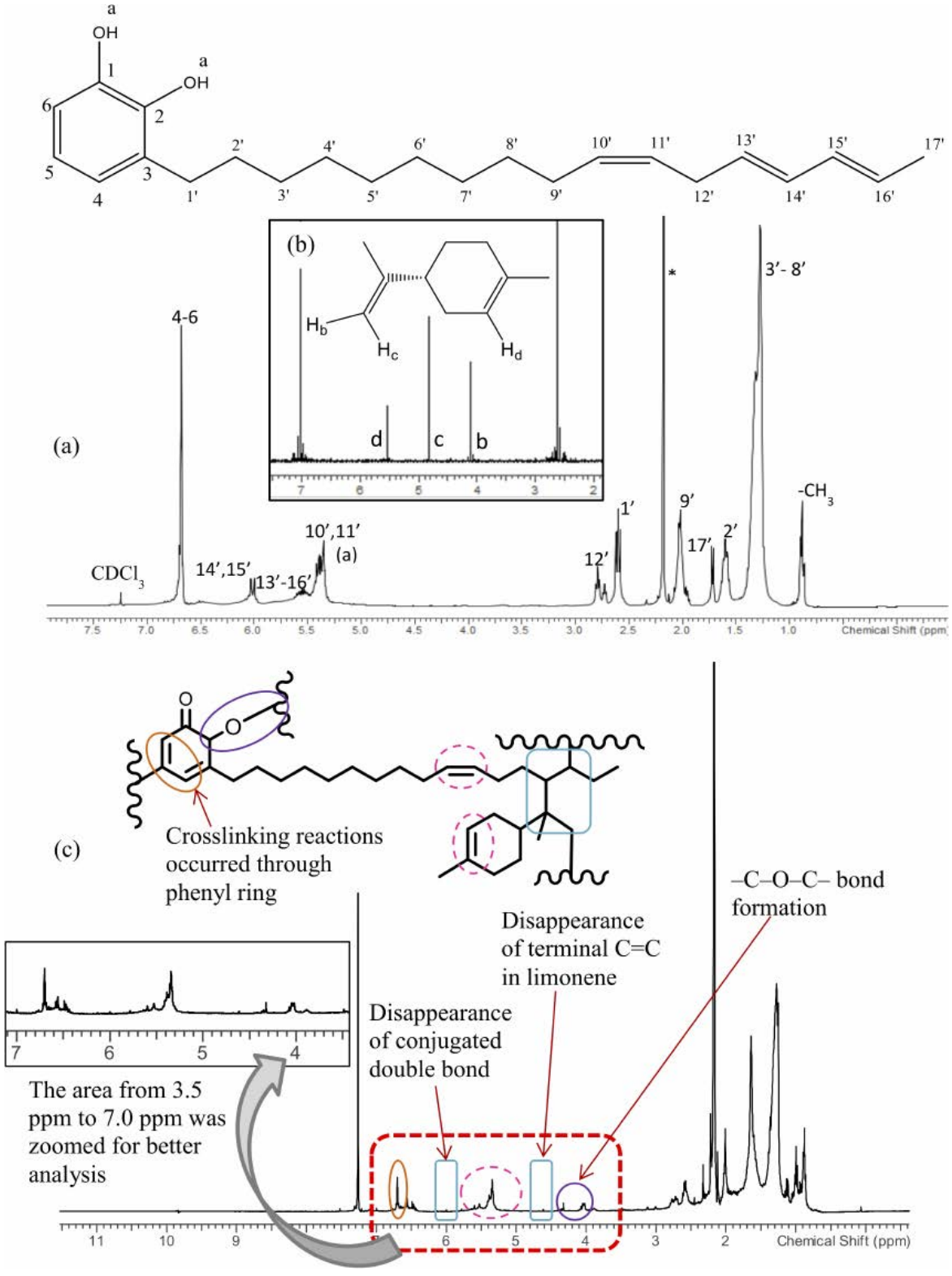

FIG. 3. NMR spectra of (a) laccol extract, (b) *d*-limonene, and (c) L-30 copolymer, *acetone. [Color figure can be viewed at wileyonlinelibrary.com]

L-30 was less than 2.000% for both control and irradiated samples. This is possible due to the removal of small molecules and residual water [13, 35]. From 200.0°C to 450.0°C temperature region, L-10 control sample weight loss percentage was 61.18% and L-30 was 65.83%. This is possible due to the copolymer degradation. After the gamma irradiation treatment, the weight loss percentages were reduced for L-10 and L-30 samples with the values of 54.69% and 64.21%, respectively. Onset temperatures for L-10 copolymer before and after irradiation were 389.1°C and 380.0°C. For L-30 copolymer onset, temperature was increased after the gamma radiation significantly with 14.72°C. Before the radiation treatment, the value was 379.0°C and after the radiation

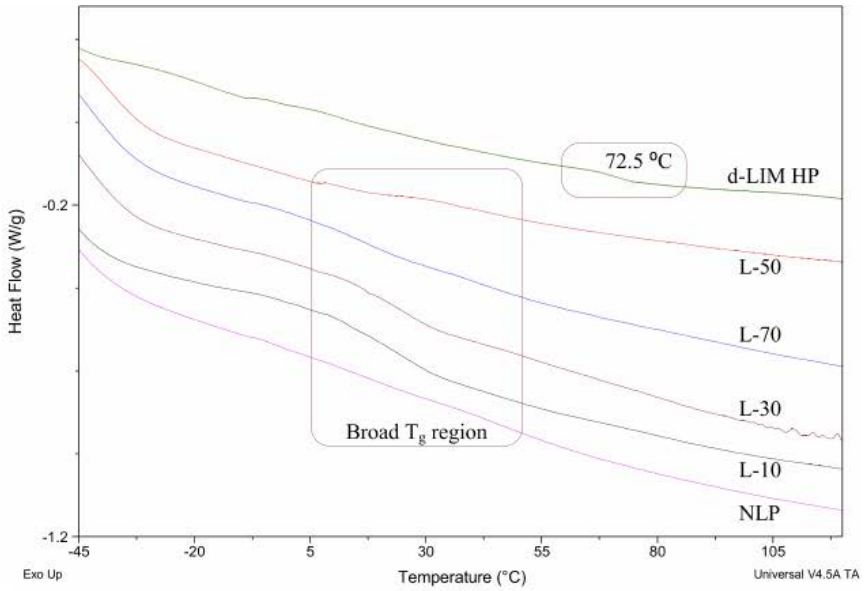

FIG. 4. DSC curves for limonene:laccol copolymers, NLP, and *d*-LIM HP at 30°C/min ramp rate. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2. T_g values and activation energies for synthesized copolymers of limonene:laccol, NLP, and *d*-LIM HP.

	T_g (°C) values at different ramp rates from DSC analysis			From rheometer	
Sample name	10°C/min	20°C/min	30°C/min	T_g (tan δ curve)	Activation energy (kJ)
L-10	14.1	18.1	25.6	20.5	243
L-30	12.6	17.9	20.3	17.1	242
L-50	13.0	34.4	35.4	23.4	258
L-70	14.1	33.0	41.2	21.8	245
NLP	14.6	36.7	45.6	15.4	244
d-LIM HP	10.3	45.9	72.5	—	—

treatment it was 393.7°C. These observations provide clear evidences for further curing of copolymers due to the gamma radiation. In addition, these copolymers illustrated high thermal stability after radiation treatment leaving significant amount of residuals. After 600.0°C for L-10, control sample has 24.26% residual and irradiated sample has 26.81% residual. For L-30 sample, this was 18.35% (control) and 19.12% (irradiated sample) after 650.0°C. These results further supporting the statement of curing through crosslinking due to gamma radiation.

Shore Hardness Analysis

Hardness of the copolymers was measured using Shore A durometer due to the soft nature of the materials. Scale is driven through 0–100 in the durometer and higher numbers depicted greater resistance to indentation; hence, harder materials [45]. The hardness was increased for all the limonene:laccol copolymers after the gamma irradiation due to further curing through crosslinking (physical and chemical) compared to control samples according to the results illustrated in Fig. 8. Increment of the

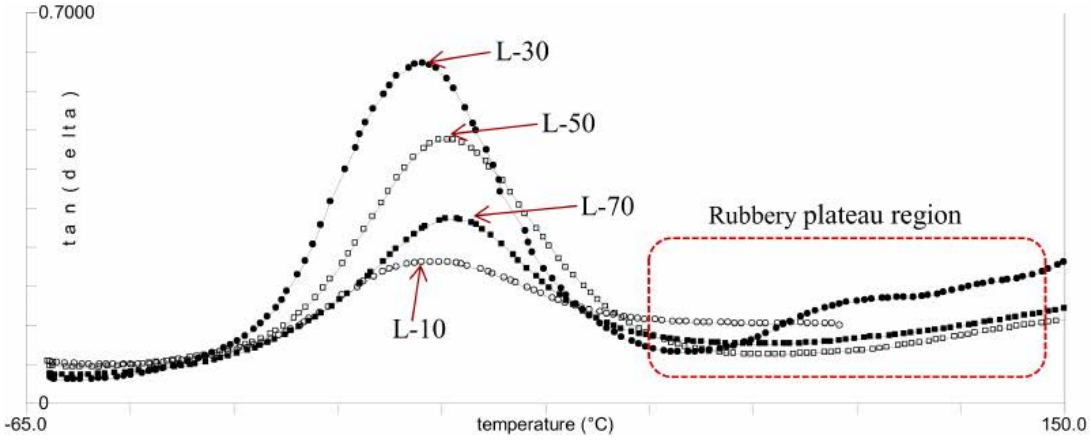

FIG. 5. Tan δ curves of limonene:laccol copolymers. [Color figure can be viewed at wileyonlinelibrary.com]

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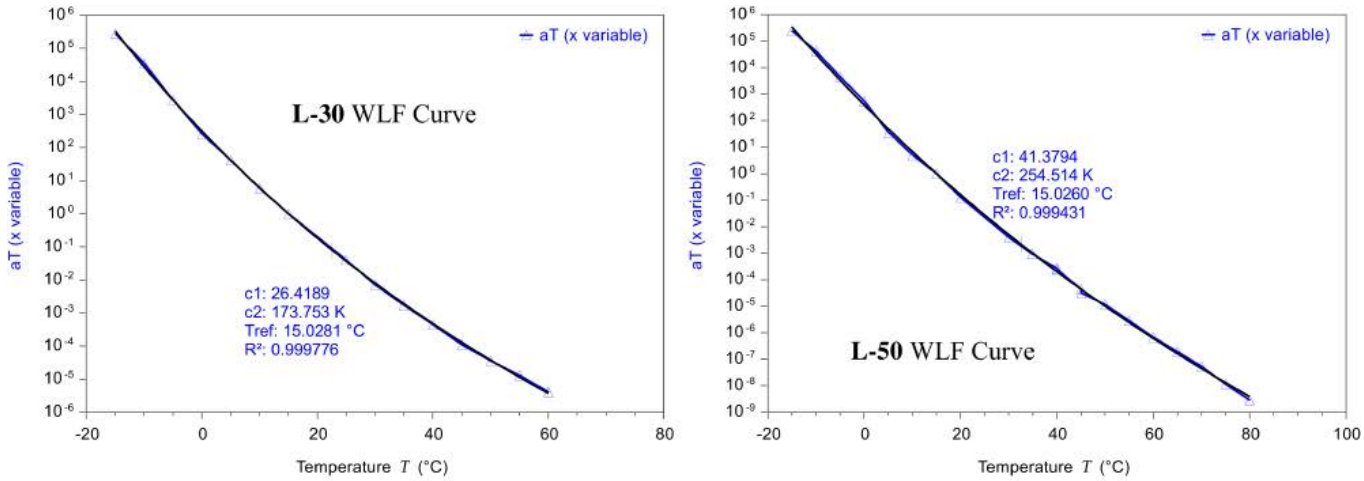

FIG. 6. WLF graphs for L-30 and L-50. [Color figure can be viewed at wileyonlinelibrary.com]

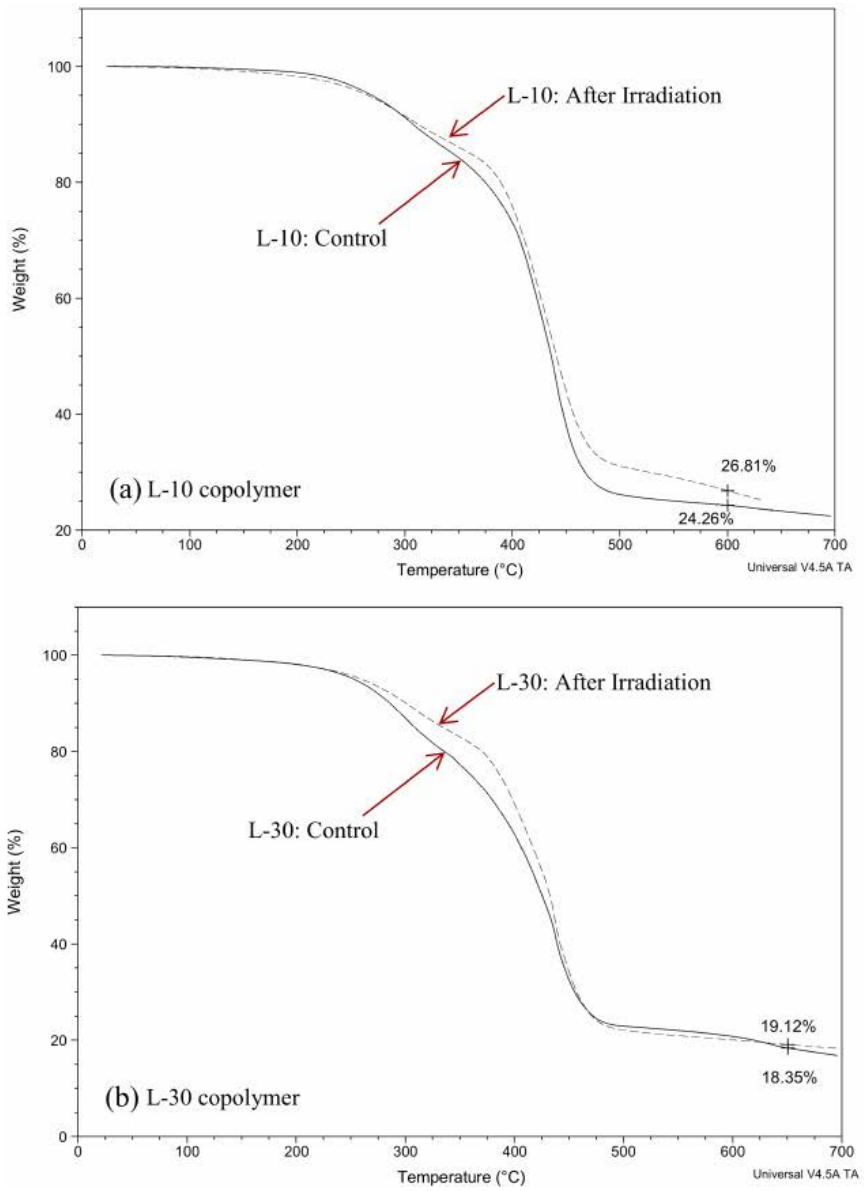

FIG. 7. TG curves of (a) L-10 copolymer and (b) L-30 copolymer; before and after gamma irradiation. [Color figure can be viewed at wileyonlinelibrary.com]

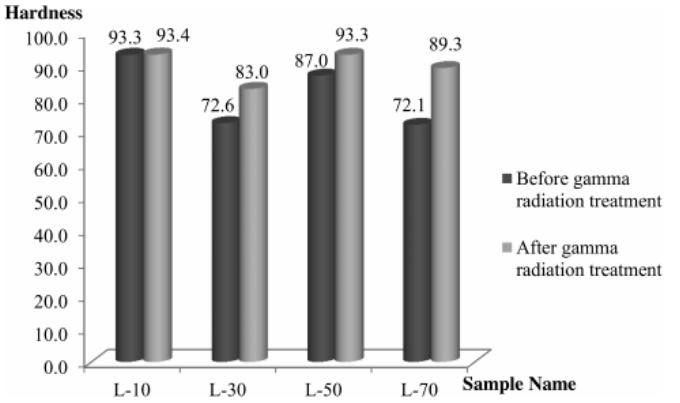

FIG. 8. Shore A hardness data for synthesized copolymers; before and after irradiation.

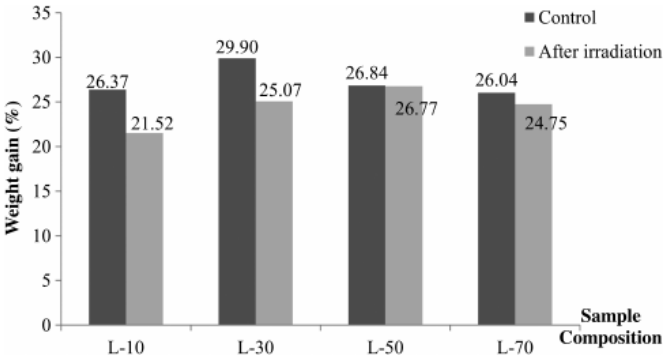

FIG. 9. Percent weight gain of copolymers; before and after gamma irradiation.

hardness was observed for L-30, L-50 and specifically for L-70 sample which has 70% of limonene on its weight. This is possibly due to the reactions occurring with the radiation. Gamma radiation could induce radical formation and other reactions inside the materials which could increase the ability of copolymers to undergo more crosslinking other than the cationic polymerization. When the amount of limonene is increased, these side reactions were more feasible because of the smaller size of the limonene molecule. Smaller the size, there is a higher possibility to penetrate the 3D polymer network by limonene to react with laccol phenyl ring due to radiation treatment according to the results shown in Fig. 8. Elevated temperatures also increase the hardness of copolymers.

Swelling Analysis

The swelling properties depend on many factors such as polymer network density, nature of the solvent and polymer–solvent interactions [46]. Swelling analysis was conducted in toluene solvent to identify the crosslinking nature of the synthesized limonene:laccol copolymers [29, 30]. Percent weight gain of copolymers was calculated before and after gamma radiation treatment as illustrated in Fig. 9. For control samples, the percent weight gain remained mostly in the same range since the only difference in the materials were monomer mixing ratios. When the crosslinking density increases, free volume inside the polymer network is decreased; hence, percent weight gain is reduced accordingly [47]. According to the obtained results, L-10, L-30, and L-70 copolymers were shown a significant reduction of percent weight gain after gamma irradiation. This provides a clear evidence of more physical and chemical crosslinks formation during the radiation treatment. With radiation, radical formation is increased and this could provide more freedom to form crosslinks inside the polymer network which ultimately led to lesser free volume for solvent uptake. Obtained results depicted this phenomenon for all the synthesized copolymers after gamma radiation treatment.

CONCLUSIONS

Synthesizing environmentally friendly sustainable limonene and laccol copolymers via cationic polymerization [48, 49] was successfully achieved using $AlCl_3$.EtOAc coinitiator. Copolymerization was occurred through mainly trans conjugated double bonds in the laccol monomer side chain and terminal double bond of the limonene. Internal double bond of the limonene also involved in the reaction for lesser extent compared to major reaction, as illustrated in Scheme 1. Alterations occurred to the peaks 1,644 and 887 cm^{-1} which are relevant to terminal C═C bond of limonene, 802 cm^{-1} for internal C═C bond of limonene, 987 cm^{-1}, 968 cm^{-1} vibrations of trans conjugated double bonds in the IR spectra (Fig. 2) provide evidence for the successful copolymerization process. NMR data further confirms this fact, as shown in Fig. 3. Limonene was able to copolymerize with laccol up to 70% weight out of total weight is another promising outcome of this study. Glass transition temperatures and their corresponding activation energies of the T_g region were identified for processing purposes of the materials. IR data collected after gamma radiation was shown a new peak at 1,712 cm^{-1} for laccol quinones formation and similar signal pattern with some alterations compared to controls, stating the fact that the samples were not deteriorated. Thermal stability of L-10 and L-30 copolymers was increased after gamma irradiation comparative to controls. Significant amount of residual was observed for L-30 specifically even after the 650.0 °C. This is a clear evidence of further curing through physical and chemical crosslinks due to radiation. Similarly, shore A hardness was also increased for all the copolymers after gamma radiation, supporting the fact mentioned previously. Further, swelling analysis provided the clear evidence of crosslinks increment due to gamma irradiation by decreasing the percent weight gain. Gamma radiation could produce radicals which possibly induce more growing points of the polymer network ultimately led to increase of crosslink density. As per the objective of the project synthesizing environmentally friendly sustainable limonene:laccol copolymers which possess compelling radiation hardening was achieved. The significance of this study is the development of novel limonene:laccol copolymers as an alternative to petroleum-based synthetic polymers in radiation hard applications and also provide a reliable solution to citrus waste problem. L-10, L-30, and L-70 samples are the most promising candidates to serve as radiation shield or protective coatings in the high-tech industrial setup which are dealing with radiation such as nuclear reactors, medicinal sterilization plants, and outer space operations [26].

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