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Preparation and Characterization of Poly(Methyl Methacrylate) Grafted Natural Rubber Latex Films

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ABSTRACT

Poly(methyl methacrylate) (PMMA) grafted natural rubber (NR) latex was successfully prepared and solely exploited even at high MMA concentration (1.5 mol/kg-rubber) to make coherent and uniform vulcanized films without blending with other polymer to achieve excellent physical properties. High ammonia natural rubber (HANR) latex was subjected to graft-copolymerization with methyl methacrylate (MMA) monomer in the presence of tert-butyl hydroperoxide (TBHP) and tetraethylenepentamine (TEPA). High conversion, i.e., 85.12 mol%, and grafting efficiency, *i.e.,* 92.70 mol%, were obtained at 1.5 mol/kg-rubber MMA. The resulting gross PMMA grafted NR (1.5PMMA) latex was then compounded, dipped, and vulcanized to produce thin films. The tensile strength and modulus at 300 percent (M300) of vulcanized 1.5PMMA film were superior to vulcanized HANR film by 1-fold. While elongation at break (EB) was identical to each other due to the high gel content in both vulcanized films. Besides, the vulcanized 1.5PMMA film absorbed less oil compared to HANR film. The thermal stability of vulcanized 1.5PMMA film was found to be higher than that of vulcanized HANR film. Hence, it can be deduced that controlling the graft-copolymerization of PMMA in NR latex is the key to produce coherent thin films with improved properties at higher PMMA content.

1. Introduction

Researchers have begun exploring the graft copolymerization technique as a means to improve the properties of NR latex since the 1950s [1,2]. Various methods such as emulsion grafting [3,4], radiation grafting [1,5], and chemical grafting [6,7] are applied to graft various monomers onto NR latex particles. In recent years, there has been an increasing trend in the production and use of grafted NR latex. This trend is largely driven by the growing demand for sustainable and eco-friendly materials, as well as the desire to upgrade the material performance. Although NR latex has always been a superior material for some applications such as dipped products, tires, and many others due to its greater performance in tear resistance, outstanding flexibility, and excellent biodegradability. However, NR also exhibits certain drawbacks such as low heat and abrasion resistance, poor aging

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properties, low oil resistance, and poor flame resistance. Hence grafting may impart the good attributes of other materials to compensate for the drawbacks of NR.

Poly(methyl methacrylate) (PMMA), a thermoplastic polymer with widespread application, is often used as a substitute for glass in products such as shatterproof windows. The polymer is noted for its rigid and hard characteristics that give it great transparency, strong impact resistance, and exceptional weather resistance [8]. Thus, grafting MMA monomer onto NR latex may offer products with improved and enhanced characteristics. In the past, PMMA grafted NR latex was prepared, blended with NR latex, or coated on the NR particles [4,9]. At certain ratios of blending, the resulting properties of the latex were found to improve physical strength [5,9], such as the tensile strength and modulus of the film and rubber. Additionally, the heat stability [10,11], oil resistance [12], roughness [13], and friction coefficient [4] were further improved in the presence of PMMA.

However, studies reported [3,4,11,14] that the grafted NR latex that contained more than 10 wt% of PMMA content was unsuccessful in forming good thin film formation, i.e., cracking issues, and faced difficulty in processing, either when it was solely used as a starting material or blended. Furthermore, the procedure involves grafting, followed by blending, which would incur costs, inefficient time, and energy consumption during the processing. On the other hand, there were also very limited works on vulcanized thin film preparation, and their properties from PMMA grafted latex alone have been documented previously, which motivates the research as discussed in this current work.

Hence, this work attempts to prepare a suitable PMMA grafted NR latex that could be used to produce a thin vulcanized film without blending with other latexes and, subsequently, characterize the properties of the resulting film. The tensile, gel content, and oil absorption percentage measurements were carried out for those films. While the thermal stability of the films using a thermogravimetric analyzer (TGA) was also studied.

It is hoped that with the growing emphasis on sustainability in various industries, the utilization of renewable resources such as NR could further add to the appeal of the derivative material produced, aligning with the industrial direction.

2. Methodology

2.1 Materials

High ammonia natural rubber (HANR) latex preserved with 0.7 wt. % ammonia was purchased from Getahindus (M) Sdn Bhd. The chemicals used for graft-copolymerization such as methyl methacrylate (MMA) monomer, tert-butyl hydroperoxide (TBHP), and tetraethylenepentamine (TEPA) were purchased from Merck (Germany). While for compounding and dipping such as calcium nitrate (CN), potassium hydroxide (KOH), and calcium carbonate (CC), were bought from Systerm Sdn Bhd (Malaysia). The dispersions of accelerator, activator and crosslinker were bought from Excelcos Sdn Bhs (Malaysia). The solvents such as toluene, chloroform, tetrahydrofuran (THF), and acetone used in this work were purchased from Sigma Aldrich. All chemicals used in this work were without further purification.

2.2 Graft-Copolymerization of Methyl Methacrylate onto NR Latex

The HANR with total solid content (TSC) of about 60 wt% was adjusted to 30 w/w% before graft-copolymerization using distilled water. Then, the diluted HANR latex was charged with N_2 gas for 15 minutes at room temperature and copolymerized with MMA in the presence of a redox initiator system comprising TBHP and TEPA. The reaction was performed for 3 hours at a temperature of 50

°C under a nitrogen (N_2) atmosphere [15]. Conditions for graft-copolymerization are shown in Table 1. The monomer content, conversion and grafting efficiency were calculated gravimetrically based on the Eq. (1)-(3).

Table 1
Conditions for graft-copolymerization

MMA monomer (mol/kg-rubber)	0.75, 1.0, 1.5, 2.0
Initiator concentration (mol/kg-rubber)	$3.3\text{x}10^{-2}$
Reaction period, hr	3
Reaction temperature, °C	50

$$\text{Monomer content (mol\%)} = \frac{(\text{Mole of MMA unit in gross polymer})}{(\text{Mole of cis} - 1{,}4 - \text{isoprene unit}) + (\text{Mole of MMA unit})} \times 100 \qquad (1)$$

$$\text{Conversion (mol\%)} = \frac{(\text{Mole of MMA unit in gross polymer})}{(\text{Mole of MMA feed})} \times 100 \qquad (2)$$

$$\text{Grafting efficiency (mol\%)} = \frac{\text{Mole of MMA unit linked to cis} - 1{,}4 - \text{polyisoprene}}{\text{Mole of MMA unit produced during graft} - \text{copolymerization}} \times 100 \qquad (3)$$

2.3 Particle Size Analysis

The size of particles and their distributions were determined using a Horiba Partica LA-960 Laser Scattering Particle Size Distribution Analyser. 2 drops of latex were diluted with 20 mL of distilled water and pipetted into the instrument's built-in water bath. The particle size distributions were then calculated when the laser transmitted between 80 to 90%.

2.4 Compounding Formulations and Dipping Procedures

Table 2 shows the compounding formulation to prepare vulcanized films. Firstly, KOH and K Laurate were added into HANR and PMMA grafted NR latexes, respectively before adding the vulcanizing chemicals. The latex mixtures were then stirred for 30 minutes at room temperature. After that, the latexes were kept at room temperature for 24 and 48 hours for maturation before underwent the dipping procedure. The size of the produced dipped film is 5 cm x 12 cm with thickness ranging from 0.11 to 0.13 mm. The experimental design is summarized in Table 3.

Table 2
Formulation of vulcanized films prepared from HANR and PMMA grafted NR latexes

Ingredients	Formulation 1 (phr)
Latex	100
Accelerator	1.2
Activator	1.0
Crosslinker	1.25

Table 3
Experimental design for HANR and PMMA grafted NR latexes dipping process maturated at 24 and 48 hours, respectively

	MMA concentrations (mol/kg-rubber)
HANR	0
0.75PMMA	0.75
1.0PMMA	1.0
1.5PMMA	1.5
2.0PMMA	2.0

Prior to the dipping procedure, the total solid content (TSC) of the compounded latex was first adjusted to 30 percent. The coagulant dipped films were prepared following an in-house dipping procedure. The ceramic plate was pre-heated at 70 ^{o}C and dwelled in a coagulant bath containing 20% calcium nitrate solution before dipping in the compounded latex for 30 seconds. The wet-gelled films were then leached in a hot water bath at 70 ± 2ºC for 2 minutes before the post vulcanization was carried out at 100 ± 2ºC for 30 minutes. The dried vulcanized films then once again leached in a hot water bath at 70 ± 2ºC for 2 minutes and air-dried before stripping off the ceramic plate former. Finally, the characterizations were carried out for the properties of the resulting vulcanized films.

2.5 Tensile Strength (TS), Elongation at Break (EB) and Modulus at 300 Percent (M300)

The vulcanized dipped films were measured for tensile strength, elongation at break, and modulus at 300 percent using an Instron Tensile Machine 5565 (INSTRON) with a 500 mm/min crosshead speed according to the ISO 37 test method [16]. The test was performed with five replicates at room temperature.

2.6 Gel Content

A film weighed of 0.1 gram was dissolved in 100 ml of toluene and was kept in the dark for a week. Then, the rubber solution was then filtered, and gel fraction was recovered and dried in the vacuum oven at 50 ^{o}C for 2 days. The gel content was calculated using the weights of dried gel fraction and initial rubber according to Eq. (4):

$$\mathrm{Gel\ content, wt\%} = \frac{\mathrm{Weight\ of\ dried\ gel,\ g}}{\mathrm{Weight\ of\ rubber, g}}\ \mathrm{x}\ 100 \tag{4}$$

2.7 Oil Absorption Percentage

The film, with a thickness of ± 0.01 mm, was cut into a circular shape with a diameter of 23 mm. The weights of the rubbers before and after immersing them in cooking oil were taken. Before taking the weight, the surface of the oil-swelled rubber was patted with filter paper to remove excess oil. The weight was taken after 1, 2, 3, and 24 hours of oil immersion. The oil uptake was calculated based on Eq. (5) below:

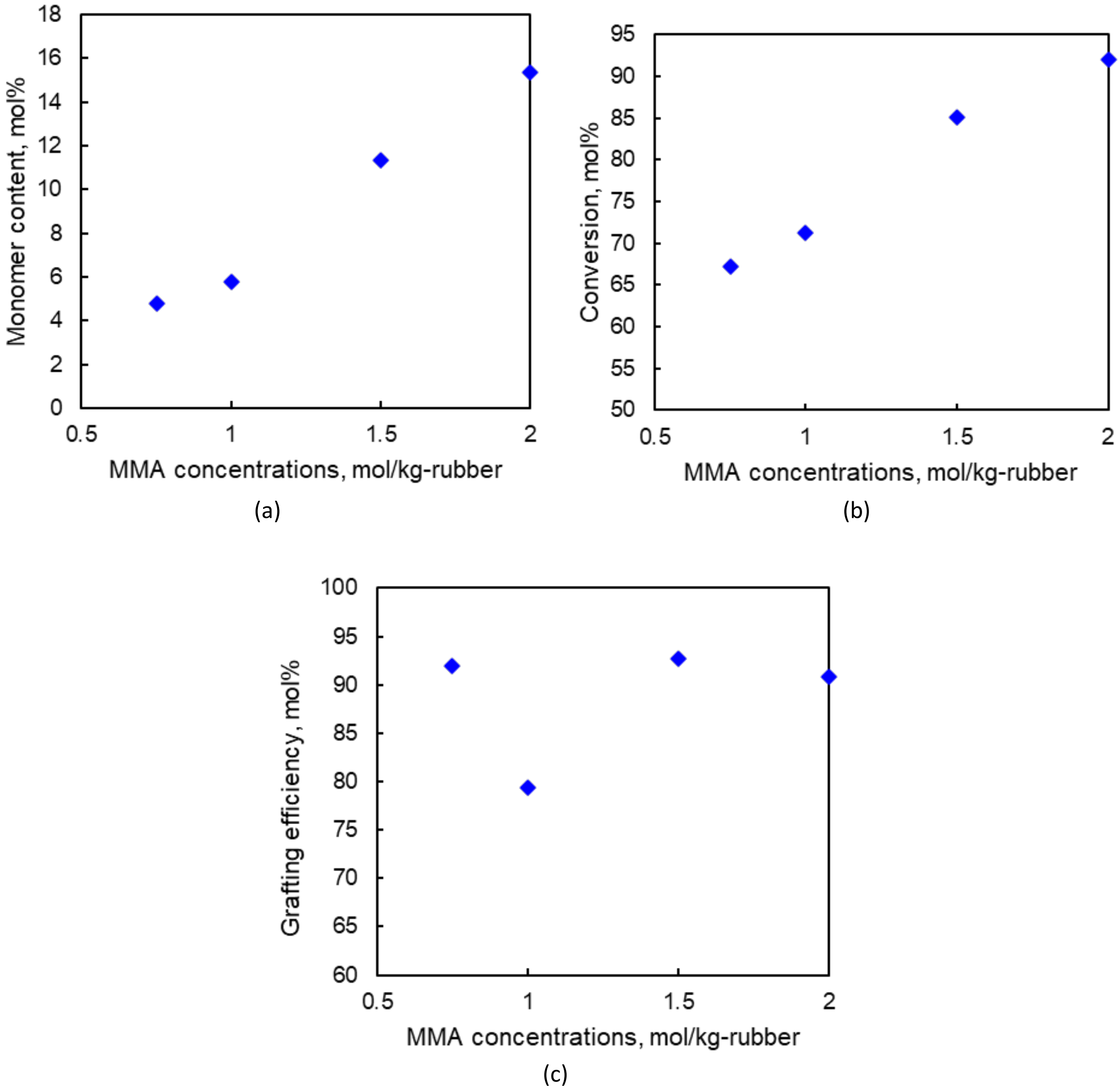
$$Oil\ uptake\ percentage, wt\% = \frac{Weight\ of\ oil\ swollen\ rubber, g}{Weight\ of\ initial\ rubber, g}\ x\ 100 \tag{5}$$

2.8 Thermal Gravimetric Analysis (TGA)

The ceramic pan was filled with 20 mg of rubber before being positioned on the thermo-balance. Then, it was heated and decomposed at a high temperature ranged from 30 to 800 °C at a heating rate of 20 °C/min under nitrogen gas flow, using TGA (Perkin Elmer TGA-STA 6000). The weight changes as a function of temperature were measured and recorded as a thermogram.

3. Results

Figure 1 shows the monomer content, conversion, and grafting efficiency of PMMA grafted NR with MMA concentrations ranging from 0.75 to 2.0 mol/kg-rubber. In Figure 1(a), the monomer content increased monotonically with the MMA concentrations. The higher the MMA concentration, the higher the monomer content. This is expected since a higher amount of reacted MMA are formed when high MMA concentration is added during graft-copolymerization.



(a) (b)

(c)

Fig. 1. Monomer content (a), conversion (b) and grafting efficiency (c) of PMMA grafted NR latexes with MMA concentrations ranged from 0.75 to 2.0 mol/kg-rubber

The conversion of PMMA grafted NRs is then calculated and shown in Figure 1(b). The conversion for all the MMA concentrations was more than 50 mol%, while the highest was determined to be 91.96 mol% at 2.0 mol/kg-rubber MMA concentrations. The tendency was identical to monomer content, whereby the conversion was dependent on MMA concentrations. Higher reacted MMA may eventually convert to more MMA polymer, i.e., PMMA lead to the increase of conversion.

In the case of grafting efficiency of PMMA grafted NRs, Figure 1(c), the highest value was determined to be 92.7 mol% at 1.5 mol/kg-rubber, while the lowest was 79.32 mol% at 1.0 mol/kg-rubber. For 1.5 mol/kg-rubber MMA concentration, the highest grafting efficiency obtained from high conversion, i.e., 85.12 mol%, which imply that most of the PMMA formed during graft-copolymerization may possibly be converted to the grafted polymer. However, for 1.0 mol/kg-rubber MMA concentrations, the lowest grafting efficiency obtained from moderate conversion, i.e., 71.20 mol%, may possibly be due to the formation of more homopolymer compared to grafted polymer.

Figure 2 shows the particle size distributions of HANR, 0.75PMMA, 1.0PMMA, 1.5PMMA, and 2.0PMMA latexes. HANR latex as a control showed a bimodal distribution which is composed of two peak modes, i.e., 0.34 mm and 0.79 mm. This is consistent with the previous finding [17] where NR latex has a wide range of particle sizes due to its naturally occurring polymer.

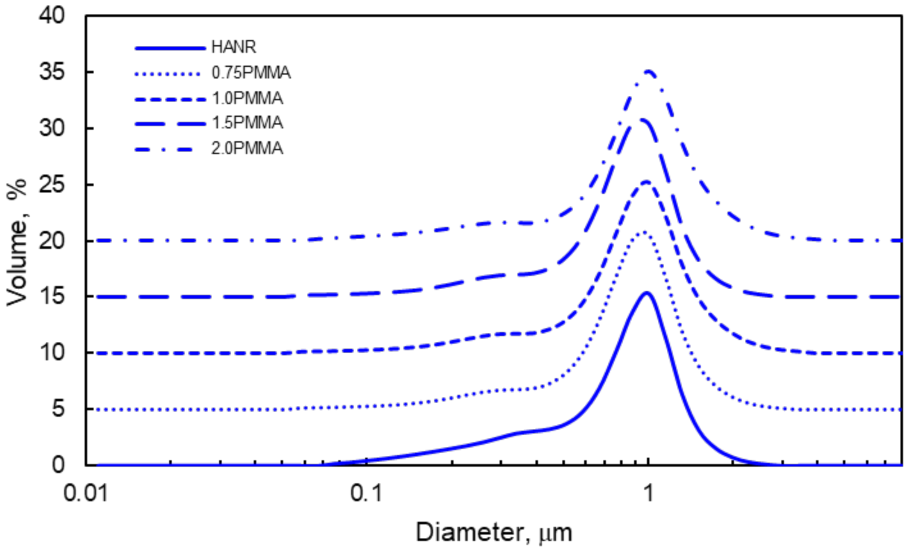


Fig. 2. Particle size distributions of HANR, and PMMA grafted NRs; 0.75PMMA, 1.0PMMA, 1.5PMMA and 2.0PMMA latexes

For PMMA grafted NR latexes, the distributions were broader as the MMA concentrations increased. According to Table 4, the median particle size increased with the increase of MMA concentrations, which were from 0.79, 0.82, 0.85, 0.86, and 0.88 mm in order of HANR, 0.75PMMA, 1.0PMMA, 1.5PMMA, and 2.0PMMA latexes. This finding supported the increment of monomer content and conversion with MMA concentrations, as shown in Figure 1. During graft-copolymerization, the grafted PMMA are attached to rubber particles and homopolymers are also formed. These occurrences could shift the particle size towards the larger region due to the increase in hydrodynamic size of grafted particles and homopolymer particles in the latex system.

Table 4
Median of particle size for HANR, and PMMA grafted NRs

	HANR	0.75PMMA	1.0PMMA	1.5PMMA	2.0PMMA
Median (mm)	0.79	0.82	0.85	0.86	0.88

Here, 1.5PMMA latex were chosen to prepare vulcanized film due to its highest grafting efficiency. The properties of the vulcanized 1.5PMMA film were then compared with vulcanized HANR film (control). Figure 3 shows the tensile strengths of vulcanized HANR and vulcanized 1.5PMMA films that underwent 24 and 48 hours of maturation, respectively. The aged HANR films were relatively higher than the unaged films. While the tensile strength for unaged HANR 48H film i.e., 8.59 MPa, was slightly increased by 2 MPa, compared to unaged HANR 24H film, i.e., 6.76 MPa. However, both aged HANR films showed identical strengths despite their maturation hours.

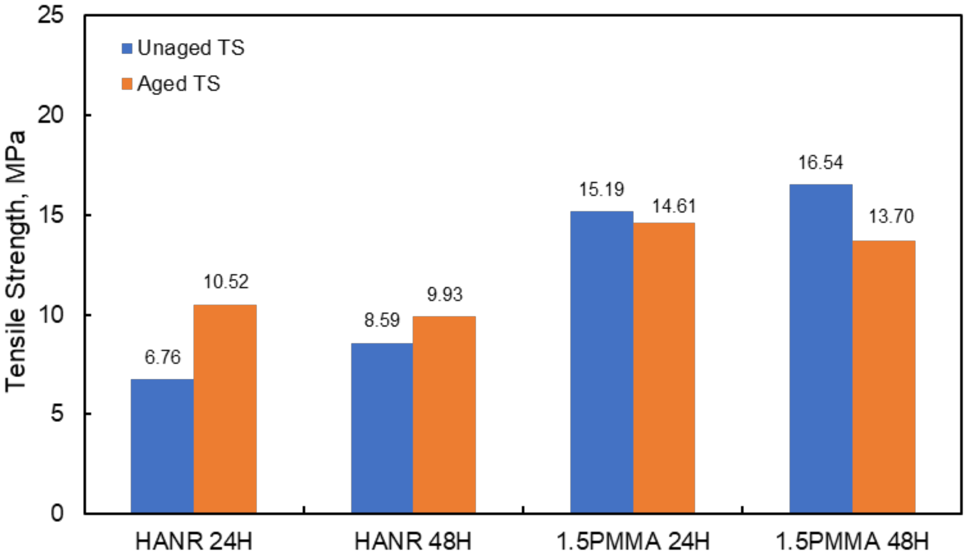


Fig. 3. Tensile strength of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H and 1.5PMMA 48H films

In the case of 1.5PMMA films, the tensile strength was substantially higher than HANR films. For instance, the tensile strength of unaged 1.5PMMA films, i.e. 15 – 16 MPa showed an increase of 1-fold compared to unaged HANR films, i.e., 6 – 9 MPa. This may be due to the presence of PMMA in the NR, which enhanced the strength of the film. On the other hand, the tensile strength of PMMA films showed a slight decrease after ageing. This suggests that the presence of heat (ageing) allows further vulcanization to occur and the existence of hard segments of PMMA, resulting in rigid films.

Based on the previous research [3,11,14], using MMA concentrations greater than 10 wt% (equivalents to 1.0 mol/kg-rubber) would have an incoherent film, whereby a crack was formed. Due to this reason, the grafted latex was blended with HANR latex to form non-crack vulcanized films. Surprisingly, such findings contradicted with the current findings, in which MMA concentrations of more than 10 wt% (at 1.5 mol/kg-rubber) were used and the grafted latex was solely used to make vulcanized films. The resulting films were found to be coherent, smooth and uniform, as shown in Figure 4.

Fig. 4. Coherent, smooth and uniform surface of vulcanized PMMA graft NR film

The elongation at breaks (EB) of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films are shown in Figure 5. The EB for aged films was found to be relatively higher than for unaged films, indicating that aged films were tougher than unaged films.

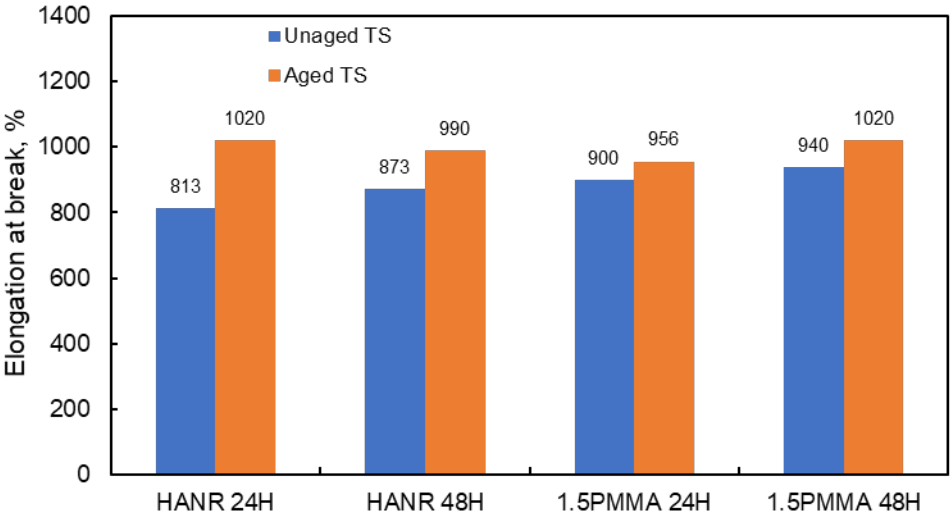


Fig. 5. Elongation at breaks of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H and 1.5PMMA 48H films

Interestingly, the EB for HANR films was about similar to 1.5PMMA films regardless of the conditions, i.e., aged, unaged, and maturation hours. The EB may be influenced by the crosslink points or 3-D networks formed in the films. Thus, to confirm the postulation, the gel content of the vulcanized films was determined. Table 5 shows the gel content of vulcanized HANR and 1.5PMMA films. The gel content for both films was high, which was above 80 wt%. This implies that high gel content may reflect the high entanglements and crosslink points that surge the toughness of the film.

Table 5
Gel content of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films

	Gel content, wt%
HANR 24H	87.07
HANR 48H	88.14
1.5PMMA 24H	80.88
1.5PMMA 48H	80.92

Figure 6 exhibits the M300 of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films. M300 measures the stress at 300 percent of film strain. According to the previous work [18,19], M300 indicates the occurrence of crystallization upon straining. From the graph, the M300 of 1.5PMMA films was abruptly higher than HANR films by 40–70 percent. This can be said that the presence of PMMA promotes strain-induced crystallization and simultaneously enhances the strength of the film.

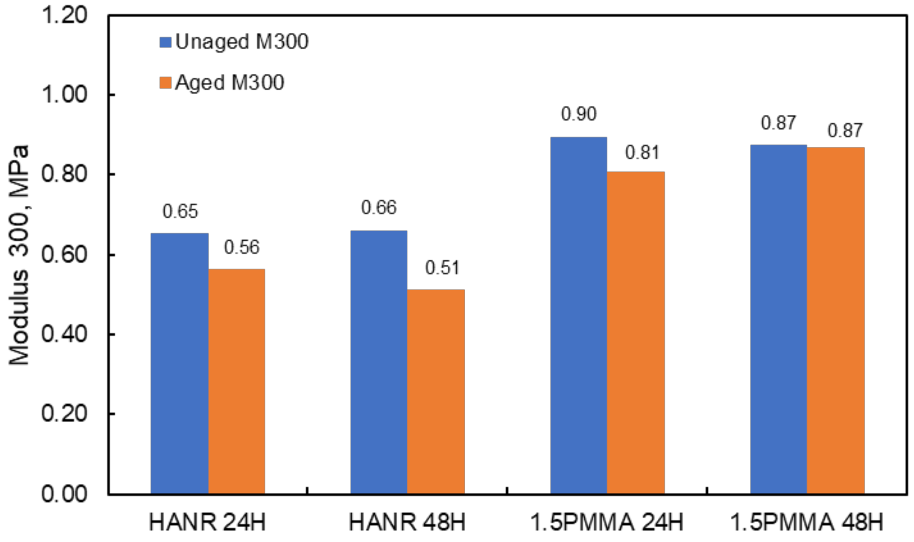


Fig. 6. Modulus 300 (M300) of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H and 1.5PMMA 48H films

The oil absorption percentages for vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films are shown in Figure 7. The oil absorption percentages for HANR 24H and HANR 48H increased as the immersion period increased. The longer the immersion period, the higher the amount of oil absorbed into the films. In contrast, the 1.5PMMA 24H and 1.5PMMA 48H showed different tendencies, where the oil absorption percentages were almost constant with the immersion period, up to 24 hours. Hence, it can be deduced that the 1.5PMMA films showed better oil resistance compared to the HANR films.

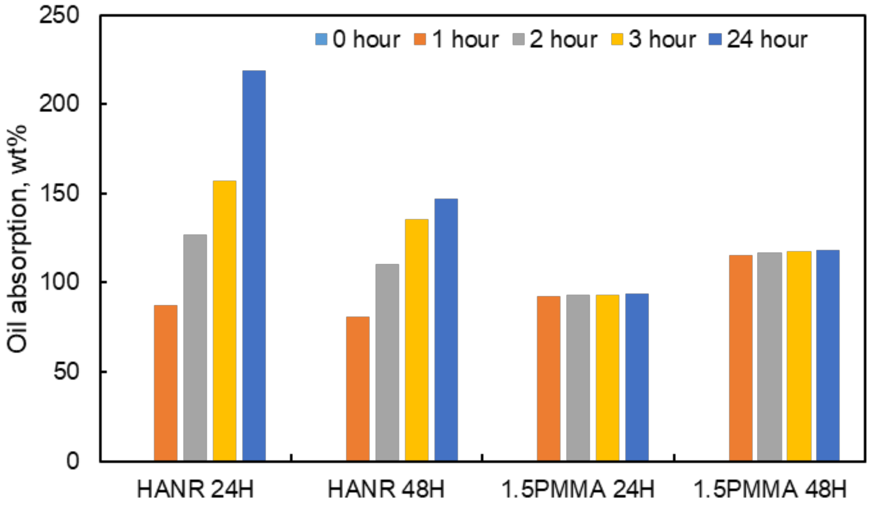


Fig. 7. Oil absorption percentage for vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films

Figure 8 illustrates the TG curves for vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films. The TG curves showed a single-step decomposition for HANR 24H and HANR 48H, which was consistent with the previous finding [20], while two-step decomposition was observed for 1.5PMMA 24H and 1.5PMMA 48H. This may be explained to be due to the degradation of two different types of polymers that formed after graft-copolymerization, which were PMMA homopolymer and PMMA grafted NR.

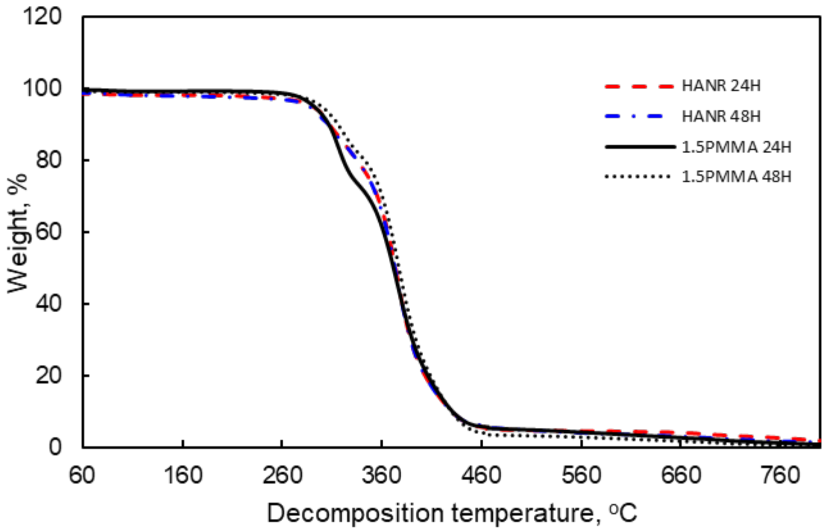


Fig. 8. Thermal gravimetric (TG) curves for vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H and 1.5PMMA 48H films

Table 6 shows the onset and maximum decomposition temperatures of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H, and 1.5PMMA 48H films. The onset decomposition temperatures for HANR films, i.e., 339–341 °C were higher than those for 1.5 PMMA films, i.e., 293 and 301 °C, respectively. A lower molecular weight of PMMA homopolymer may decompose earlier compared to high molecular weight PMMA grafted NR, resulting in a lower onset decomposition temperature in 1.5 PMMA films which were 316 and 320 °C, respectively. In the case of maximum decomposition temperature, HANR films, i.e., 374 and 376 °C showed lower temperatures compared to 1.5PMMA films, i.e., 376 and 378 °C. It is assumed that the hard segment of grafted PMMA may inhibit the motion of NR chains during heating. While the maximum decomposition temperature for 48 hours of maturation showed higher than for 24 hours of maturation which reflected the hindrance of early decomposition due to higher crosslinking points at longer maturation hours.

Table 6
The onset and maximum decomposition temperatures of vulcanized HANR 24H, HANR 48H, 1.5PMMA 24H and 1.5PMMA 48H films

	Onset Decomposition Temperature (°C)	Maximum Decomposition Temperature (°C)
HANR 24H	339	374
HANR 48H	341	376
1.5PMMA 24H	293	316
	360	376
1.5PMMA 48H	301	320
	359	378

4. Conclusions

PMMA grafted NR latex was successfully prepared by graft-copolymerization of MMA monomer onto NR latex. The highest conversion and grafting efficiency were obtained at 1.5 mol/kg-rubber MMA concentration (1.5 PMMA). Without blending with NR or other polymers, the grafted latex was then compounded, dipped, and vulcanized. The films produced were coherent and uniform; no crack was observed even at higher PMMA content (> 1.0 mol/kg-rubber), which contradicted the previous findings. Due to good film formation, the characterizations of these films were effectively carried out. The overall properties showed the vulcanized 1.5PMMA film was excellent compared with the vulcanized HANR film, suggesting the PMMA in the NR, either grafted or homopolymerized, governed the resulting properties of the film. On the other hand, graft-copolymerization of MMA in NR latex should be controlled to obtain a high PMMA content without sacrificing the film formation and properties of the resulting vulcanized films. Moreover, using solely PMMA grafted latex could reduce time, cost, and energy consumption.

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