

Fabrication and Properties of Smart Temperature Epoxidized Natural Rubber

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Research Article

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Fabrication and properties of smart temperature epoxidized natural rubber

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Abstract

Temperature-responsive polymers are smart materials due to responding to change in surrounding temperature and are applicable for different applications. Here, we prepared the smart rubber from epoxidized natural rubber (ENR) latex, N-vinylcaprolactam (NVCL) as monomer, poly(vinyl alcohol) (PVA) as a surfactant and potassium persulfate (KPS) as free radical initiator. The temperature responsiveness of the grafted copolymers was investigated using water swelling and compared with that of pure ENR. The lower critical solution temperature (LCST) of the grafted copolymer was found to be in the range 20-40 °C whereas the ENR was not responsive to temperature. The temperature-responsiveness of the grafted copolymer near human body temperature can be utilized to be fabricated as biomedical materials. Based on this study, the temperature-responsive ENR-graft-NVCL would potentially be used as a novel responsive rubber-based material in various applications.

Keywords: Natural rubber; Biopolymer; Smart polymer; Chemical modification; Green

Introduction

Epoxidized natural rubber (ENR) is a derivative polymer from natural rubber latex (NRL) consisting poly(*cis*-1,4-isoprene) rubber [1-2]. ENR was used to many fields due to the reactivity of epoxy groups and the high polarity of OH groups. Previous work [3] studied rick husk/ENR as polymer matrix for encapsulation of urea to control release. Results suggested that the increasing of temperature has increased the rate of urea release from polymer matrix in the water. ENR was

used to improve the mechanical properties of starch/chitosan blend [4]. The tensile strength and elongation at break of the starch/chitosan blend increased with the ENR content due to reaction between the reactive functional groups of the chitosan and the additives with the epoxy groups of ENR. Here, we try the preparation of smart rubber which sensitives to detect external stimuli such as liquids organic gases [5], thermal field [6] and mechanical strains (Mahmoud & Al-Bluwi, 2020) [7], are becoming very attractive because of the rapid development of robotics as well as the need for a continuous monitoring of human health. Due to the presence of hydrophilic and hydrophobic groups in its structure [8], PNVCL is a suitable polymer for biomedical applications in vivo because unlike most polyacrylamides, its hydrolysis does not yield small organic molecules [9] and due to its amphiphilic character as block copolymer, it can be used as a carrier for drug delivery of active molecules with controlled release of active ingredients. PNVCL can be covalently linked with CMC to get the more valuable graft copolymer through conventional free radical polymerization process [10]. It has been successfully carried out in the present work, which provided highly antioxidative and antibacterial natural polymer-based material. In case of ENR, many works studied modification of the ENR such as cured ENR with hexamethylene diamine [11], cured ENR with zinc diacrylate-cured [12], blending ENR with thermoplastic starch-chitosan blended [13]. ENR was blended with sulfonated poly (ether ether ketone) (SPEEK) to form membrane [14]. The water uptake and methanol permeability of membrane were found to be decreased with increasing of ENR. But the proton conductivity of membrane was improved and it can be listed as one of the potential proton electrolyte membranes. ENR was blended with NR to improve the damping performance of NR near room temperature [15]. It possesses the best comprehensive performance than that in random superposition and sequential superposition way which is qualified for application standards of rubber damping materials. Elastomeric conductive

composites (ECCs) [16] was made from NR and reduced graphene oxide to play a significant role in the field of smart sensors due to their excellent flexibility, high and wide-spectrum sensitivity as well as fast response to external stimuli. Recently, new material having thermal/magnetic/light triggered shape memory from polylactide, epoxidized natural rubber and ferriferrous oxide (Fe_3O_4) [17]. Results show that the smart material could quickly recover to their initial shape in an alternating magnetic field or under near-infrared light, which showed great potential in intelligent medical devices. Previous work [18] studied the preparation of poly(N-vinylcaprolactam)-g-collagen (PNVCL-g-Col) by grafting collagen with carboxyl group-terminated thermosensitive PNVCL-COOH. PNVCL-g-Col exhibited a temperature-dependent phase transition around human physiological temperature (at ~ 38.5 °C), and temperature-dependent tunability and temperature-dependent release of the model drugs, lidocaine hydrochloride and bovine serum albumin. To the best of our knowledge, it is for the first time that this kind of study is being reported here wherein potassium persulfate is used as an initiator to achieve grafting of PNVCL onto the ENR. The influences of NVCL on the physical properties including swelling ratio, moisture content, moisture absorption, tensile strength, elongation at break and contact angle on the ENR—grafted-NVCL were investigated. The chemical structure of the ENR and ENR-grafted-NVCL was FTIR and $^1\text{H-NMR}$ was measured. XRD was used to check the crystalline of these samples. The temperature sensitive of this sample was analyzed. Moreover, the biodegradation was also measured.

Experimental

Materials

High-ammonia NR latex (60% dry rubber content (DRC)) was purchased from the Department of Agriculture, Thailand. All other chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. NVCL was purified by recrystallization in methanol. Organic

solvents (Labskan, AR) were used as received. Deionized (DI) water was used throughout the experiments. The curcumin was purchased from Sigma-Aldrich (St. Louis, MO, USA).

Methods

Preparation of ENR

68 g of natural rubber was diluted with deionized water (10 M) and then blended with non-ionic surfactant 15 g Triton™ X-100 (20% by weight) under constant stirring (210 rpm, 30 °C, 15 min). Subsequent, the mixture was gently acidified with formic acid 12 g (85% by weight) and gradually added hydrogen peroxide 50 mL while maintaining temperature at 30 °C. The reaction reached for 8 h.

Preparation of smart epoxidized natural rubber (ENR-graft-NVCL)

The ENR latex (100 g) was placed in 100 mL round-bottom flask. Then, the NVCL monomer (50-150 phr with respect to dry rubber content) was added continuously and the reaction mixture was heated at 80 °C for at least 30 min with continuous stirring. Subsequently, KPS (0.5 phr with respect to dry rubber content) as an initiator was dissolved with a slight amount of water and slowly charged into the reactor. The polymerization reaction was performed at the desired polymerization temperature (80-100 °C). The reaction mixture was allowed to react for a specified length of time (4-8 h). After that, the reaction mixture was cooled down to room temperature and sample was poured on glass sheet. The modified product was purified by soxhlet extraction in acetone for 24 h to remove contaminants, unreacted monomer and homopolymer. The grafted product was dried under vacuum at 60 °C overnight. After drying, the grafted product was characterized.

Application

Curcumin-loaded ENR-graft-NVCL samples were prepared by an aqueous chemistry route. Briefly, curcumin (5 mg in 1 ml ethanol) and ENR-graft-NVCL were mixed together under stirring for 5 min at low rpm. The loaded grafted product was dried under vacuum at 60 °C overnight. After drying, the curcumin loaded grafted product was characterized.

Characterization

The ENR-graft-NVCL and ENR samples were analyzed by attenuated total reflection (ATR)-FTIR using a Bruker Equinox 55 measuring in the range of 4000–500 cm^{-1} . Solution-state NMR spectroscopy was performed with an Ascend TM 600/ Avance III HD, NMR spectrometer (Bruker, Switzerland) for the ENR, NVCL and ENR-graft-NVCL (10 mg for ^1H NMR measurements), which was dissolved into chloroform- d without tetramethylsilane (TMS) (~ 3.4 ml) in a 5-mm ϕ tube. The ^1H NMR measurement at 499.65 MHz and 300 K was performed by 500 scans with a pulse repetition time of 7 s at 45° pulse of 1.7 μs and a relaxation delay of 3.24 s. X-ray diffraction (XRD) measurements were done at room temperature using an XRD, PW3710X-ray diffractometer with Cu-K α radiation ($\lambda = 0.13406$ nm). The 2θ scanning range was 10–90°, and the step size was 0.02° with a scan speed of 1 s per step.

The swelling ratio was determined by the following equation (1):

$$\text{Swelling ratio (\%)} = (W_s - W_d) / W_d \times 100 \dots (1)$$

Where, W_d and W_s are the weight of the samples before and after immersion in water (g), respectively. An average value of the three replicates for each specimen was reported.

The ENR-graft-NVCL was measured in terms of its swelling and deswelling abilities in a buffer solution at pH of 7.0. The samples were immersed in deionized water for 2 h at a range of temperatures from 20 to 40 °C. After removing the surface liquid gently with tissue paper, the

weight of the materials was measured and the swelling percentage was calculated to determine the LCST from the following equation: at each temperature was measured according to Eq. (1) at consecutive time intervals (60 min).

Moisture content was measured the loss weight before (W_i) and after (W_f) drying in oven at 110 °C for 2 h and then was calculated as follow equation (2):

$$\text{Moisture content (\%)} = (W_i - W_f) / W_i \times 100 \dots \dots \dots (2)$$

Moisture absorption was calculated based on the weight measurement before and after moisture treatment. A sample was cut into 1×1 cm² size and dried at 90 °C for 120 min. The dried samples were placed in a desiccator containing copper sulfate (RH~98%). The weight of samples was measured every specific time until reaching a constant weight. The moisture absorption was calculated as follows (3):

$$\text{Moisture absorption (\%)} = (W_t - W_0) / W_0 \times 100 \dots \dots \dots (3)$$

Where, W_0 is the weight of dried sample and W_t is the weight gain at time. An average film thickness was measured using the dial thickness gauge (SM-112, Teclock; Japan) in a random 5 positions. The chemical structure and interaction bonding were characterized by IR spectrometer (Spectrum 100 PerkinElmer; USA) equipped with an attenuated total reflectance device for solid analysis. The analysis performed in the range of 4000 to 500 cm⁻¹ with 4 scans recorded at a 4 cm⁻¹ resolution. The tensile tests were determined with dumbbell specimens according to ASTM D638 (6 mm width in cross section) by using a Universal Testing Machine (Instron Model 2701) with a crosshead speed of 100 mm/min. Tensile experiments were done to the samples during every stages of biodegradation to determine the mechanical properties. Test specimens with a length of 30 mm and a width of 10 mm were cut from composite sheets. The samples were approximately

cut 10 mm × 1 mm × 6 mm (length × thickness × width). Contact angle measurements were taken at room temperature by a goniometer, model of Manual Krüss Easydrop DSA 15E (produced by Krüss, Germany) using the sessile drop method. A 5 µL water drop was deposited onto the surface of the film using a micrometer syringe fitted with a stainless steel needle. The contact angle on both sides of the drop was measured to ensure symmetry. JSM 7800F (JEOL, Japan) scanning electron microscopy was used to observe the surface and cryogenically fractured surfaces which were sputter-coated with gold prior observation.

Encapsulation of curcumin

For *in vitro* quantification of curcumin, a standard solution of curcumin in ethanol was prepared by dissolving 5 mg of curcumin in 100 ml ethanol solution. A serial dilution from 0.2 to 2 ml was taken and diluted up to 25 ml and assayed the system at 428 nm using (UV-1700 Pharma Spec) UV spectrophotometer. The data were plotted to get a straight line for the quantification of unknown drug in the ENR-graft-NVCL. A known amount of the ENR-graft-NVCL sample (50 mg) encapsulating curcumin was dispersed in 10 ml phosphate buffer, pH 7.4, and the solution was divided into 30 glass test tubes (50 ml each). The tubes were kept in a thermostable water bath set at two different temperatures as 20 °C (below LCST) and 40 °C (above LCST). The released curcumin was redissolved in 3 ml ethanol to assay spectrophotometrically at 428 nm. The percentage of curcumin released was determined from the following equation (4).

From the slope and intercept of the plot of $\log (M_t/M_\alpha)$ against $\log (t)$, the kinetic parameter n was calculated.

$$M_t/M_\alpha = kt^n \dots\dots\dots(4)$$

where M_t/M_α is the released fraction at time t , n is the release exponent, and K is the release factor. From the slope and intercept of the plot of $\log (M_t/M_\alpha)$ against

$\log(t)$, the kinetic parameter n was calculated.

Biodegradation

Biodegradation of the ENR-graft-NVCL were measured for 30 days related to previous work [19]. Soil was taken from the surface layer (Khlung Luang, Pathum Thani, Thailand) which was removed inert materials to obtain homogeneous mass. The samples (1cm×1cm) were weighted and buried at a depth of 2 cm in selected soil 100 g under ambient temperature (27-30 °C). Moreover, they do well in high density culture, and are very tolerant to a wide range of environmental conditions. Water was sprayed once a day to sustain the moisture of the soil and was taken out at the fixed periods. Each week, the samples were carefully removed, rinsed with distilled water to remove the soil and dried in a desiccator at 50 °C for 1 day before being reweighed (W_r).

The biodegradation was calculated as follows (5):

$$\% \text{Biodegradation} = (1 - W_r/W_1 \times 100) \dots \dots \dots (5)$$

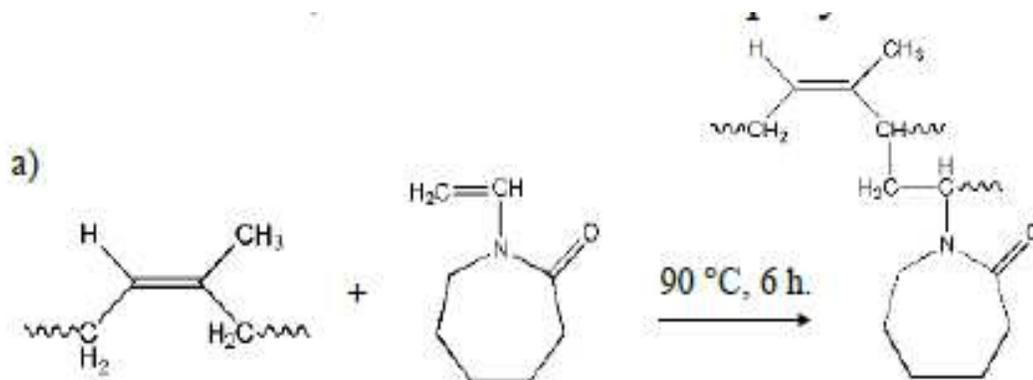
Results and discussion

The ENR-graft-NVCL was prepared via free radical grafting in aqueous system using KPS as an initiator. The formation of grafting copolymer is believed to proceed by two possible pathways: a reaction between the free radicals and double bonds of the isoprene units and a hydrogen abstraction mechanism as shown in Fig. 1. The ENR-graft-NVCL was purified by soxhlet extraction in acetone in order to remove impurities, unreacted NVCL, and PNVCL homopolymer. Photograph images of the ENR and the ENR-graft-NVCL with different NVCL contents are shown in Fig. 1(b). In this Fig., the pure ENR film is almost clear, the ENR-graft-NVCL at 0.5% NVCL film is yellow, the ENR-graft-NVCL at 1.0% NVCL film is almost

milky, and the ENR-graft-NVCL at 2% NVCL is bold yellow. The thickness of the modified ENR film is increased by the addition of NVCL, and the physical and mechanical properties of the films are reported in detail in latter.

FTIR, $^1\text{H-NMR}$ and XRD studied

The ENR-graft-NVCL was characterized using FT-IR techniques and compared with the ENR and NVCL. The FT-IR spectrum of ENR-graft-NVCL showed signature signals of both ENR and NVCL (Fig. 2). The FT-IR signals at 3440, 3255, 1631, and 1379 cm^{-1} corresponded to O-H stretching, N-H stretching, C=O stretching and C-N stretching of caprolactam ring of NVCL, respectively. The signal at 1442 cm^{-1} corresponded to C=C stretching of the polyisoprene. The FT-IR results are consistent with those in previous work [19].



b)

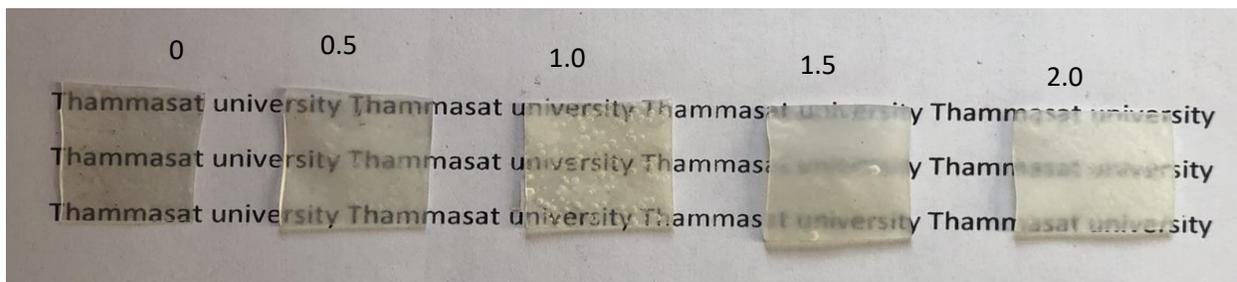


Fig. 1 A) Schematic representation for the synthesis of the ENR-graft-NVCL from the ENR and NVCL and B) Photograph images of ENR-graft-NVCL with different NVCL contents

In previous work [20], they synthesized the graft copolymer between chitosan and PNVCL and it was confirmed by FTIR. They found that the -NH groups was found at 3325 cm^{-1} and 1654 cm^{-1} .

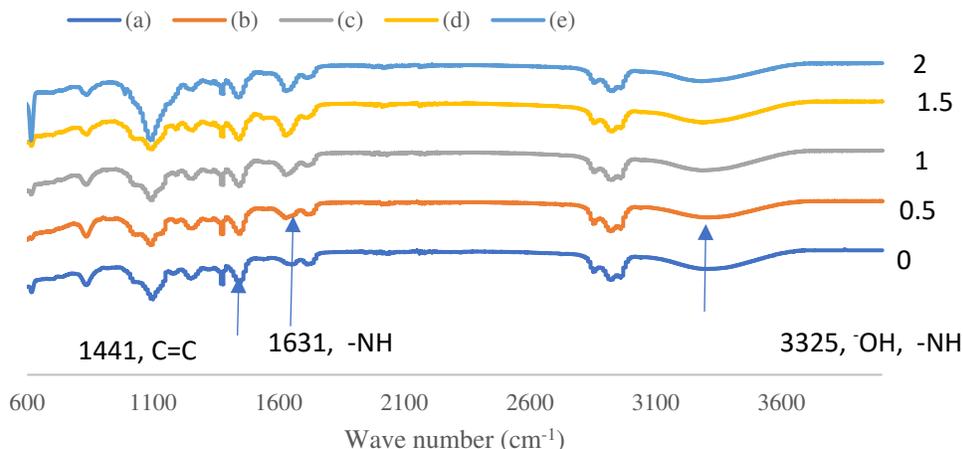


Fig. 2 ATR-FTIR spectra of ENR-graft-NVCL with different NVCL contents

The chemical structure of the ENR-grafted-NVCL was confirmed by ¹H NMR. The ¹H-NMR signals at 4.4, 3.3, 2.5, and 1.8 ppm were observed in the NVCL, corresponding to CH-NH, CH₂-NH, CH₂-CO, and CH₂ respectively as shown in Fig. 3. The ¹H-NMR signal of the ENR-graft-NVCL showed at 4.4 ppm corresponded to CH-NH of the PNVCL and the signal at 4.97 ppm corresponded to C-H of the isoprene units from the ENR [21].

3.3, CH₂-NH

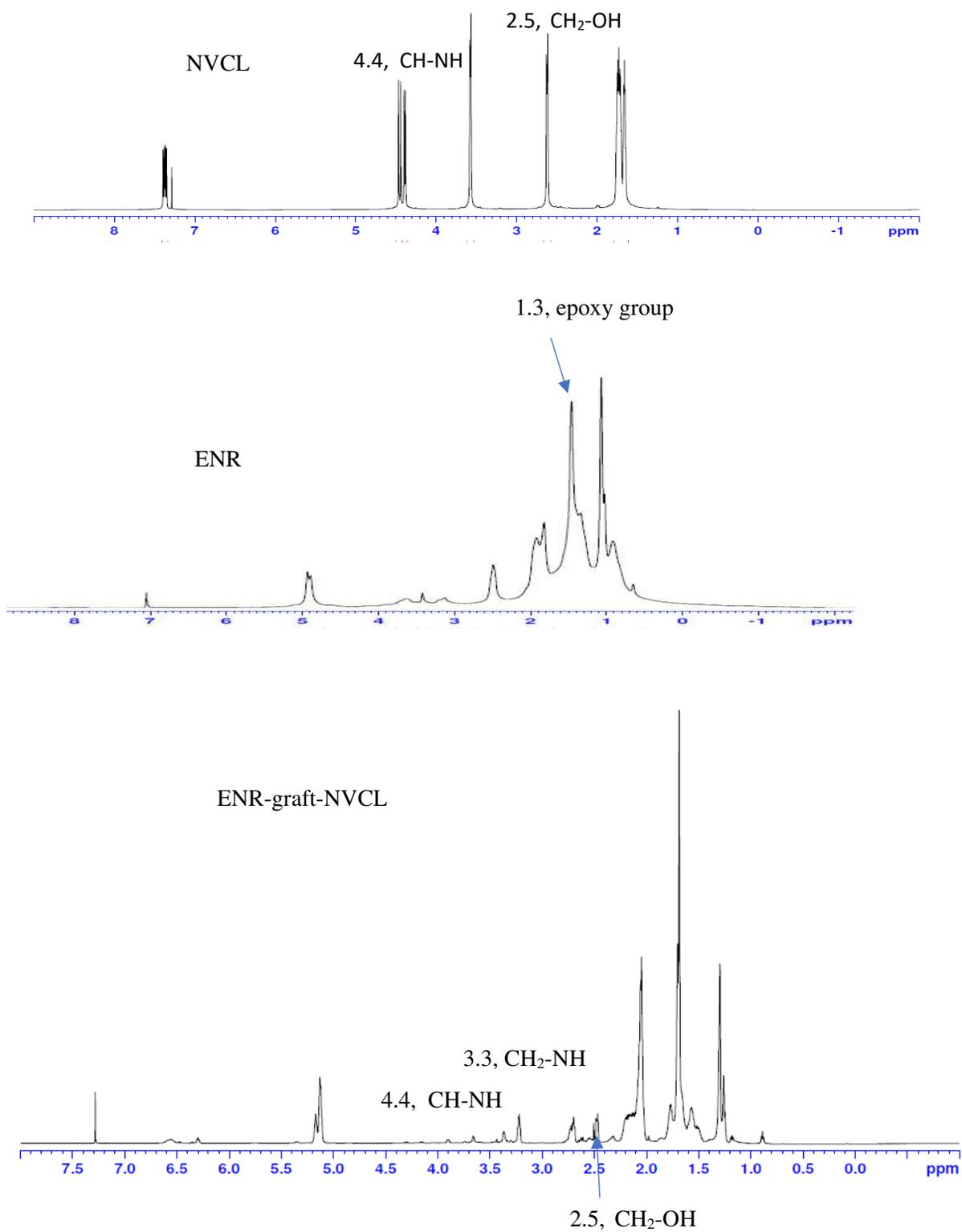


Fig. 3 $^1\text{H-NMR}$ spectra of the NVCL, ENR and ENR-graft-NVCL in CDCl_3

In previous work [22], the C-H in isoprene of the ENR 50 was located at 4.97-5.1 ppm. In the case of ENR, the methyl, methylene and unsaturated methine proton of *cis*-1,4- isoprene unit in ENR appeared at 1.7, 2.1 and 5.1 ppm, respectively. Moreover, two signals characteristic of epoxy group appeared at 1.3 and 2.7 ppm, which were assigned to methyl and methine proton of resulting epoxy group, respectively which are found in this work.

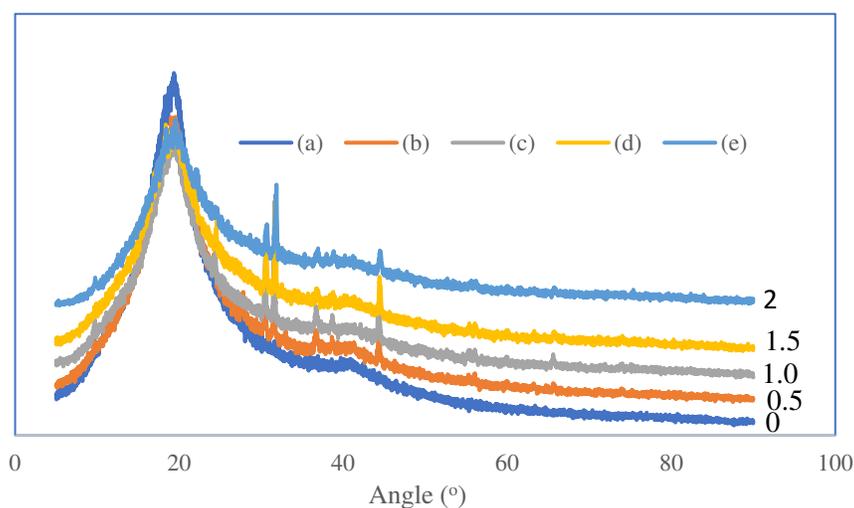


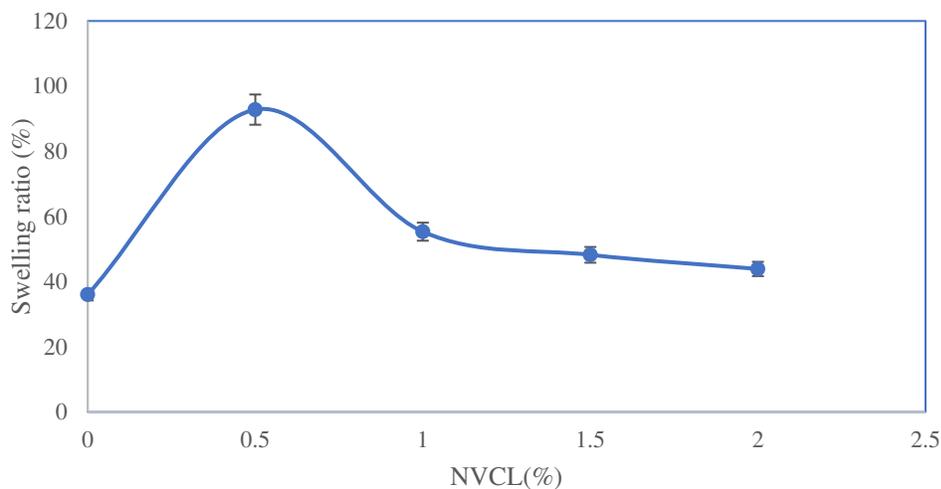
Fig. 4 XRD patterns of ENR-graft-NVCL/PVA blend with different NVCL contents.

The ENR-graft-NVCL show an initial broad diffraction peak of epoxy matrix at 2θ range in between 20° and 45° as shown in Fig. 4. Based on the previous findings, the XRD pattern of pristine ENR shows an intense basal reflection peak at $2\theta = 20.5^\circ$, which is amorphous portion. In previous work [19], it was found that the broad peak of the hydrated crystalline structure of PVA in the ENR shows the same tendency as that observed for the peak at 19° . It is vital to note that there are two halos cited at 19.5° which is a crystalline peak and 40.5° referring to a low intensity and broad shape and corresponds to noncrystalline zones within the crystalline polymer matrix. In

previous work [23], the X-ray diffraction pattern of native PVCL hydrogel has three peaks with the first peak of the intermolecular interactions of C–C polymer chains, second peak attributed to both inter- and intramolecular correlations.

Swelling ratio, contact angle and moisture content/moisture absorption

Swelling studies indicated that equilibrium swelling of the ENR-graft-NVCL had been reached after being immersed in water for 30 min and results are recorded in Fig. 5. The influence of the CL on the swelling ratios of the ENR-graft-NVCL/PVA blend with different CL contents and results are reported in Fig. 5. Results showed that the swelling ratio of the ENR-graft-NVCL without CL was 40%. The incorporation of CL into the ENR-graft-NVCL has shifted the higher value comparing to the sample without CL. When the amount of CL increased from 0.5 to 1.0 %CL, the swelling ratio of the sample decreased due to chemical interaction between CL and the ENR-graft-NVCL. The results indicated that swelling ratio decreased as the amount of CL increased due to more chemical interaction.



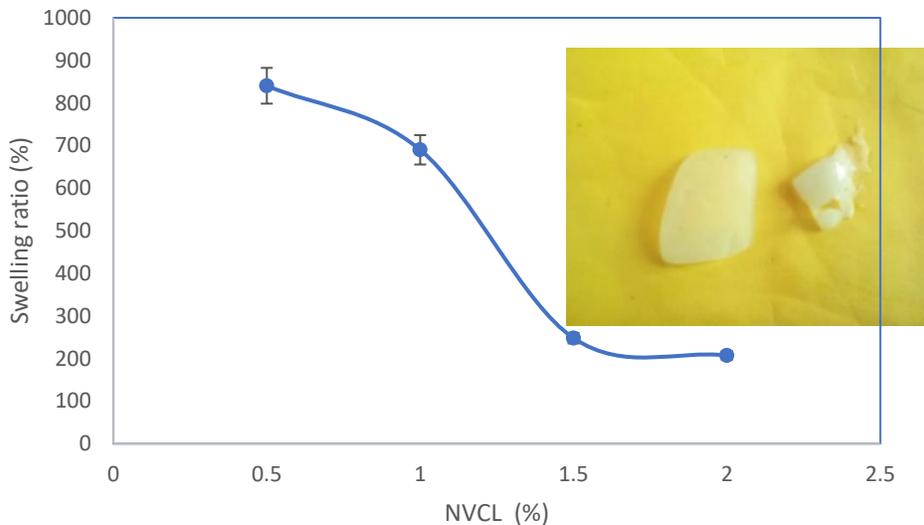


Fig. 5 Swelling ratio of the ENR-graft-NVCL contents in water and toluene

Previous work [24] studied the effect of hydrolyzed epoxy soybean oil-graft-hydroxyethyl cellulose (H-ESO-HEC) on the swelling ratio of N-vinylcaprolactam (NVCL) hydrogels. Results showed that the swelling ratio decreased as function of H-ESO-HEC content due to increasing hydrophilic groups of H-ESO-HEC. In case of toluene, the effect of CL on the swelling ratio was studied and all data are reported in Fig 5. The swelling ratio decreased with increasing CL. The swelling ratio of the the ENR-graft-NVCL was 850% when using 0.5%CL. However, the amount of CL was over 0.5%, the swelling ratio of the ENR-graft-NVCL decreased as a function of CL. The lowest swelling ratio was found when using 2% CP. Our previous work [25] studied the swelling ratio of biopolymer from natural rubber grafted cassava starch and maleate epoxidized natural rubber. Results showed that the swelling ratio dramatically decreased as a function of MENR content owing to the chemical interaction between the MENR and the NR-graft-CSt through the esterification.

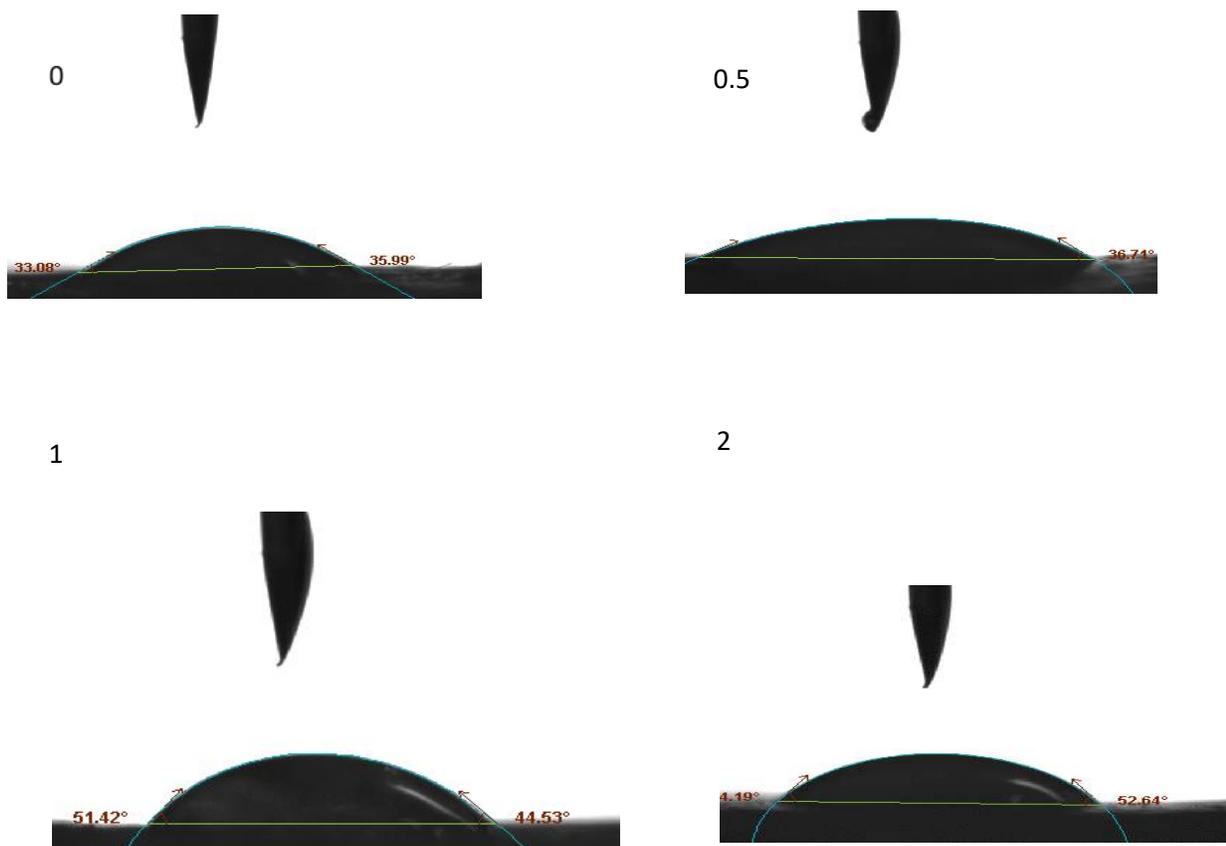


Fig. 6 Contact angle of the ENR and ENR-graft-NVCL/PVA blend with different NVCL contents

Surface composition and the surface topography of substrates is greatly influenced wettability or water-repellancy of substrates. The hydrophilic surface of the the ENR-graft-NVCL was observed by the contact measurement and results are recorded in Fig. 6. The polar nature of the film surface is correlated well with the presence of the exuded nonionic surfactant materials at the film surface. The surface free energies of the latex films are comparable to that for synthetic cis-polyisoprene latex film [26]. These are in turn in reasonable agreement with the surface free energies of some common solid polymer surfaces. The contact angle of the ENR was the lowest, indicating hydrophic surface character due to epoxide group and non-ionic surfactant. After the addition of the NVCL into the ENR sample, the ENR-graft-NVCL had relatively similar contact angles showing hydrophobicity. The contact angle of this sample increased as a function of the NVCL contents. We measured the change in moisture content and moisture absorption according to

storage time and is shown in Fig.7. Results show that the moisture content of this sample decreased as a function of the CP contents. These were might be due to the hydrophobic nature. The moisture content of the ENR was 14. When the addition of NVCL was 0.5%, the moisture content of this sample was 11%. The minimum of moisture content was found when using 2% and its value was 3% owing to high chemical interaction [27].

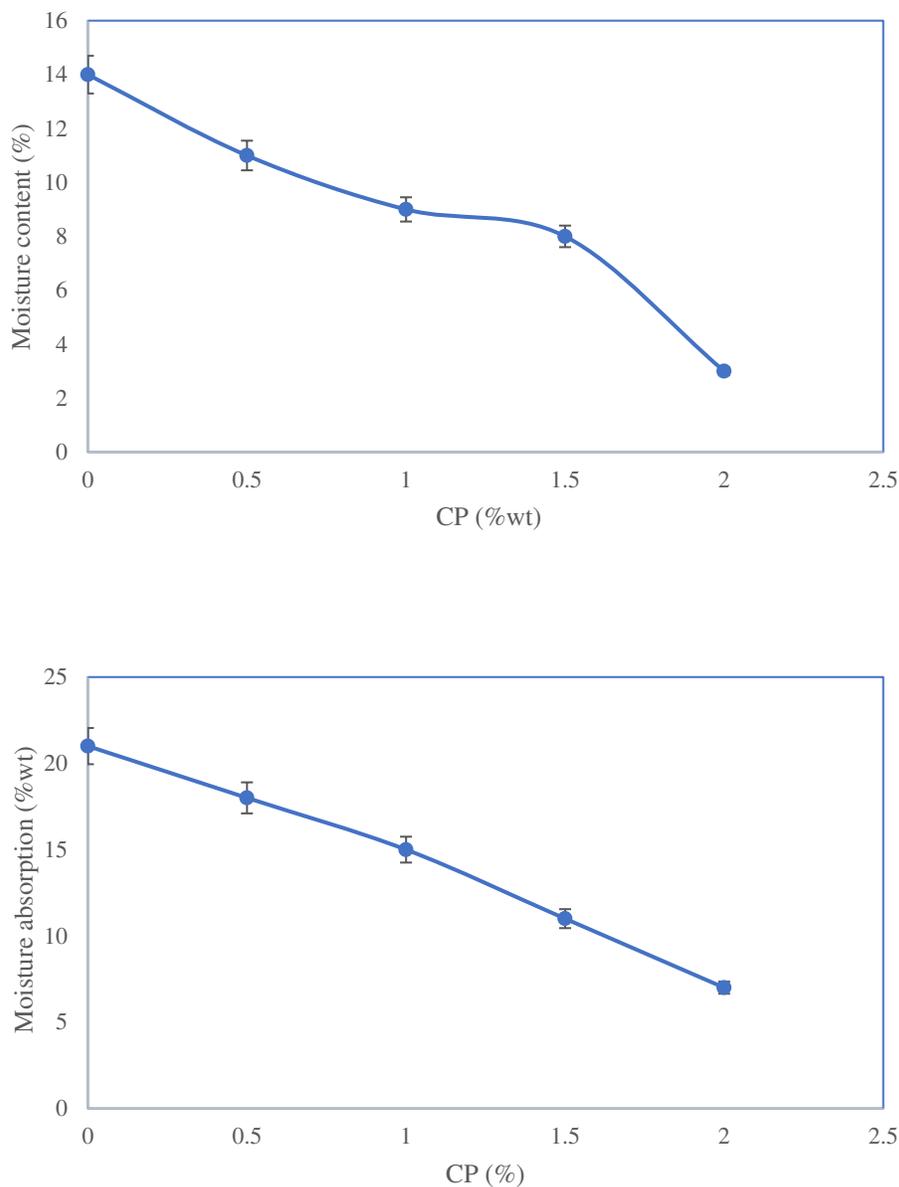
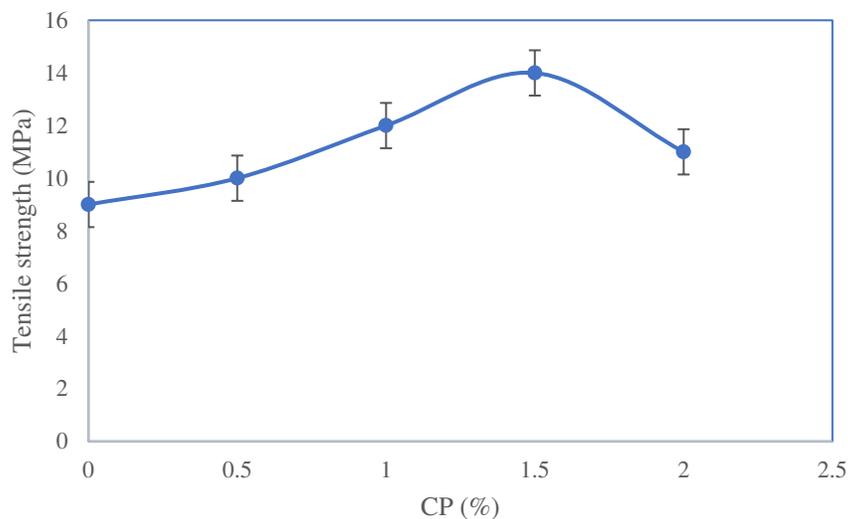


Fig. 7 Moisture content and moisture absorption of the ENR-graft-NVCL

The moisture absorption of these sample show the same trend with moisture content. The moisture absorption of the ENR was 22%. When the adding NVCL into the ENR, the moisture absorption of these sample decreased as NVCL contents. With an increase in NVCL content, the moisture content of the ENR-graft-NVCL films decreased, which can be attributed to the chemical interaction of the ENR-graft-NVCL films, owing to the presence of hydrophobic group polymer chains caused by the incorporation of NVCL.

Mechanical properties and morphology

The tensile strength curves of the ENR-graft-NVCL with different NVCL contents are presented in Fig. 8. As can be clearly seen, tensile strength of the ENR-graft-NVCL were all improved with increasing the content of NVCL. For example, tensile strength increased from 8.5 and 13.5 MPa with addition of only 1.5 phr NVCL, showing an increasement of about 60 %.



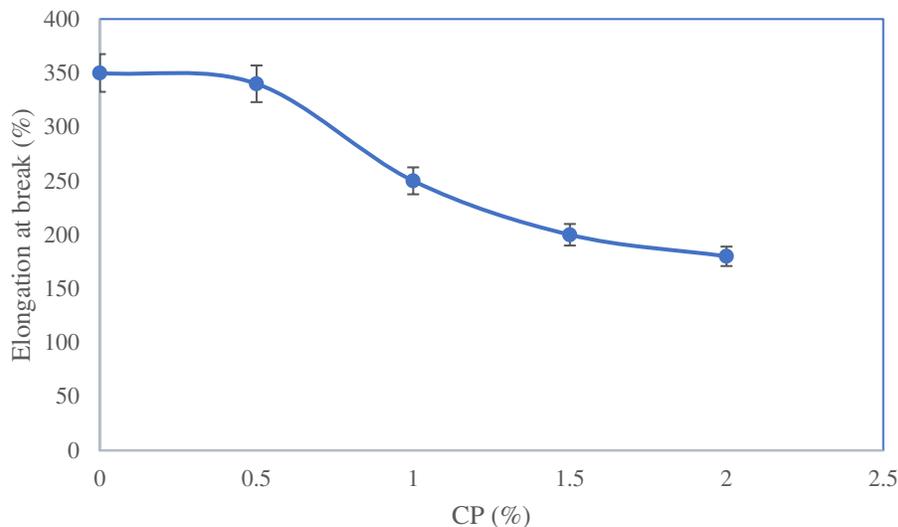
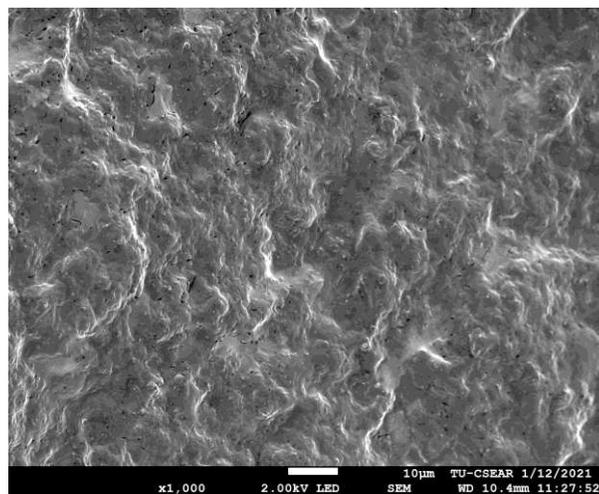
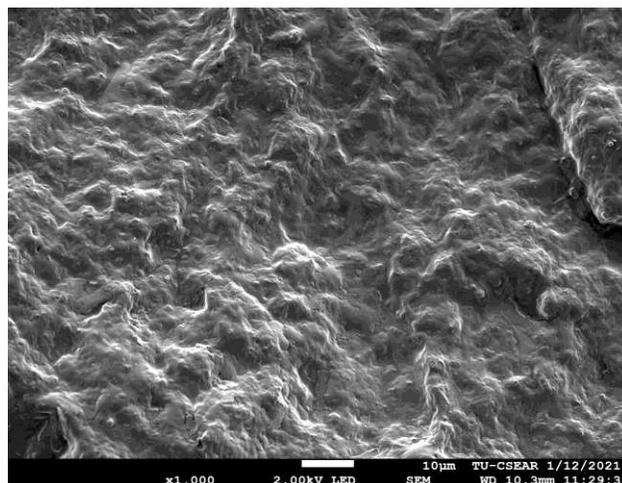


Fig. 8 Tensile strength and elongation at break of the ENR-graft-NVCL with different NVCL contents

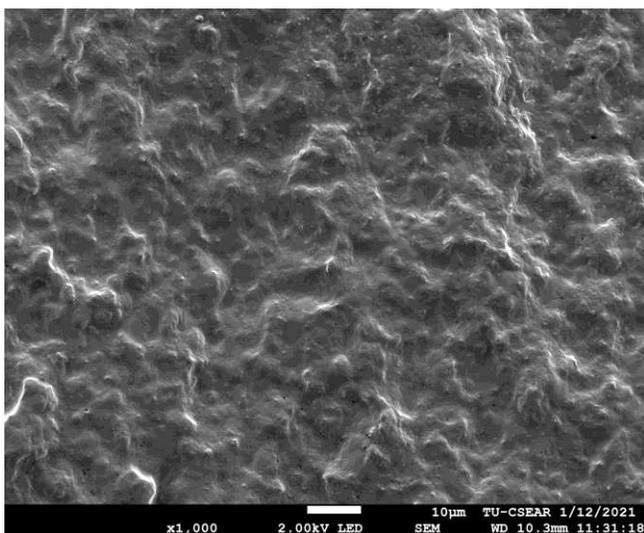
In previous work [27], the effect of NVCL on the mechanical properties of silicone rubber (SR) to provide SR with temperature-responsive hydrophilic nanobrushes coating for encapsulation of lysozyme. The mechanical properties of the ENR-graft-NVCL were remarkably altered after a moderate grafting of the ENR-graft-NVCL. It was explained by the fact that gamma irradiation may cause flexibility loss of the grafted films due to induced crosslinking processes between the polydimethylsiloxane chains. The dispersion of the NVCL in the ENR-graft-NVCL was observed by SEM and results are recorded in Fig. 9. Pristine ENR film showed an irregular topography because of marks of its manufacturing process and surfactant residual. Results showed that the good dispersion of NVCL in the ENR-graft-NVCL was found. These results are referred that the good polymer compatibility between the ENR and NVCL.



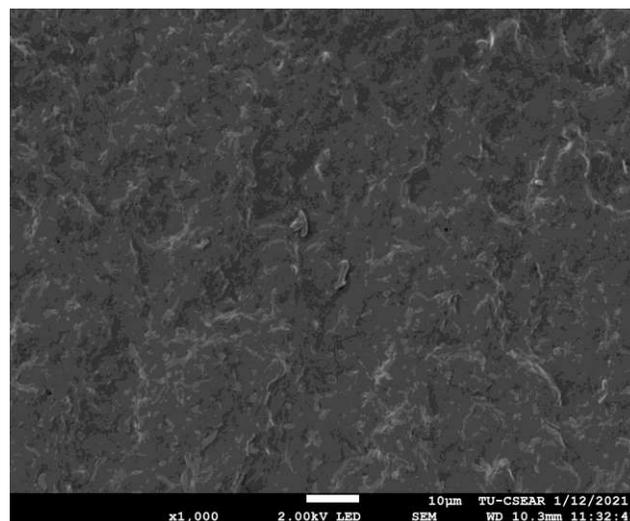
0.5



1.0



1.5



2.0

Fig. 9 SEM images of the ENR-graft-NVCL with different NVCL contents

These results are correlated with the mechanical properties. In previous work (Pino-Ramos et al., 2018), the morphology of the SR changed after it was grafted with NVCL. The morphology showed flakes form on the entire surface of the film. This result was referred that the good chemical interaction between the SR and NVCL.

Application in temperature sensitive and encapsulation of curcumin

The ENR-graft-NVCL in water were characterized at a temperature range of 28-33 °C. At 28 °C, ENR-graft-NVCL swelled by 150 % of its original weight and about 8 times more than the ENR, due to the presence of hydrophilic NVCL units and results are recorded in Fig. 10. The ENR-graft-NVCL can be thus considered as a hydrogel-like material. As the temperature was increased, the percentage of swelling of the ENR did not change, whereas that of the ENR-graft-NVCL started to decrease when the temperature of water exceeded 30 °C and became constant above 34 °C (Fig. 5). The water uptake of the conjugated polymer is influenced by temperature. Water uptake of ENR-graft-NVCL copolymer was higher at +4 °C (at which hydrophilicity is maximum). Water molecules penetrated into the hydrogel structure more easily because of increased hydrophilicity, i.e., the increase in hydrogen bonds between water molecules and hydrophilic chain segments. Above the LCST, the bound water was released from the ENR-graft-NVCL copolymer. In turn, hydrophobic interactions between the NVCL chains in the ENR-graft-NVCL increased.

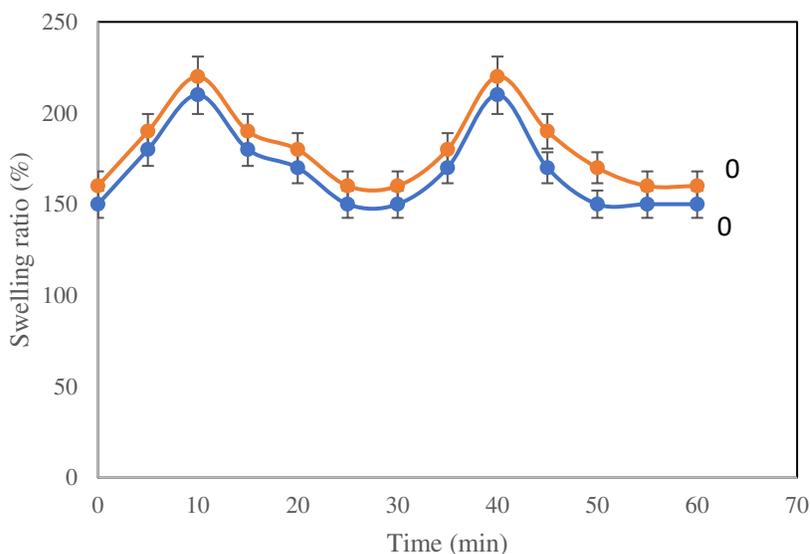


Fig. 10 Temperature sensitive of the ENR-graft-NVCL

The previous work [28] studied the preparation of temperature-responsive polymers from N-vinylcaprolactam and deproteinized natural rubber (DPNR) latex, with 2,20-azoisobutyronitrile

(AIBN) as the free radical initiator. Results show that the graft copolymer was found to be temperature responsive in the range 32-34 °C, which is near the human body temperature, it can be used to fabricate biomedical and sensing materials. Here, the ENR-graft-NVCL was used a polymer matrix for encapsulated of curcumin. The effect of releasing time and temperature medium on the curcumin which is a natural antioxidant with potential health benefits against cardiovascular problems, inflammatory diseases and certain cancers from the ENR-graft-NVCL matrix was evaluated. In order to investigate in vitro drug release, The sustained release of curcumin from the ENR-graft-NVCL was observed at 20 °C and 40 °C . The release kinetics from the sample shows two stages: an initial fast release before the inflections (stage I) followed by a slow and constant release (stage II) [29-30]. In stage I, there were initial rapid release from the electrospun mats, then the release ceased and the remainder of the drug was released in stage II. In the process of electrospinning, FA molecules exist both at the outer and inner surface of the nanofiber mats [31]. During the release processes, curcumin present on the surface dissolved in ethanol. For the ENR-graft-NVCL sample at 20 °C, there was an initial burst release 24% within 0.5h (Fig. 6C). The drug loaded ENR-graft-NVCL composite nanofibers showed a relatively sustained curcumin release from the sample. In the following 0.5 h to 24 h, the amount of drug released reached 53%. The release percentages of the loaded curcumin sample at 40 °C at 72 h was much lower than that of the sample at 20 °C. The sustained release profile of curcumin from the sample is due to the fact that the soluble structure affect the kinetics of drug release.

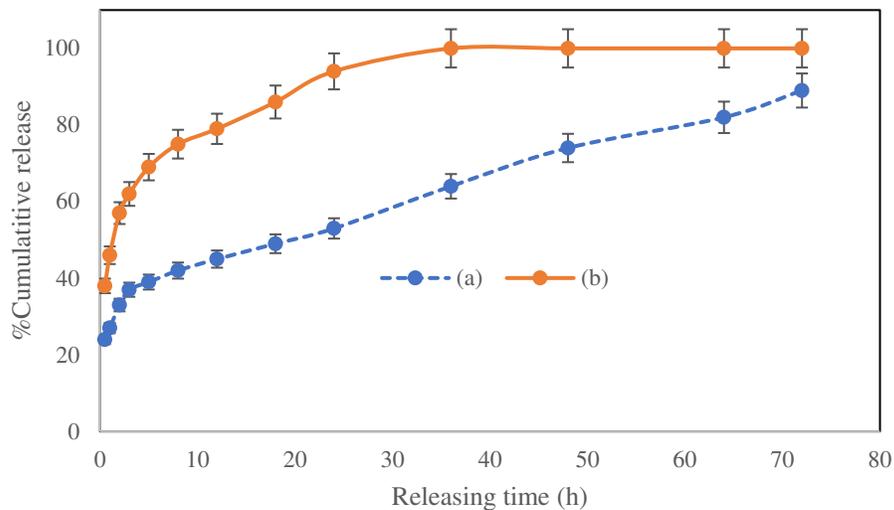


Table 1

Values of kinetic parameter for releasing mechanism of curcumin from the ENR-graft-NVCL film

Temp (°C)	n	k/min ⁻¹	R ²
20	0.4145	2.4689	98.4443
40	0.4321	2.3568	98.9753

The kinetic parameters for the cumulative release of curcumin from the loaded ENR-graft-NVCL composite film were measured and results are recorded in Table 1. Results show that the R² values of curcumin encapsulated by the ENR-graft-NVCL composite reflect this linearity. The release mechanism can be elucidated from the n values, which represent the release exponent. The diffusion exponent values of curcumin loaded ENR-graft-NVCL composite at 20 and 40°C was

0.4145 and 0.4321, respectively, indicated that release occurred via Fickian diffusion, the molecular diffusion of curcumin due to a chemical potential gradient [31].

Biodegradation

Enzymes involved in rubber biodegradation, particularly enzymes catalyzing cleavage of the rubber backbone, were one of the last obstacles to biopolymer degradation and were unknown until recently and results are recoded in Fig. 11. Chemical analysis of degradation products which were transiently formed due to incomplete biodegradation, analysis of mutants not capable of using natural rubber as a carbon source for growth, and finally identification of the first genes coding for enzymes catalyzing cleavage of polyisoprene revealed some information about the biochemistry of rubber biodegradation [32-33].

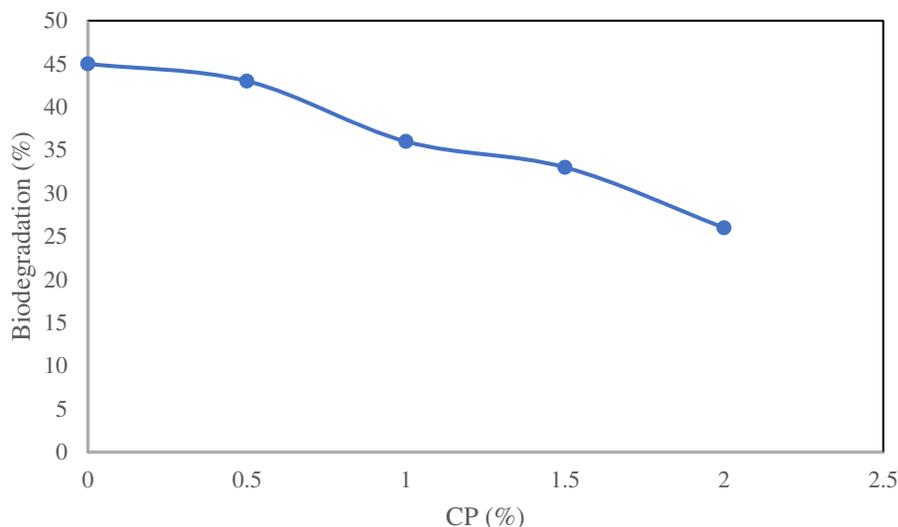


Fig. 11 Biodegradation of the ENR-graft-NVCL in natural soil

The biodegradation of the ENR was around 45%. After the addition of the NVCL into the ENR-graft-NVCL, the biodegradation slight decrease as a function of NVCL content. This was might due to the chemical interaction between the ENR and NVCL. The previous work [34] studied the biodegradation of the degradation rate of poly-acrylic acid grafted natural rubber (NR-g-PAA is very fast in the beginning first week. Afterwards, the weight loss of the samples increased slowly in the following 2 weeks. During the biodegradation test, the NR-g-PAA

powders transitioned to a loose structure and could be easily milled. The mechanism of enzymatic degradation can be proposed by binding the enzyme to the polymer chains which act as a catalyst for a hydrolytic cleavage [33-34].

Conclusions

In this work, the grafted copolymers between the NVCL and ENR/PVA blend were successfully prepared via grafting reaction in emulsion using KPS as an initiator. ENR-graft-NVCL/PVA blend was studied by water swelling experiment that showed an LCST around 32-34 °C, which was close to the phase transition of NVCL due to the presence of hydrophilic NVCL units. The ENR-graft-NVCL showed a good polymer matrix for the encapsulation of curcumin. These temperature-responsive rubbers will be useful for a variety of biomedical applications. The biodegradation of the ENR-graft-NVCL slight decrease as a function of NVCL content in soil. Potential consumer products include, smart bandages and facial masks with the ability to efficiently release medicine or healing ingredients upon contact with human skins.

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