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ГИДРОКСИЛИРОВАНИЕ МАСЛА КАУЧУКОВЫХ СЕМЯН С ПОМОЩЬЮ МУРАВЬИНОЙ КИСЛОТЫ/H_2O_2 ДЛЯ ИСПОЛЬЗОВАНИЯ В КАЧЕСТВЕ ВТОРИЧНОГО ПЛАСТИФИЦИРУЮЩЕГО СРЕДСТВА В СОСТАВАХ ПВХ

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В данном исследовании масло семян каучукового дерева (RSO) было успешно гидроксилировано с использованием пероксиуксусной и пермуравьиной кислот. Химическая структура гидроксилированного масла семян каучукового дерева (HRSO) была подтверждена методами ядерного магнитного резонанса (ЯМР) и инфракрасной спектроскопии с преобразованием Фурье (FTIR). Пластифицирующая способность HRSO исследовалась с помощью дифференциальной сканирующей калориметрии (ДСК) и испытаний на растяжение. Смешиваемость и миграционное поведение HRSO в качестве пластификатора оценивались с помощью тестов на летучесть и экстракцию. В качестве основного пластификатора был выбран коммерческий диоктилфталат (DOP), который использовался в качестве контроля. Добавление HRSO к DOP снизило температуру стеклования на 14 °C. Присутствие HRSO также снизило летучесть и миграцию пластификатора благодаря его более высокой молекулярной массе и совместимости с DOP. Механические свойства ПВХ, пластифицированного DOP/HRSO, были несколько хуже, чем у ПВХ, пластифицированного DOP. HRSO продемонстрировал хороший потенциал в качестве вторичного пластификатора ПВХ.

Ключевые слова: эпоксидированное масло семян каучукового дерева (ERSO), гидроксилированное масло семян каучукового дерева (HRSO), пластификатор, ПВХ

HYDROXYLATION OF RUBBER SEED OIL BY FORMIC ACID/H_2O_2 FOR USING AS SECONDARY PLASTICIZER IN PVC FORMULATION

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In this study, rubber seed oil (RSO) was successfully hydroxylated using peracetic and performic acids. The chemical structure of hydroxylated rubber seed oil (HRSO) was confirmed by nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopy. The

plasticizing efficiency of HRSO was investigated using differential scanning calorimetry (DSC) and tensile testing. The miscibility and migration behavior of HRSO as a plasticizer were evaluated by volatility and extraction tests. Commercial dioctyl phthalate (DOP) was chosen as the primary plasticizer and used as a control. The addition of HRSO to DOP reduced glass transition temperature by 14 °C. The presence of HRSO also decreased the volatility and migration of the plasticizer due to its higher molecular weight and its compatibility with DOP. The mechanical properties of DOP/HRSO-plasticized PVC were slighly inferior to those of DOP-plasticized PVC. HRSO showed good potential as a secondary PVC plasticizer.

Keywords: epoxidized rubber seed oil (ERSO), hydroxylated rubber seed oil (HRSO), plasticizer, PVC

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INTRODUCTION

PVC is a thermoplastic widely used in many applications such as cables, floors, wall panels, packaging materials, toys, medical supplies, etc. [1-4]. However, pure PVC has the disadvantage of being hard, brittle and having poor heat resistance. To enhance its processability and expand its application range, it is necessary to use plasticizers and thermal stabilizers. PVC plasticizers play an important role in improving flexibility by inserting themselves between PVC polymer chains, breaking the interactions of the polymer chains and lowering the glass transition temperature. A good plasticizer can also improve the heat resistance of the material and is compatible with other additives [5]. Some traditional plasticizers such as dioctyl phthalate (DOP), although widely used, are gradually being restricted due to toxicity concerns. Therefore, they should be replaced with biobased or renewable, environmentally friendly resources [6-8]. The modified vegetable oil such as epoxidized or hydroxylated vegetable oil is very suitable because it contains many epoxy or hydroxy groups and has renewable sources [2, 9, 10]. Moreover, it is not only known as a plasticizer but also contributes to improving the thermal stability of PVC [11]. There are many types of modified vegetable oils such as soybean oil [12-14], linseed oil [15-18], and sunflower oil [19] that have been used as primary or secondary plasticizers and/or thermal stabilizers for PVC. Among them, rubber seed oil and its derivatives have not only been used for a long time [20, 21] but are also very popular because it is an inedible oil [22]. Epoxidized rubber seed oils were used as plasticizer and thermal stabilizers for PVC plastisol [11, 20, 21, 23, 24] but hydroxylated rubber seed (HRSO) oil has not been studied much.

In this study, we synthesized hydroxylated rubber seed oil and used it as a secondary plasticizer for PVC. The synthesis process of hydroxylated rubber seed oil is similar to the epoxidation process of rubber seed oil with some modifications such as temperature and reaction time. The hydroxylated rubber seed oil product is then blended with DOP and a heat stabilizer during the PVC formulations. Characteristics of PVC such as tensile properties, migration, leaching and thermal property were investigated.

MATERIALS AND METHODS

Materials

The Vietnamese rubber seed oil (RSO) was obtained from EC Company, Vietnam. Formic acid (88 wt. %), and hydrogen peroxide (30 wt.%) were obtained from Xilong Scientific, China. Glacial acetic acid (99 wt.%), ethyl acetate (technical grade), K_2CO_3 (99 wt.%), H_2SO_4 (98 wt.%) and Na_2SO_4 (99 wt.%) were obtained from Merck. All of which were used without further purification. PVC powder with a trade name of SG660, original from Thailand, was obtained from TPC VINA (Vietnam) – Density: 1.45 g/cm^3, molecular wieght 89000 amu. Dioctyl phtalate (DOP) (technical grade, from China) was supplied by a local company.

Preparation of hydroxylated rubber seed oil

The hydroxylation was carried out according to the process reported by Okieimena *et al*. [25], with minor modification. A certain amount of 40.0 g of rubber seed oil was introduced into a 250 mL three-necked

flask equipped with a mechanical stirrer, dropping funnel and reflux condenser. Subsequently, 0.12 mol of HCOOH or CH_3COOH (approximately 5.0 ml) and 0.5 ml of 96% H_2SO_4 solution (0,009 mol) were added to the mixture. The reaction vessel was cooled in an ice-salt bath to 0 °C. Then, 42.0 ml of 30% H_2O_2 solution (0.411 mol) was added dropwise into the reaction vessel over approximately 30 min. After all the H_2O_2 was added, the reaction mixture was continously stirred at room temperature for 1 h, and subsequently was heated at a predetermined temperature (60, 70, 80 and 90 °C) for 8 h. When the reaction finished, the reaction mixture was cooled to room temperature, extracted with ethyl acetate and washed with distilled water until pH = 7. The organic phase was dried over Na_2SO_4 and filtered. The filtrate was then refluxed with activated carbon for about 30 min and then filtered again. The ethyl acetate solvent was eliminated by rotary evaporation. The obtained hydroxylated rubber seed oil (HRSO) is in dark orange yellow color.

PVC plastisol preparation

To evaluate the behavior as the secondary plasticizer for PVC, HRSO was gradually substitued for DOP in the plasticizer formulation. The ratio of plasticizer and thermal stabilizer were kept at 30 phr and 2 phr, respectively, and the sample with 30 phr of DOP was used as reference. The PVC plastisol and dog-bone sample were prepared following procedure below: PVC powder, plasticizer of different composition (30 phr, as shown in the Table 1) and a thermal stabilizer (Ca/Zn stearate, 2 phr) were blended for 30 min, using a high speed mechanical mixer. The temperature of mixture could reache approximately 80 °C. The resulting mixtures were poured into stainless steel mould and cured for 5 min under pressure using a heat press. The cured temperatures are listed in the Table 1. After curing, dog-bone specimens (Fig. 1, 2.0 mm ± 0.04 mm thickness) were obtained.

For reference sample, PVC was mixed only with thermal stabilizer Ca/Zn (2 phr) and then cured using the same heat-press procedure.

Characterization

The iodine value and free fatty acid (FFA) value of the oil product was determined according to ASTM D5554-95 and ISO 660:2009 standards by automatic titrator TitroLine 5000 (SI Analytics). Functional groups of RSO and HRSO were analyzed by Fourier transform infrared spectrometer (FTIR Tensor 27, Bruker) with a resolution of 4 cm^{-1} and a scanning range of 400-4000 cm^{-1}. Proton Nuclear Magnetic Resonance (^1H NMR) spectra were obtained using Nuclear Magnetic Resonance spectrometer (Avance III HD 500 MHz, Bruker Biospin) operating at frequency of 500 MHz, with $CDCl_3$ as the solvent. Differential scanning calorimetry (DSC) measurements were performed on a DSC Q2500 (TA Instrument, USA) at heating rates of 5 and 10 °C/min and temperature range from -20 °C to 120 °C.

The tensile modulus, tensile strength and elongation at break of the PVC samples were measured using a Cometech universal testing machine equipped with a load cell of 20 kN (Cometech, Taiwan). The tests were performed according to the ASTM D638. The specimens were tested at a constant rate of 10 mm/min at room temperature. Each tests were repeated for five consecutive measurements.

Table 1

Composition of PVC plastisol

***Таблица 1.* Состав ПВХ-пластизоля**

Sample	PVC (phr)	DOP (phr)	HRSO (phr)	Ratio of HRSO in plasticizer formulation (%)	Curing temperature (°C)
PVC0	100	-	-	-	190
PVC1	100	30	-	0	150-160
PVC2	100	24	6	20	150-160
PVC3	100	18	12	40	160-170
PVC3’	100	15	15	50	160-170
PVC4	100	12	18	60	160-170
PVC5	100	6	24	80	170-180
PVC6	100	-	30	100	170-180

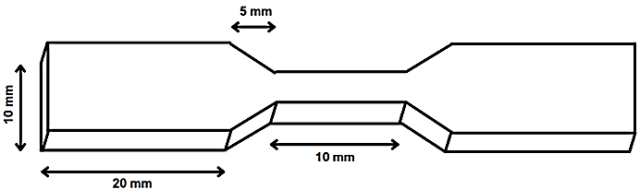

Fig. 1. PVC specimen for mechanical testing

Рис. 1. Образец ПВХ для механических испытаний

The volatility of plasticizer was determined according to the following procedure [26]: PVC samples with an initial weight w_0 were placed between two filter papers and then dried in an oven at 40 °C. After 72 h, the samples were taken out and weighted again (weight w_1). The volatility of plasticizers were calculated using the following equation:

$$\text{Volatility} = \%\text{weight loss} = \frac{w_0 - w_1}{w_0} \cdot 100.$$

The leaching tests were conducted according to the following procedure: the specimens were immersed in five different solvents: distilled water, ethanol 30% (w/w), acetic acid 30% (w/w), n-hexane and cooking oil at room temperature for 24 h. After immersion, the PVC samples were rinsed and dried in a vacumm oven at 30 °C for 24 h. The amount of plasticizer leached into solvent were determined using the following equation:

$$\text{Leaching} = \%\text{weight loss} = \frac{w_0 - w_1}{w_0} \cdot 100$$

RESULTS AND DISCUSSION

Hydroxylation of rubber seed oil

To investigate the effect of temperature and reaction time on the conversion of double bonds into hydroxy groups, rubber seed oil was hydroxylated with acetic acid or formic acid and hydrogene peroxide (H_2O_2), catalyzed by sulfuric acid (H_2SO_4), at different temperatures (60, 70, 80, and 90 °C) for various reaction times ranging from 4 to 10 h. The products obtained after purification were characterized and the results were summarized in Table 2 and Table 3.

Table 2

Effect of temperature and reaction time on the hydroxylation of rubber seed oil

Таблица 2. **Влияние температуры и времени реакции на гидроксилирование масла семян каучукового дерева**

Sample	Acid	Temperature (°C)	Reaction time (h)	Double bond conversion (%)
HRSO1	CH_3COOH	60	8	66.5
HRSO2	CH_3COOH	70	8	67.1
HRSO3	CH_3COOH	80	8	68.8
HRSO4	CH_3COOH	90	8	86.9
HRSO5	HCOOH	60	8	92.3
HRSO6	HCOOH	70	8	92.7
HRSO7	HCOOH	80	8	96.5
HRSO8	HCOOH	90	8	96.9
HRSO9	HCOOH	80	4	68.5
HRSO10	HCOOH	80	6	89.8

Table 3

Comparaison of Physiochemical Properties of RSO and HRSO

Таблица 3. **Сравнение физико-химических свойств RSO и HRSO**

Property	RSO	HRSO
Color	Dark yellow	Dark orange
Density at 25 °C (g/cm^3)	0.943	0.950
Free fat acid (%)	36.33	21.0
Iodine value (mg I_2/100 g)	138.76	18.09

The obtained HRSO exhibited higher density than raw RSO. This increase in density can be contributed to the addition of oxygent atoms to C=C double bond, and followed by hydroxylation. This addition also results in the decrease in iodine value from RSO to HRSO, as the double bonds were converted. Fig. 2 shows the ^{1}H-NMR spectrum of rubber seed oil before (RSO) and after hydroxylation (HRSO). In the spectrum of RSO, the peak at 5.3-5.4 ppm is characteristic of the proton of the double bond (–CH=CH–). This peak gradually disappeared during the epoxidation and subsequent hydroxylation process, and became insignificant in the spectrum of HRSO after 8 h of reaction.

The results show that the peak in the range of 0.8-1.0 ppm corresponds to the proton of the $–CH_3$ group, the peak in the range of 1.2-1.4 ppm is characteristic of the proton of the $–CH_2–$ group, the peak at 1.6 ppm is characteristic of the proton of the β-$\mathbf{CH_2}$–(C=O)O– group and the peak at 2.3 ppm is characteristic of the proton of the α-$\mathbf{CH_2}$–(C=O)O– group. All these peaks are present in both ^{1}H-NMR spectra of RSO and HRSO and did not changed during the epoxidation and hydroxylation process. These signals can be used as reference peaks to determine the conversion of double bonds during the epoxidation and hydroxylation reactions.

Reaction yields were determined by evaluating the integration values of both the appearing and disappearing signals. To illustrate this, the hydroxylation of methyl oleate is presented step by step, as shown in Fig. 3. A clear decrease in the peak area at 2.01 ppm, corresponding to the –$\mathbf{CH_2}$–CH=CH–$\mathbf{CH_2}$– protons were observed, while new signals were arising at 1.50 (–$\mathbf{CH_2}$–CHOCH–$\mathbf{CH_2}$–) and 3.40 ppm (–**CH**(OH)-**CH**(OH)–). When comparing the reactivity of two acids, formic acid exhibited significantly higher double-bond conversions than acetic acid. At decent temperature, the conversions with CH_3COOH were from 66% to 69%, and could reach 86.9% only at 90 °C. In contrast, HCOOH achieved more than 90% of double-bond even at 60 °C, and with conversion increasing from 92 to 96.5% as the temperature rose from 60 °C to 80 °C. From 80 to 90 °C, the conversion changed insignificultly. Influence of reaction time was also investigated. Hydroxylation using HCOOH at 80 °C converted 68.5% and 89.9% of double-bond after 4 and 6 h of reaction, respectively. The conversion yield was further confirmed by the reduction of iodine value from 138.8 to 18.1.

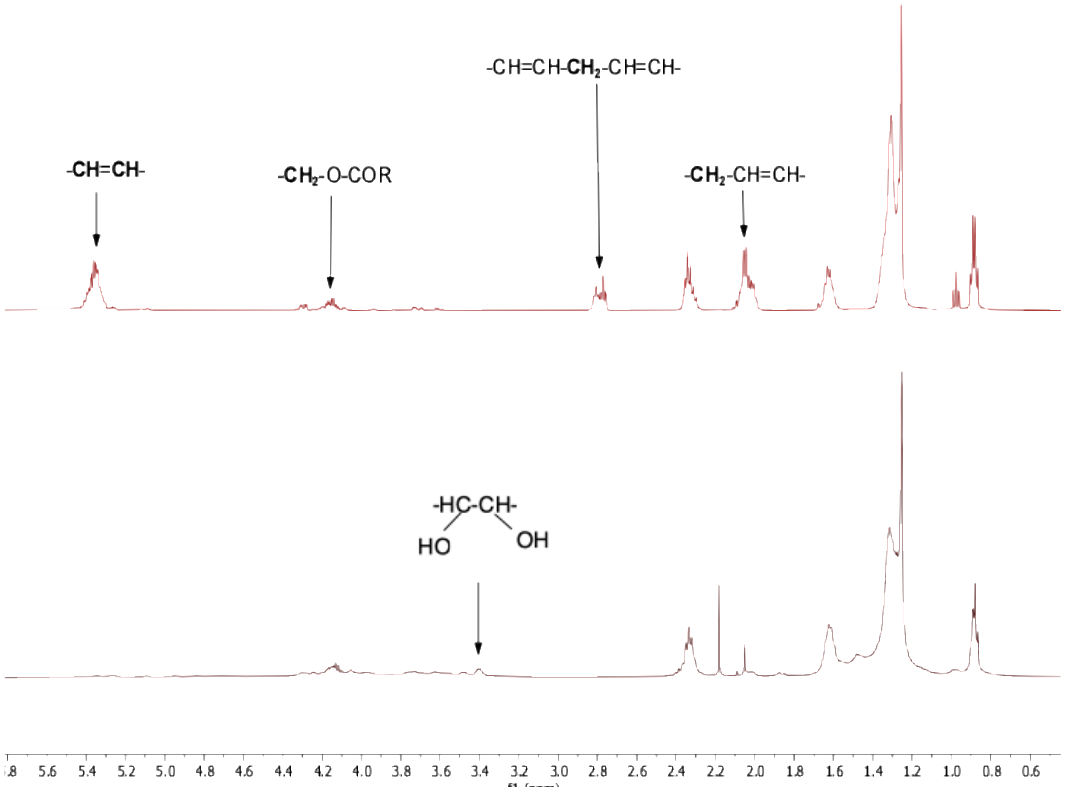

Fig. 2. ^{1}H NMR spectra of rubber seed oil RSO (above) and hydroxylated rubber seed oil HRSO (below)
Рис. 2. Спектры ^{1}H ЯМР масла семян каучукового дерева RSO (сверху) и гидроксилированного масла семян каучукового дерева HRSO (снизу)

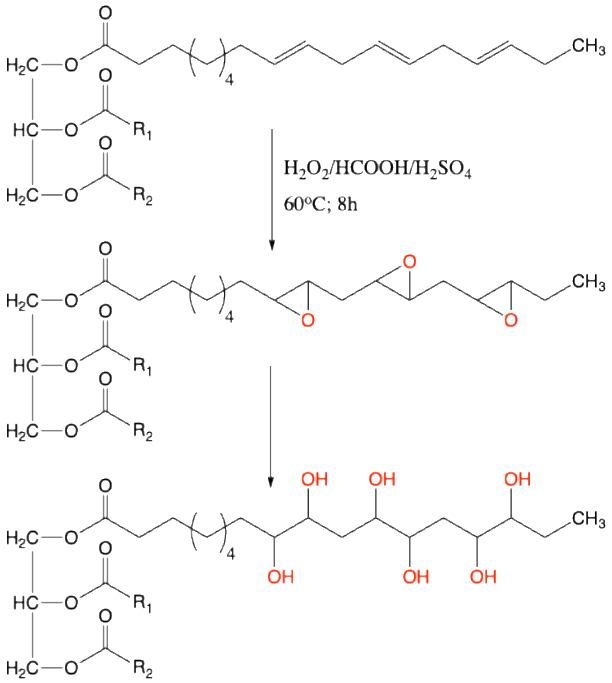

Fig. 3. Hydroxylation reaction of using H_2O_2/HCOOH/H_2SO_4
Рис. 3. Реакция гидроксилирования с использованием H_2O_2/HCOOH/H_2SO_4

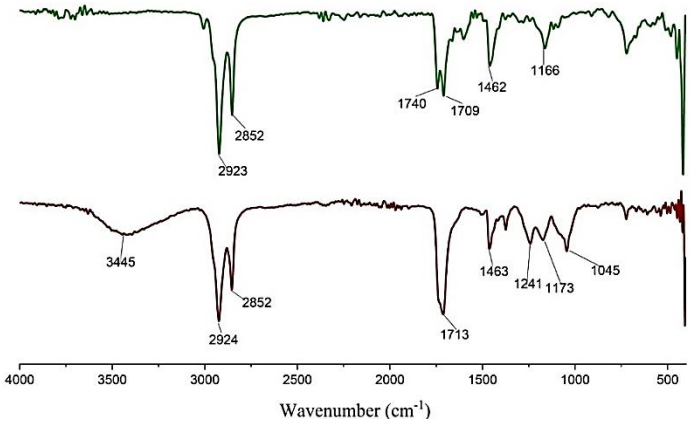

Fig. 4. FTIR spectrum of RSO (above) and HRSO (below)
Рис. 4. ИК спектр RSO (сверху) и HRSO (снизу)

Table 4

Assignement of FTIR spectrum of RSO and HRSO
***Таблица 4.* Анализ ИК спектров RSO и HRSO**

	RSO (cm^{-1})	ERSO (cm^{-1})
O-H	(-)	3445
C-H (CH_2; CH_3)	2923-2852	2924-2852
C=O (-COO-)	1740-1709	1712
C-H (stretching)	1462	1463
C-O-C	1166	1173
C-OH	(-)	1241

The hydroxylation of RSO was also confirmed by infrared spectroscopy. The FTIR spectra and their assignments for RSO and HRSO are shown in Fig. 4 and Table 4. The stretching vibrations of C-H groups was clearly observed at 292-2852 cm^{-1}, while theis bending vibrations appeared at 1462 cm^{-1} [27]. The strong absorption band at 1740-1709 cm^{-1} correspoinded to the stretching vibrations of C=O bond in ester groups, whereas C-O-C groups in glyceride gave a signal at 1166 cm^{-1}. In the spectrum of HRSO, new broad signal appeared at 3445 cm^{-1} and at 1241 cm^{-1}, which was characteristic of the O-H stretching vibration (alcohol) and C-OH group, respectively [28].

Glass transition temperature

The results for the glass transition temperatures of the PVC samples are presented in Table 5. The virgin PVC, containing Ca/Zn stearate thermal stabilizer, exhibited a glass transition temperature (T_g) of 84.78 °C. When DOP was added at 30 phr, the T_g decreased to 56.22 °C. As DOP was gradually replaced by HRSO, T_g continued to decreased and reached minimum value of 51.46 °C, about 5 °C lower than that of PVC plasticized with DOP alone, and only a single T_g was observed. This indicates that HRSO had good compatibility with both DOP and PVC. The lowest T_g was determined at PVC3' sample, 42.37 °C, when 50% of DOP was replaced by HRSO. However, when the proportion of HRSO was higher than DOP, T_g increased again and for PVC plasticized solely with HRSO, T_g reached 58.12 °C. It showed that HRSO can act as a secondary plasticizer and partially replace DOP in PVC formulation.

Table 5

Glass transition temperature of PVC samples with different plasticizer compositions

***Таблица 5.* Температура стеклования образцов ПВХ с различным составом пластификаторов**

Sample	Glass transition temperature T_g (°C)
PVC0	84.78
PVC1	56.22
PVC2	51.46
PVC3'	42.37
PVC6	58.12

Volatility and leaching tests

The migration stability is an important property of PVC plasticizer. It is defined as the amount of plasticizer migrating from polymer specimen to other media, such as liquids (leaching test) or gases (volatility test). The migration of plasticizer depends on severaon factors, including the polymer – plasticizer compatibility, the structure and polarity of the plasticizer, temperature, the surrounding environment, and other conditions. The weight loss of plasticizer during volatility testing is shown in Fig. 5.

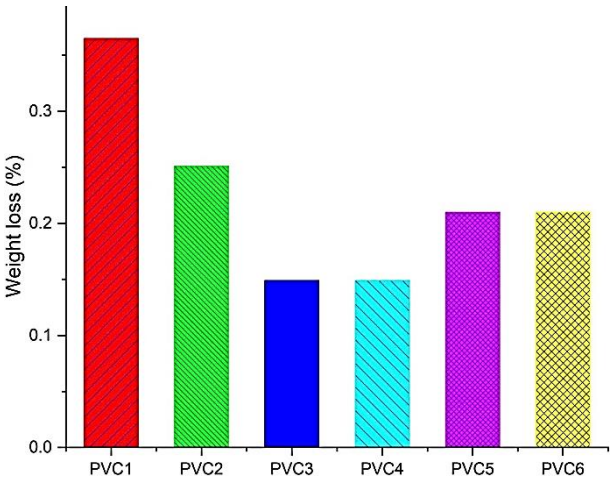

Fig. 5. Degree of volatility stability of different PVC blends

Рис. 5. Степень летучести различных смесей ПВХ

The volatile weight loss of plasticizer were determined for DOP and other compositions. Interestingly, the weight loss reduced when HRSO was used as secondary plasticizer. The lowest weight loss were found at PVC3 and PVC4 samples, where the ratio of HRSO/DOP attained 2/3 and 3/2 (w/w) respectively. After that, when the ratio of HRSO was higher, the weight loss were increased but remained inferior than of PVC plasticized solely with DOP. This could be attributed to the higher molecular wieght of HRSO which limits its volatility. It also proved the good misiblity of HRSO and DOP, HRSO-DOP-PVC resulting in reduced plasticizer migration compared with the PVC-DOP system alone.

The results of the leaching tests are presented in Figure 6. In polar solvent such as distillated water, ethanol 30% and acetic acid 30%, the extraction of plasticizer from PVC2 to PVC4 initially increased and then decreased for PVC5. In contrast, when HRSO was use alone as the primary plasticizer, the extraction in n-hexane was about three times higher than DOP alone. This indicates that HRSO, when used as secondary plasticizer together with DOP, exhibits a similar level of migration as DOP. However, without DOP, the leaching of HRSO increased significantly, which demonstrated its lower compatibility with polymer matrix.

Mechanical Properties

Mechanical properties could be used to evaluate the plasticization efficiency of polymers. In the presence of a plasticizer, the tensile strength of PVC typically decreased, whereas the strain turned higher [29]. Fig. 7 shows the summarized mechanical properties of plasticized PVC with different compositions, and Table 6 summarizes the tensile stress, elongation at

break and modulus of the PVC blends. As can be seen, the mechanical properties of PVC varied with the composition of plasticizer. When HRSO was incorporated into the plasticizer system, both tensile strength and modulus increased. The highest tensile strength (26.69 Mpa) was observed at PVC6 sample, which contained only HRSO. In contrast, elongation at break of PVC2 was 119.245%, approximately 18% lower than that of DOP, and it decreased as the HRSO ratio increased. Interestingly, from PVC3 to PVC6, the strain did not changed significantly.

It had been reported the plasticizing impact of epoxidized and hydroxylated vegetable oil to PVC mechanical properties. The polarity of C=O and C-OH bonds enhanced the miscibility of HRSO with DOP and improved its compatibility within the PVC matrix. However, the presence of unreacted double-bonds may reduced the plasticizing efficiency of HRSO compared with DOP.

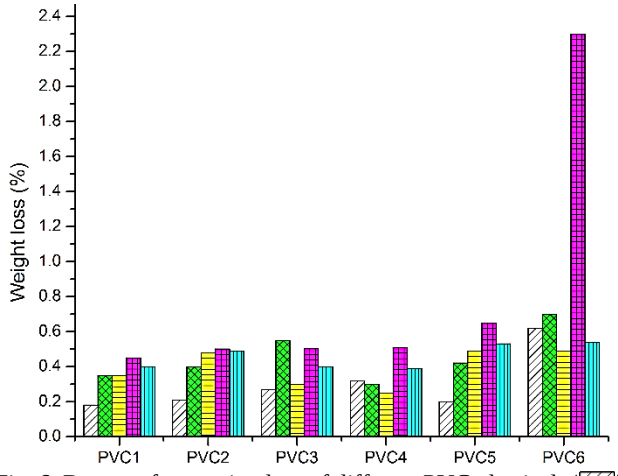

Fig. 6. Degree of extraction loss of different PVC plastisol: (▨) Water; (▩) Ethanol 30%; (▭) Acetic acid 30%; (▭) N-hexane; (▭) Cooking oil

Рис. 6. Степень потерь при экстракции различных ПВХ-пластизолей: (▨) вода; (▩) этанол 30%; (▭) уксусная кислота 30%; (▭) н-гексан; (▭) растительное масло

Table 6

Mechanical properties of different PVC blends

***Таблица 6.* Механические свойства различных смесей ПВХ**

Sample	Stress at break (Mpa)	Strain at break (%)	Modulus (Mpa)
PVC0	37.03	36.41	249.84
PVC1	15.13	145.23	18.44
PVC2	18.48	119.25	28.43
PVC3	22.35	20.43	38.83
PVC4	22.83	18.59	39.33
PVC5	25.01	21.02	41.26
PVC6	26.69	18.00	51.81

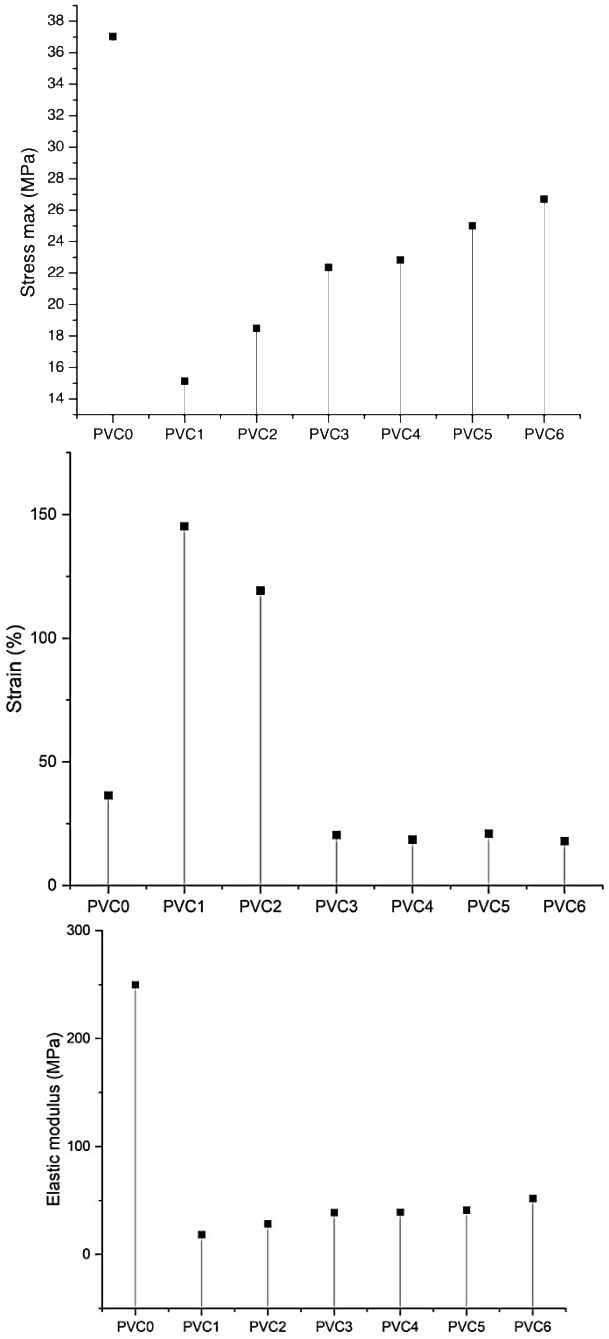

Fig. 7. Stress at breaks, Strain and modulus of different PVC formulations

Рис. 7. Напряжение при разрыве, деформация и модуль упругости различных составов ПВХ

CONCLUSIONS

In this work, rubber seed oil (RSO) was succesfully hydroxylated with using peracid such as peracetic and performic acid. Performic acid exhibited better reactivity in hydroxylation reaction, resulting in a more efficient conversion of double bonds into hydroxyl groups. The glass transition temperature indicated good miscibility of HRSO with DOP and PVC, with the 50/50

(w/w) DOP/HRSO ratio exhibited lowest T_g. Interestingly, the presence of HRSO reduced the volatility and migration of plasticizer. Mechanical tests revealed that the plasticizing efficiency of HRSO was still slightly lower than that of DOP, perhap due to the unreact double bonds. This study demonstrated the potential of HRSO as secondary plasticizer for PVC.

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