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ORIGINAL PAPER

Physicochemical properties of liquid natural rubber bearing fluoro groups for hydrophobic surfaces

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Abstract The modification of liquid natural rubber (LNR) has attracted interests among chemists as it brings improvements to several of its properties and widens its application to various fields. LNR can be modified into fluorinated LNR (F-LNR) which is of interest to industries due to its remarkable properties, including low surface energies, high thermal stabilities, together with its significant hydrophobic characters. In this work, a new route to prepare fluorinated rubber was presented. Hydroxylated LNR (OH-LNR) was initially synthesized in good yield via oxidation in the presence of tungsten complex catalyst and acetic acid with hydrogen peroxide as an oxidant. The optimum hydroxyl content of 57.0% was obtained within 6 h reaction time at 90 °C. In the second step, the esterification of OH-LNR using pentadecafluorooctanoyl chloride (PDFOC) under mild conditions was conducted, leading to LNR bearing fluoro groups in the side chain of LNR (F-LNR). ATR-FTIR spectroscopy was used to elucidate the structure and determine any changes in the functional groups that may have been induced during the reaction. ^{1}H NMR spectroscopy was employed to reveal that a high fluorine content of 48.6% was obtained using 3:1 molar ratio of OH-LNR:PDFOC for 8 h at 50 °C. The microstructure of F-LNR was further analyzed using ^{19}F NMR and ^{13}C NMR spectroscopies, and the results confirmed the presence of fluorine in LNR. Thermogravimetric analyses also indicated that the modification improved thermal stability of the LNR. Contact angle measurements were also conducted to verify the hydrophobicity of the fluorinated rubber and the results obtained showed that F-LNR exhibited higher hydrophobicity than LNR.

Keywords Modified liquid natural rubber · Hydroxylated rubber · Fluorinated rubber · Hydrophobic surface

Introduction

Synthetic rubbers are artificial elastomer which are mainly synthesized from petroleum byproducts and are mainly used in the rubber and plastics industries nowadays. However, synthetic rubbers manufacturing processes are highly polluting and contribute to global warming due to the emission of carbon dioxide to the environment. Therefore, there are major concerns about the use of industrial materials derived from natural sources. To achieve this goal, attention has turned to natural polyisoprenoids; a generic name for polymers derived from plants comprising an isoprene unit. The natural rubber (NR) extracted from *Hevea brasiliensis*, exhibits good elasticity, high resilience, and excellent mechanical strength [1]. Due to its high-performance properties, it is used extensively in many applications and products, either alone or in combination with other materials. However, due to the unsaturation of carbon-carbon double bond of the isoprene backbone, NR can be degraded when exposed to sunlight, ozone or oxygen, thus limiting its applicability especially

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for high performance and high functional materials. In order to improve these undesirable properties and to produce new polymeric materials with specific and functional properties, chemical modification of NR is necessary [2]. Since chemical reactivity of C = C of NR is similar to that of simple olefins, organic reactions of olefins can be applied to NR.

Typically, NR has the number average molecular weight (M_n) of more than 1.0×10^6 that must be reduced during the manufacturing processes [3]. The processing of rubber that requires heavy equipment and high-power input has brought about the need for it to be available in liquid form. The availability of NR in this form will provide NR with a higher added value and gives the desired combinations of properties for specific and demanding applications. Moreover, the fact that NR has a low-molecular-weight enables it to be easily modified into various useful products. Liquid natural rubber (LNR), which is a reduced form of NR, is an important rubber derivative that can be produced by photosensitized degradation of NR and it has the same monomer as the rubber 1,4-isoprene unit [4]. The short polymeric chains of LNR and its ability to flow at room temperature offers many possibilities of chemical transformations involving the highly reactive carbon-carbon unsaturated groups and thus expands the applicability of LNR in various fields [5, 6].

Chemical modification of NR/LNR is an active field of research due to the technological importance of the modified products, in which most research aim at improving the NR/LNR properties and widening its range of use. Epoxidized NR (ENR), hydrochlorinated NR, and chlorinated NR, are some examples of commercially available modified NR [7, 8]. Chlorinated NR (CNR) is used as a raw material for paint because of its resistance to acids and alkalis, and its wear resistance, ageing resistance and corrosion resistance in seawater [9]. Hydrogenated NR (HNR) also gained much interest from users and manufacturers as it improves the thermal properties of NR and is also a practical method of preparing perfectly alternating copolymer of ethylene and propylene (EPDM rubber), which cannot be prepared by direct polymerisation [10, 11].

Fluorine-containing polymers are a class of polymers that contain multiple strong carbon – fluorine bonds and possess remarkable properties, including low surface energies, high chemical and thermal stabilities, unique water and oil repellency, self-cleaning property and low dielectric constants and refractive indices when compared to their non-fluorinated counterparts [12, 13]. Due to these outstanding properties, they are an excellent choice for various applications such as in automotive and aerospace parts, optics and sensors [14, 15]. Fluoropolymers have attracted vast interests over recent decades since they exhibit enhanced hydrophobicity and resistance to swelling for the use in humidity sensing applications. Furthermore, fluoropolymers can be used as a coating as it exhibits high resistance to corrosion and UV light as well as low permeability to various gases. These unique properties can be attributed to fluorine's high electronegativity and small atomic radius. Some of the polymers that have been fluorinated by other researchers include polydienes, polyacrylates, polystyrene, polyolefins, and polyethers [16–20]. Even though the modification of fluorination by synthetic rubber has been extensively reported, so far no serious attempts have been made with liquid NR [21–23]. For this purpose, a combination of advantages emerging from both the fluoropolymers and NR, are anticipated with the fluorination of NR/LNR.

At present, most of the commercial fluoropolymers are prepared by polymerization of fluorine-containing monomers. However, the high cost, low productivity and limited availability of many fluorinated monomers, restricts the preparation of various types of fluoropolymers using this route. Hence, these limitations prohibit the development of a large basis of such materials. Another modification route that is normally utilized for the synthesis of fluorinated polymers is by incorporating the fluorine-containing moieties into a non-fluorinated parent polymer. For this chemical reaction to take place, the parent polymer should possess a functional site for modification. Among the functional groups, the hydroxyl groups attract much attention, because they can be easily converted from the epoxidized NR due to the residual strain of the three-membered ring structure. Furthermore, the presence of hydroxyl groups as the functional site of a polymer strongly attracts other functional crosslinking agents such as isocyanate, acyl chloride, and amine, which form strong crosslinking junctions and act as a good precursor for further modification [24]. In the last two decades, the oxidation of NR has been carried out to prepare the NR with epoxy and hydroxyl groups. Very recently, hydroxylated LNR was successfully generated via in situ multi-step reactions, which was found to contain high loadings of hydroxyl groups [25].

This paper described the achievement of LNR modification as a route to the production of fluorinated LNR (F-LNR). It was carried out via a simple chain reaction by introducing fluorinated moieties into LNR containing a precursor of reactive hydroxyl groups, which was obtained from the ring opening of an oxirane ring in epoxidized LNR. This method of modification of LNR is of immense interest and to us has the best prospect because it overcomes the disadvantages of toxic reagents and increased the possibility to vary and control the surface properties. We have also studied the physicochemical properties of the fluoropolymers by using several characterization

techniques. The contact angle of the fluoropolymers was also discussed.

Experimental

Materials

In this work, we used natural rubber from the Malaysian Rubber Board. Toluene, hydrogen peroxide, and ethanol were supplied by R&M Chemicals. Anhydrous tetrahydrofuran, pentadecafluorooctanoyl chloride (PDFOC), perfluorobutyryl chloride (PFBC), methylene blue, rose Bengal, anhydrous pyridine, anhydrous methanol and sodium carbonate were purchased from Sigma Aldrich. Sodium tungstate was purchased from Acros Organics. Acetic acid was purchased from Systerm. Deuterated chloroform was purchased from Merck.

Preparation of liquid natural rubber (LNR)

LNR was synthesized by photosensitized degradation, according to a method described by Kargarzadeh et al. [26]. Dried NR was cut into small pieces and dissolved in toluene with catalytic amounts of methylene blue and rose Bengal. The solution was stirred using a mechanical stirrer in the presence of visible light with the storage temperature of 80 °C, for 2 weeks, until the rubber mixture transformed into a golden-yellow viscous liquid. Toluene was added to the mixture constantly while stirring until the NR settled down. Finally, the LNR was centrifuged for 4 min at 3000 rpm.

Preparation of hydroxylated LNR (OH-LNR)

OH-LNR was synthesized by oxidation reaction, according to a method described by Zhang et al. [27] . LNR was dissolved in toluene, followed by an addition of acetic acid in a 250 mL round bottom flask, fitted with a reflux condenser and magnetic stirrer. Then, sodium tungstate dissolved in hydrogen peroxide solution, was added dropwise, while the solution was stirred at 90 °C. After the completion of the reaction, the products were precipitated with ethanol, followed by soaking in 1% sodium carbonate solution for 24 h. Then, the white solid products were washed with deionized water and dried in vacuum oven at 60 °C overnight.

Preparation of fluorinated LNR (F-LNR)

F-LNR was synthesized by an esterification reaction, according to a method described by Politakos et al. [28]. OH-LNR was dissolved in anhydrous tetrahydrofuran (THF) and anhydrous pyridine, under an inert atmosphere. Then, PDFOC was added into the mixture through a rubber septum. The yellow solution was constantly stirred at 50 °C for 24 h. The reaction was terminated with the addition of anhydrous methanol. After the completion of the reaction, the products were precipitated and rinsed several times in a mixture of MeOH/H_2O. Then, the deep yellow solid products were dried in a vacuum oven at 60 °C, overnight. For comparison, PFBC was also used as the fluorine source.

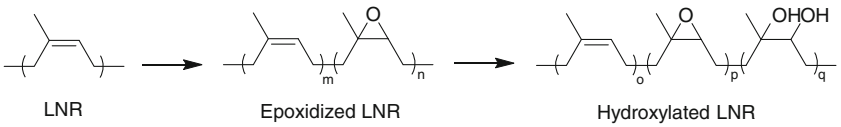
Characterization

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (Perkin Elmer) was used to determine any changes in the functional groups that may have been induced as a result of the hydroxylation and esterification reactions. The samples were analyzed using Perkin-Elmer Spectrum BX in a transmittance mode in the wavenumber range of 650–4000 cm^{-1}.

Nuclear magnetic resonance (NMR) spectroscopy was used to analyze the chemical structure of the products using the Bruker FT-NMR 600 MHz Cryoprobe spectrometer. Deuterated chloroform ($CDCl_3$) was used as the solvent in all cases. The integration of signals from ^1H NMR was used to estimate the percentage conversion from OH-LNR to F-LNR.

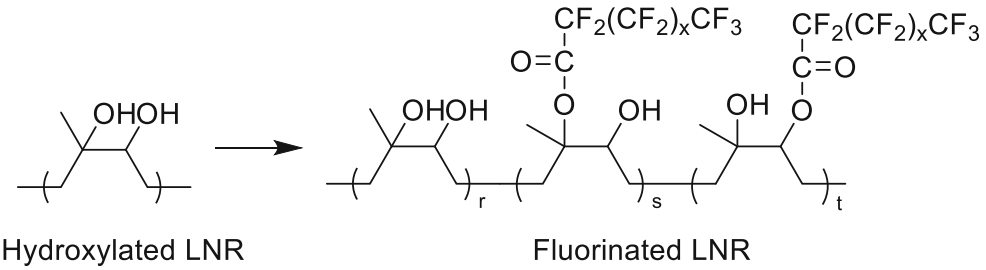
X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra spectrometer with an Al K_α X-ray source operated at 150 W. The spectra were calibrated by the C1s peak of the C-C bond at 284.6 eV.

Gel permeation chromatography (GPC) was employed to investigate the molecular weight (M_w) and the polydispersity index (PDI) of the products in THF with polystyrene as standard (Waters 1515 Isocratic HPLC pump equipped with a Waters 2414 Refractive Index detector, Waters Corporation, USA).



Scheme 1 Oxidation of LNR in the presence of $NaWO_4$, CH_3COOH and H_2O_2 at 90 °C to give epoxidized LNR which ring-opened to generate OH-LNR

Scheme 2 Esterification reaction between diol groups in OH-LNR and fluorinated acyl chloride to give F-LNR (where x = 1 for PFBC or x = 5 for PDFOC)



Thermogravimetric analysis (TGA) was carried out to determine the degradation temperature of the samples using instrument from Mettler Toledo Company (TGA/SDTA 851^e). The sample was heated from room temperature to 600 °C at a constant heating rate of 10 °C/min.

Contact angles were measured with deionized water using SEO Sessile Drop Contact Angle Analyzer with an automatic dispenser at room temperature. The film was obtained by dissolving the samples in THF to a certain concentration, and the solution was drop cast onto clean glass slides. Then, the glass slides were dried for 48 h before testing. A MilliQ deionized water droplet of 5 μL was placed on the coated surface with the syringe attached to the droplet. The liquid drop was recorded using a HDD camera. All the contact angles were determined by averaging the values measured at three different locations on each sample surface.

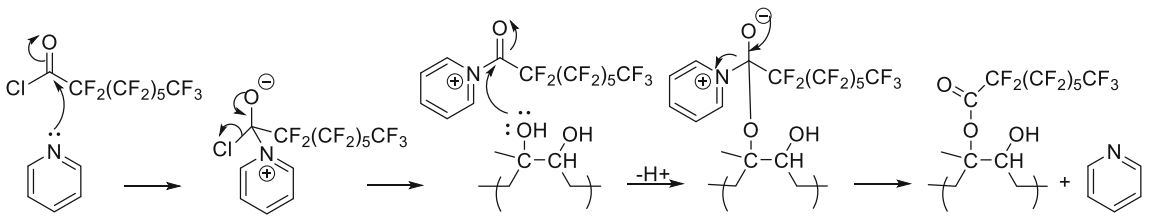
Results and discussion

Preparation of F-LNR

Initially, NR was thermally depolymerized which transformed NR into LNR. In this process, any impurities were removed but the rubber monomer unit (1,4-isoprene) remained. Chemical modification of LNR to F-LNR was performed in two steps, which was a new convenient route to prepare fluoropolymers. In the first reaction, oxidation of LNR was carried out to give the hydroxylated LNR (OH-LNR) in the presence of tungsten complex catalyst/acetic acid with hydrogen peroxide as an oxidant. Scheme 1 summarizes the route for synthesis of OH-LNR which consists of a mixture of epoxidized and hydroxylated rubber. It is well documented in the literature that LNR can be epoxidized using peracids (CH_3COOOH) and a ring opening of oxirane groups occurs during the epoxidation of LNR to give diols [25]. By prolonging the reaction time, the hydroxyl content of the product could be increased. This method of modification is of the greatest interest because a high percentage of diols can be introduced into the LNR, which serves as a good intermediate for further chemical modifications. In this study, the optimum hydroxyl content of 57.0% is obtained within 6 h reaction time at 90 °C.

In the second reaction, the esterification of OH-LNR using fluorine-containing acyl chloride was conducted, leading to modified LNR bearing fluoro groups. There are two types of fluorine-containing acyl chloride with different fluoroalkyl length used in this study which are pentadecafluorooctanoyl chloride (PDFOC) and perfluorobutyryl chloride (PFBC). Indication of successful reaction was the formation of a deep yellow solid obtained after 8 h of reaction at 50 °C. The reaction however does not fully convert OH-LNR to F-LNR as confirmed by the obtained results of FTIR and ^{1}H NMR spectroscopies. The F-LNR samples consists of a mixture of hydroxylated and fluorinated rubber as shown in Scheme 2.

A weak base like pyridine was used to remove the HCl produced in the reaction and also acts as nucleophilic catalyst to speed up the reaction [29]. The mechanism of the reaction between the fluorine-containing acyl chloride and hydroxyl group in the presence of pyridine is shown in Scheme 3. Pyridine, which is more nucleophilic than the hydroxyl, attacks the acyl chloride rapidly to form a highly electrophilic intermediate. This reactive intermediate is the acylating agent which then reacts with the hydroxyl groups to give the esterified rubber. The resulting product is precipitated in a basic solution of $MeOH/H_2O$ to minimize any side reactions that might lead to crosslinking. The



Scheme 3 The proposed mechanism for the reaction between fluorine-containing acyl chloride and hydroxyl group in the presence of pyridine

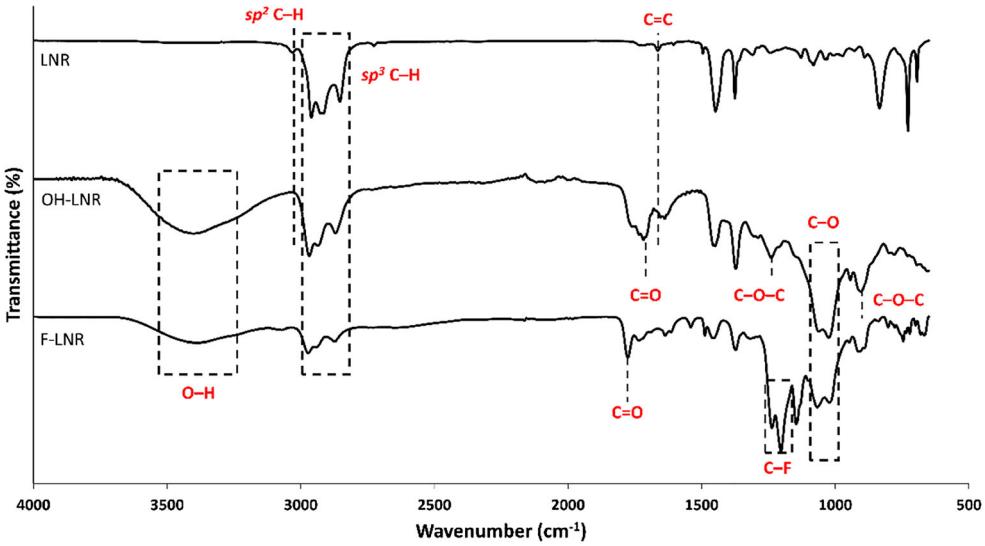


Fig. 1 FTIR spectra of LNR, OH-LNR and F-LNR

methods have advantages such as the low cost of materials and it requires easier processes than the traditional methods and the scaling-up possibilities for the production of fluorinated rubber for a variety of applications.

Microstructures of LNR, OH-LNR and F-LNR

The microstructures of LNR, OH-LNR and F-LNR are characterized using the ATR-FTIR, and the spectra are shown in Fig. 1. The main peaks for LNR are located at 3050, 3000–2850 and 1660 cm^{-1}, which correspond to sp^2 C–H stretching, sp^3 C–H stretching and C = C stretching, respectively [30]. The intensity of the C = C stretching peaks decreases upon hydroxylation, which can be attributed to the reduced amount of the unsaturated groups in the structure of hydroxylated rubber. The most apparent changes are the presence of O–H stretching (3600–3100 cm^{-1}) and C–O stretching (1020–1070 cm^{-1}) in OH-LNR which correspond to the hydroxyl functional group in the LNR chain. The other parts of the spectra,

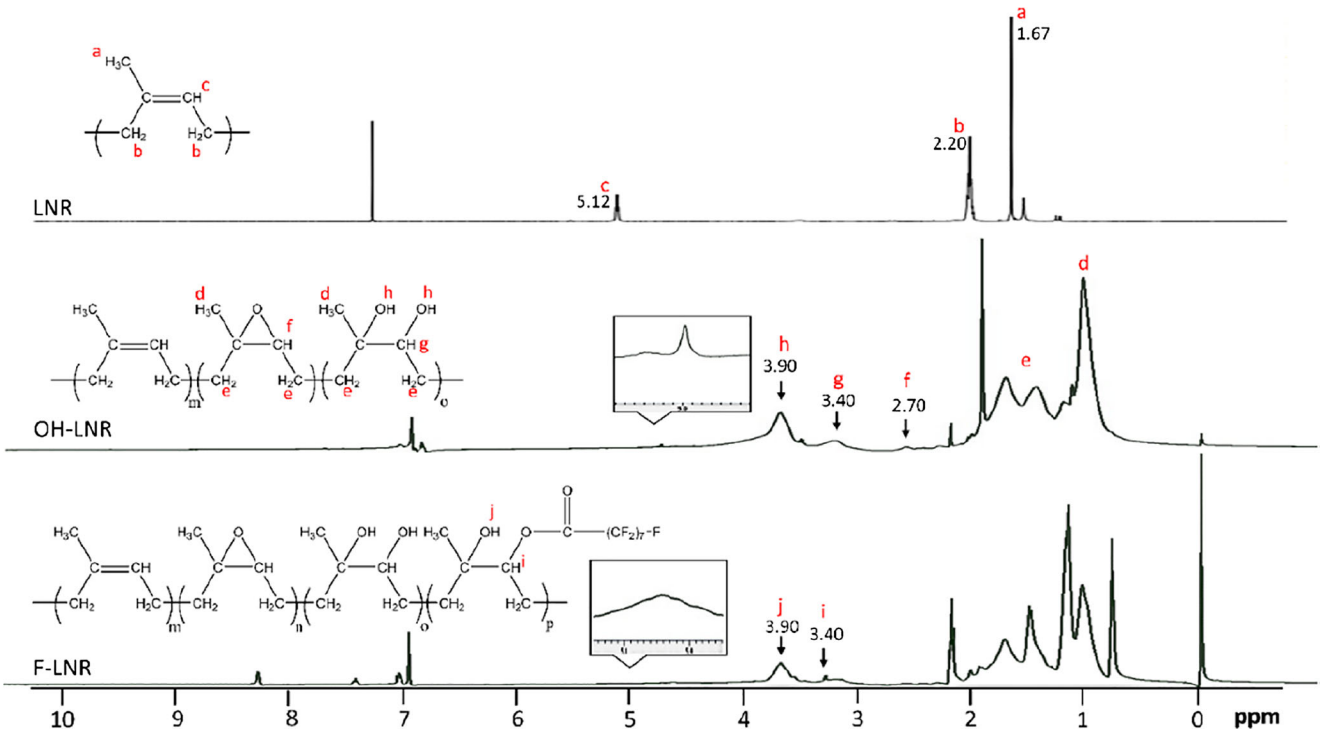


Fig. 2 ^{1}H NMR spectra of LNR, OH-LNR and F-LNR

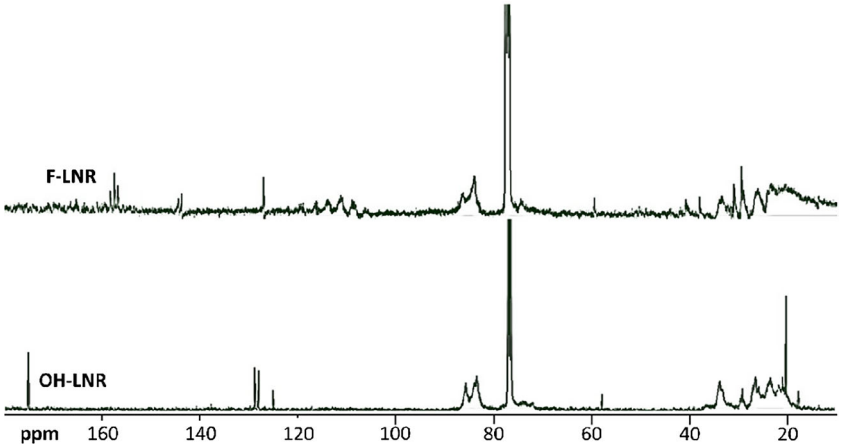


Fig. 3 ^{13}C NMR spectra of OH-LNR and F-LNR

particularly the peaks at 1241 and 900 cm^{-1} are due to the epoxide groups, indicating that there is a small amount of the epoxide groups that are still not ring-opened. The OH-LNR is known to predominantly suffer from the chain scission under an oxidative atmosphere which results in the presence of carbonyl peaks at 1710 cm^{-1} [31]. The intensity of O–H stretching bands shows a reduction after the esterification which is an indication that OH-LNR is partially modified into F-LNR. Furthermore, the appearance of new peaks can be seen in F-LNR at 1770 and 1200–1250 cm^{-1} which correspond to C = O stretching of the esterified LNR and C–F stretching vibration, respectively, which proves the formation of an ester from the attachment between the oxygen of the hydroxyl group and the carbonyl carbon of the acyl chloride. The reduction of the C–H stretching from LNR to OH-LNR and F-LNR are observed which indicates successful modification.

Figure 2 shows the ^{1}H NMR spectra of LNR, OH-LNR and F-LNR. The characteristic ^{1}H NMR signals of LNR are attributed to olefinic protons (5.12 ppm), unsaturated methylene, $-CH_2-$ (2.20 ppm), and unsaturated methyl, $-CH_3$ (1.67 ppm) which disappeared after the hydroxylation process. New signals had appeared at 2.70, 3.40 and 3.90 ppm, signifying the existence of epoxy methine proton (C-O-C**H**), α hydrogen (−C**H**-OH) and hydroxyl proton (C-O**H**) respectively. This result also agrees with a previous study, thereby indicating the formation of epoxides which are then partially converted to the hydroxyl groups [31]. The broad absorptions at 3.90 ppm confirmed the diol formation, which resulted from the ring-opening of an epoxide, as mentioned by Thames and Gupta [22]. For F-LNR spectra, the signal for the hydroxyl proton (C-O**H**) decreases which indicate the attachment of the fluorinated side groups due to the formation of ester functions from the hydroxy groups and the fluorinated acyl chloride. Some small amounts of unsaturation, indicated by a broad, weak peak around 5.00–5.10 ppm exist in all cases, which suggest that all functionalized and modified products still retain the basic characteristics of rubber. The

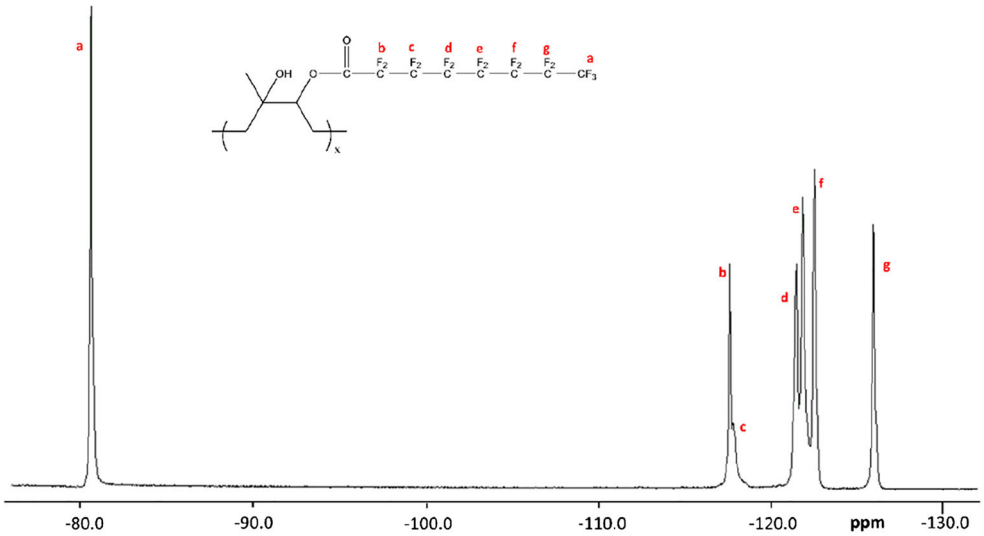


Fig. 4 ^{19}F NMR spectra of F-LNR

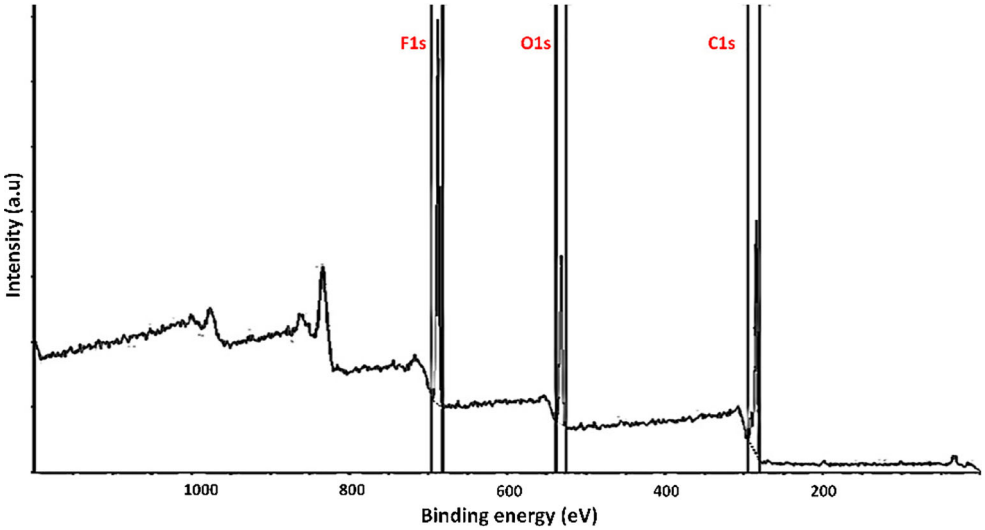


Fig. 5 XPS wide scan spectra of F-LNR

hydroxyl content is estimated by comparing the integration area of the signals from ^{1}H NMR spectra, as shown below in Eq. (1):

$$X_{hydroxyl} = \frac{\frac{I_{3.9}}{2}}{I_{2.7} + I_{3.4} + \frac{I_{3.9}}{2} + I_{5.1}} \times 100 \quad (1)$$

Meanwhile, the fluorine content was estimated from the hydroxyl content value before and after modification was carried out.

In the ^{13}C NMR (Fig. 3) analysis, the signal characteristics of LNR for methyl and methylene carbons appear at 24.0, 26.8 and 34.4 ppm. The signals appear at 58.4 ppm in the spectrum of both OH-LNR and F-LNR, which are the characteristic signals of the epoxy groups. Two signals appear at 83.0–86.0 ppm, which correspond with the carbon atoms in –**C**-OH and this result is consistent with the partially hydroxylated natural rubber as reported by Thames and He [9]. Meanwhile, the signals appear at chemical shift 125.0–130.0 ppm which correspond to the –**C** = **C** group. After the esterification with an acyl chloride, several signals newly appear in the range of 110.0–120.0 ppm which represent the carbons linking to fluorine (−**C**F_2– and –**C**F_3). Owing to the presence of carbonyl carbon (−O**C** = O) in the esterified rubber of F-LNR, the signals are recorded at 162.5 ppm.

Figure 4 shows the ^{19}F NMR spectra of the final product which reveals that the F-LNR has a chemical shift at

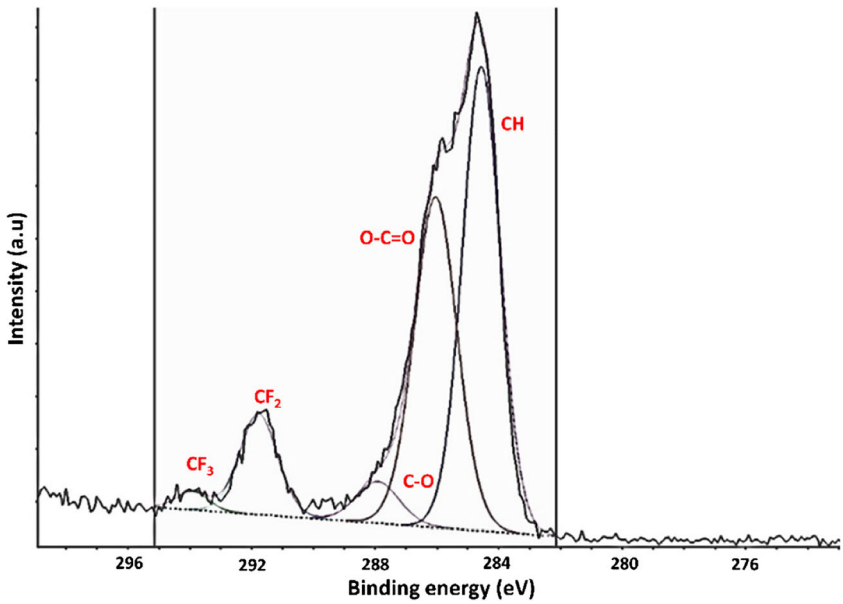


Fig. 6 XPS C1s core level spectra of F-LNR

Table 1 Molecular weight and PDI of LNR, OH-LNR and F-LNR obtained from GPC

Sample	M_n (g/mol)	M_w (g/mol)	PDI
LNR	10,900	88,400	8.11
OH-LNR	1800	3200	1.78
F-LNR (PDFOC)	11,000	19,600	1.78
F-LNR (PFBC)	8400	9900	1.18

−80.7 ppm that is attributed to the $–CF_3$. The other signals that appear in the range of −117.7 to −126.0 ppm are attributed to the $–CF_2$ [32, 33]. The ^{19}F NMR analysis confirms the presence of fluorine in the LNR.

Figure 5 shows the XPS wide scan spectra of F-LNR. The presence of three major elements can be found in the spectra, which correspond to F1 s, O1s and C1s with a binding energy at 688.916, 531.916 and 284.916 eV respectively. The corresponding C1s core level spectra in Fig. 6 shows the peak components attributable to C–H, O–C = O, C–O, CF_2 and CF_3. These results therefore, support the proposed structure of the F-LNR.

The molecular characterization results (number average molecular weight, M_n, weight average molecular weight, M_w and polydispersity indices, PDI) obtained from GPC for the LNR, OH-LNR and F-LNR are given in Table 1. From the results, the molecular weight of LNR show a significant drop upon oxidation to OH-LNR due to the degradation of the main chain. At high temperature (for example 90 °C) under acidic condition and oxidative atmosphere, the component of the long chain of LNR begin to be broken and resulted in chain scission which leads to low molecular weight rubber fragments and formation of new end groups especially ketones and carboxylic acids [31]. This finding agrees with the FTIR results which show the presence of carbonyl groups at 1710 cm^{-1} in the OH-LNR. Meanwhile, the significant increase in molecular weight of F-LNR modified using PDFOC as fluorine source strongly suggests that the long fluoroalkyl length of the acyl chloride was successfully attached during esterification. The molecular weight of F-LNR modified using PFBC which has shorter fluoroalkyl length is lower than that of PDFOC. This finding revealed that the molecular weight elevation of F-LNR was proportional to the increased fluoroalkyl chain length.

Generally, LNR has a very broad molecular weight distribution shown by high PDI value [34]. After oxidation reaction, the PDI value decrease intensely which indicate that the chain degradation enhances the distribution of the side chains towards molecular homogeneity among the molecules. The narrowing of molecular weight distribution was preserved through the esterification reaction, which suggests that the hydroxyl groups were modified without significant coupling or scission.

The effects of esterification reaction conditions on fluorine content

In this study, the effects of the reaction time and OH-LNR:PDFOC molar ratio on fluorine content were studied. The effect of the OH-LNR:PDFOC molar ratio on the fluorine content percentage was investigated and the results are shown in Fig. 7. The temperature and reaction time are kept constant at 50 °C and 4 h, respectively. The results show that, by increasing the PDFOC amount, the fluorine content decreases from 15% to 5%. These results indicate that a larger excess of PDFOC relative to rubber volume in the reaction mixture can possibly cause crosslink reaction and lower mobility of highly crosslinked LNR may exist. Thus,

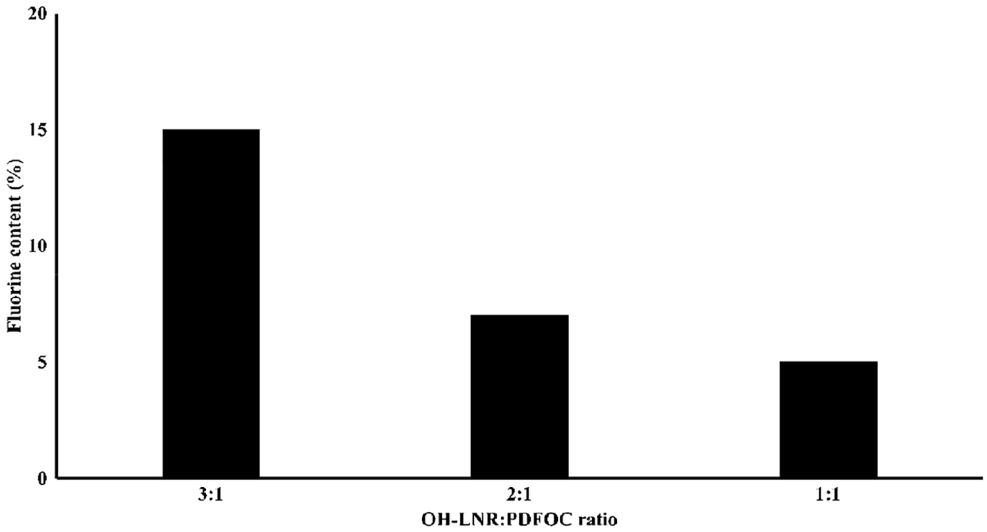


Fig. 7 Fluorine content percentage calculated from ^1H NMR spectra using different OH-LNR to PDFOC molar ratio at temperature 50 °C and 4 h reaction time

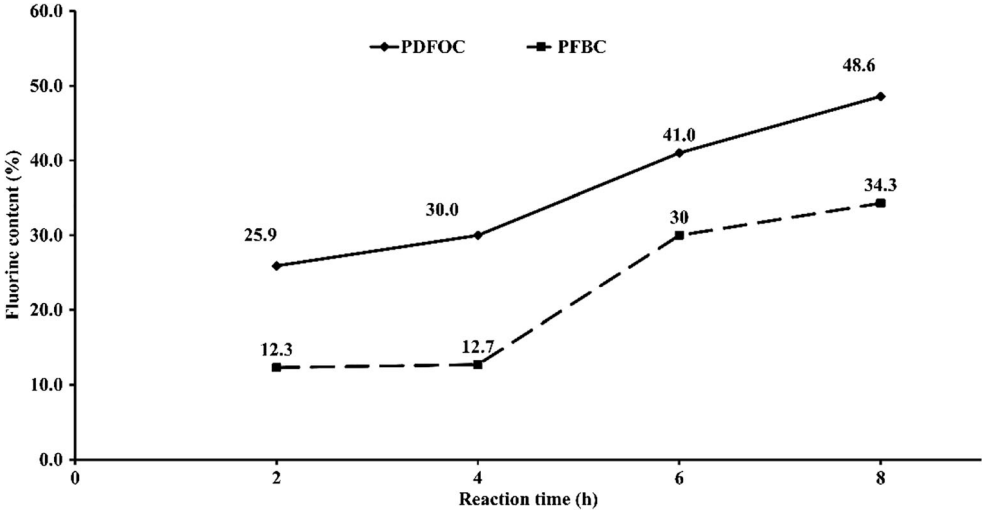


Fig. 8 Fluorine content percentage calculated from ^{1}H NMR spectra at different reaction times using PDFOC (*solid line*) and PFBC (*dashed line*) at 50 °C with molar ratio of OH-LNR to fluorinated acyl chloride equal to 3:1

the number of hydroxyl groups become less available for esterification reaction.

The effect of the reaction time on the fluorine content is evaluated by keeping the reaction temperature constant at 50 °C with molar ratio of OH-LNR to fluorinated acyl chloride at 3:1 (Fig. 8). It is found that by increasing the reaction time from 2 to 8 h. will slightly increase the fluorine content of the LNR. A reaction time of 8 h leads to a maximum fluorine content of 48.6% for PDFOC and 34.3% for PFBC. However, when the reaction time is extended to a longer time, the percentage tends to decrease, presumably due to side reactions and increasing amount of the acyl chloride lost due to evaporation. These results also suggest that more fluorine can be incorporated into LNR when the acyl chloride that has a longer fluoroalkyl length is used as the fluorine source. This is because having longer side chains provide higher possibilities of the hydroxyl groups to be converted via esterification. Overall, the reaction conditions for the preparation of F-LNR that yields the highest fluorine content is by using PDFOC with a molar ratio OH-LNR:PDFOC of 3:1 at 50 °C for 8 h.

Thermal stability

Thermogravimetric analysis (TGA) is one of the commonly used techniques for rapid evaluation of the thermal stability of chemically modified LNR's at various temperatures. Table 2 shows the decomposition temperature for LNR, OH-LNR and F-LNR. The initial decomposition temperature (T_{id}) was determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature (T_{max}) of each sample was obtained from the peak maxima of the derivatives of the TGA curves. The decomposition of LNR started around 327 °C and reached a T_{max} of 374 °C. The results obtained agreed with previous work carried out by other researchers [35]. The thermogram of OH-LNR showed the highest T_{id} and T_{max} which are observed at 339 °C and 410 °C respectively. The enhanced stability of OH-LNR is achieved because the weak π–bonds in the unsaturated units of C = C in LNR are converted to stronger C-OH sigma (σ) bonds in the saturated unit of OH-LNR. A similar behavior in the thermal properties of hydroxylated rubbers has been studied by Azhar et al. [25]. On the other hand, the modified LNR containing fluorine groups, F-LNR, possesses a generally lower thermal stability than OH-LNR which are observed at 325 °C (T_{id}) and 391 °C (T_{max}). The observed lower stability of F-LNR than OH-LNR is attributed to the greater amount of diol functionality in OH-LNR which are related to its ability to form hydrogen bonding. Hydrogen bonds have a significant influence on the physical properties of modified LNR's which then leads to

Table 2 Decomposition temperature of LNR, OH-LNR and F-LNR

Sample	T_{id} (°C)	T_{max} (°C)
LNR	327	374
OH-LNR	339	410
F-LNR	325	391

Table 3 Water contact angles and surface tension of the unmodified and fluorinated NR

Sample	Contact angle (°)	Surface tension, γ (mN/m)
Unmodified	86.4	56.8
Fluorinated	116.3	7.9

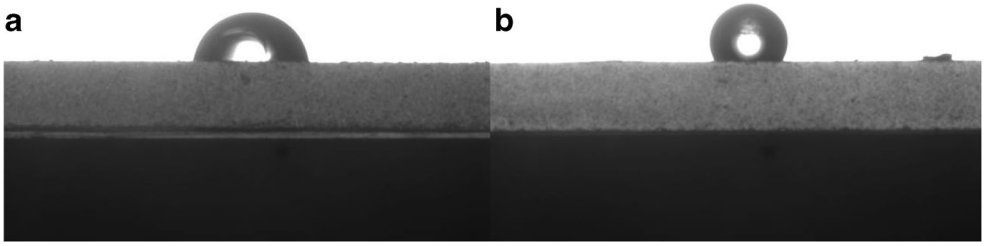


Fig. 9 Images of water droplets on the surface of glass slides coated with different type of samples: (**a**) unmodified (**b**) fluorinated

stronger intermolecular interactions and higher thermal stability. These results proved that modification reactions have significant influence on the thermal stability of LNR.

Contact angle

The contact angle is a tool to evaluate hydrophobicity of a surface. The surface properties of unmodified and fluorinated rubbers are compared in terms of their contact angle and surface tension, as summarized in Table 3. The water contact angle of the unmodified rubber is 86.4° whereby the value after modification with fluorine significantly increases to 116.3° which is evidence that the attachment of fluorine groups onto the surface of rubber will substantially expose hydrophobicity behaviour and thus impart low surface energy. The hydrophobic behaviour of F-LNR is due to the high electronegativity and small size of the fluorine atom which then results in strong chemical bonds between carbon and fluorine. Attaching fluorinated group ($-CF_2$ and $-CF_3$) on the LNR backbone would create a surface with the lowest possible surface tension [36]. In addition, interaction between F-LNR and water are also not favorable as interaction among water molecules due to the inability of F-LNR to form hydrogen bond or electrostatic interaction. Images of the liquid drops of distilled water on the rubber films are shown in Fig. 9. The images clearly show that the contact angles of the fluorinated NR are higher than that of unmodified rubber due to the increased hydrophobicity, leading to low wettability of the surface.

Conclusion

In brief, this paper reports a highly efficient work-up procedure for the preparation of fluorinated LNR and its full structural elucidation. The F-LNR was successfully synthesized by the hydroxylation of LNR and subsequent esterification with fluorine-containing acyl chloride. FTIR, NMR, XPS and GPC were used to verify the microstructure of all the modified LNR. The chemical modification of LNR with fluorine groups not only increases thermal stability but also imparts higher hydrophobicity as compared with unmodified LNR. These remarkable properties allow F-LNR to be available for a wider range of product applications such as for the design of pressure-sensitive adhesives.

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