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Surface modification of natural rubber film by polymerisation of methyl methacrylate in water-based system

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Abstract

Polymerisation of methyl methacrylate (MMA) on the surface of natural rubber (NR) film was studied in order to increase the surface hardness, roughness and, hence, to decrease the friction coefficient of rubber. We used the two-step process: (i) swelling of MMA and *tert*-butyl hydroperoxide, emulsified in an aqueous solution of sodium dodecyl sulphate, onto the NR film surface, and (ii) subsequently immersing the swollen rubber strip into an alkaline aqueous solution of ferrous ion/fructose for redox initiation. The presence of PMMA on the NR surface was examined by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). Increasing the concentration of ferrous ion caused an increase in MMA conversion. The surface morphology observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) in tapping mode revealed the aggregation of micronmetre-scale nodules on the modified surface. The surface hardness and roughness increased with increasing PMMA content.

Keywords: Surface modification; Natural rubber; Poly(methyl methacrylate); Redox initiation

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1. Introduction

Natural rubber (NR) latex has been widely used to produce the glove with regard to its excellent physical properties, comfort and feel. Unfortunately, the soft and tacky NR film results in surface friction and bunching of the glove. Therefore, it is necessary to modify glove's surface to reduce friction or tack while maintaining the characteristics of the bulk properties. Talc or other fine powdered materials such as starch is traditionally applied. However, talc can no longer be used, and starch is considered a contamination in electronic and biomedical applications. Therefore, powder-free glove treated with the halogenation process is introduced. However, high level of chlorination can cause the deterioration in its physical properties, i.e., the halogenated surface film becomes darkened, hard and brittle [1]. It has been of great interest to study the grafting, e.g., UV-induced graft copolymerisation of the plasma-pretreated NR film [2,3], plasma polymerisation and photografting of vulcanised NR film [4], and gamma radiation-induced simultaneous grafting on NR tube [5].

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An alternative technique that involves the surface swelling of monomers followed by polymerisation was applied for surface modification of elastomers. Acrylate monomer was polymerised under visible light on the surface of segmented polyurethane (SPU) after immersing the SPU film into the mixture of acrylate and photoinitiator [6,7]. It should be noticed that the processes successfully used for surface modification were solvent-based treatments. For safety and environmental reasons, the water-based system is a better method of choice. A two-step process, using an aqueous emulsion of acrylate monomer containing peroxide initiator, was designed to form interpenetrating polymer networks (IPNs) structure on the surface of vulcanised ethylene–propylene-diene terpolymer (EPDM) sheet [8]. Moreover, swelling in aqueous monomer dispersion has the advantage of a better control of the swelling kinetics. The excess of emulsion on the rubber can also be easily eliminated by simple rinsing with water which also makes the re-use of monomer possible.

In the present work, poly(methyl methacrylate) (PMMA), a hard and transparent thermoplastic, was formed on the surface of NR sheet. The aim was to increase the surface rigidity or hardness and roughness of NR, which should reduce its surface friction [9,10] in the powder-free condition. For environmental reason, the water-based system was applied, i.e., MMA swollen NR surface was obtained when dipping NR strip into an aqueous emulsion of MMA containing *tert*-butyl hydroperoxide (*t*-BuHP). The swollen NR sheet was then immersed in an aqueous solution of ferrous ion to activate a redox initiation [11,12]. The reason of initiation by using *t*-BuHP/ferrous redox system was its advantage in yielding desirable initiation rate at moderate temperature. The problem of high decomposition temperature of the thermal initiator which caused the degradation of NR was consequently avoided. In this case, the polymerisation loci were expectedly confined near the interface between the swollen NR sheet and polymerising medium where ferrous ion activated the decomposition of *t*-BuHP. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) was principally applied to characterise the modified NR surface. The surface morphology was examined under scanning electron microscopy (SEM) and atomic force microscopy (AFM) in the tapping mode [2,3,13–15]. The roughness and hardness of the rubber sheet were also determined.

2. Experimental

2.1. Surface modification of NR sheet

An aqueous emulsion was prepared by dispersing MMA (Fluka, Purum) (62.5 g), purified by passing through an aluminium oxide column, mixed with 70% *t*-BuHP (Fluka, Purum) (6.7 g) into 2% aqueous solution of sodium dodecyl sulphate (SDS, Fluka, Biochemika) (191.2 g) in a glass container while stirring at 400 rpm for 1 h. The unvulcanised rubber strip ($0.15 \times 2 \times 5\ \mathrm{cm}^3$), casted from commercial NR latex concentrate (Rayong Bangkok Rubber Co., Ltd., Thailand), was held on a poly(ethylene terephthalate) (PET) film, without using any adhesive. The sample was then immersed into the MMA emulsion at room temperature. After a given immersion time, its surface was washed with distilled water and blotted with filter paper. The MMA swollen NR was subsequently polymerised in a capped tube containing an aqueous solution (30 ml) of ammonium iron (II) sulphate hexahydrate (Riedel de Haën, Reagent grade) and D-(−)-fructose (Fluka, Biochemika) at pH 10. The sample surface was rinsed with distilled water before drying under vacuum at room temperature until it reached the constant weight, and the percent conversion of MMA was gravimetrically determined.

2.2. Surface characterisation of modified NR sheet

The surface of modified NR was characterised by using FTIR (Bruker, EQUINOX 55). ATR-FTIR spectra (32 scans with a resolution of $4\ \mathrm{cm}^{-1}$) were recorded by using a ZnSe crystal with multi-reflection mode. The change of the characteristic absorption peaks at 1730 and $1376\ \mathrm{cm}^{-1}$, corresponding to C=O stretching of PMMA and CH_3 deformation of NR, respectively, was investigated. The depth of penetration (d_p) of IR beam into the sample is given by the following equation:

$$d_{\mathrm{p}} = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}} \tag{1}$$

where λ is the wavelength of light, θ is the angle of incidence of IR beam (45°), n_1 and n_2 are the refractive indices of the crystal (2.4) and the sample (1.5), respectively.

The surface morphologies of samples, coated with a thin layer of gold, were studied under SEM (Hitachi, S-2500) operated at 15 kV. The AFM measurements, by using Multimode AFM equipped with Nanoscope IIIa controller (Digital Instrument), were conducted under ambient condition. The spring constant and resonance frequency of silicon cantilever probe (Veeco Probes, RTESP7) in AFM tapping experiments, as reported by the manufacturer, were 40 N/m and 300 kHz, respectively. The surface mean roughness (R_a) was directly calculated from Nanoscope software by using the following equation:

$$R_a = \frac{1}{n}\sum_{j=1}^{n}|Z_j| \tag{2}$$

where Z_j is the current difference between the height and the mean plane and n is the number of points in the image.

The hardness of unmodified NR and NR sheets modified by PMMA was measured by using a Shore A scale hardness tester (Wallace, H17A) according to ASTM D2240.

3. Results and discussion

3.1. Swelling of MMA into NR

The amount of MMA, consisting of *t*-BuHP, diffused from the emulsion into NR sheet was gravimetrically determined. The total weight uptake in NR sheet plotted as a function of immersion time is presented in Fig. 1.

Results showed that the weight uptake in NR sample was proportional to the immersion time. It might be due to the fact that monomer droplets came to contact with the NR surface and then diffused into the rubber. Besides the collision of MMA droplets to the rubber surface, the amount of swollen MMA into NR sheet possibly resulted from the soluble MMA in an aqueous medium (the water solubility of MMA is 1.5 wt.% at 25 °C [16]). In order to prove this hypothesis, the weight uptake of the NR sample after immersing into water, saturated with MMA, was determined at various immersion times and the data are also shown in Fig. 1. As expected, the weight of MMA swollen in the NR increased with the immersion time. However, the slope of the latter was not as steep as that of the emulsion case, i.e., the total amount of monomer diffused from the water soluble MMA into NR was three times less than that from the MMA emulsion. The small droplets in the emulsion with high surface area were responsible for the high rate of MMA transferred into the substrate. It should be remarked that the swelling of MMA into NR took place in spite of the difference in the solubility parameters (δ) (δ of MMA and NR are 16.6 and 18.0 $(\mathrm{J/cm^3})^{1/2}$, respectively [17]). It should also be emphasised that *t*-BuHP, classified as partially water-soluble peroxide, could transfer into the NR sheet together with MMA.

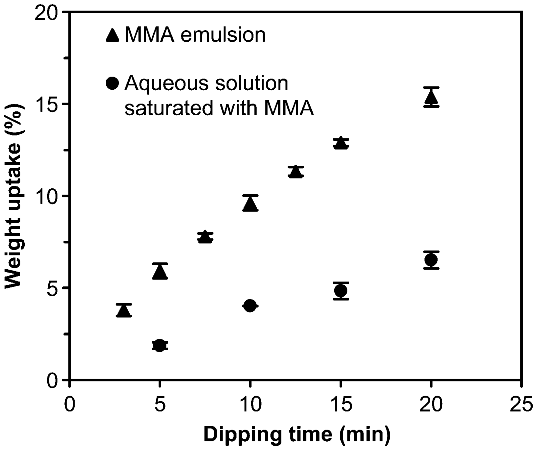


Fig. 1. Weight uptakes in NR sheet after immersing in the MMA emulsion compared with that in an aqueous solution saturated with MMA at various dipping times.

3.2. Effect of redox initiation

It is well known that the thermal initiator, e.g., an organic peroxide, generally used in the radical chain polymerisation is decomposed at high temperature. Since the half-life of *t*-BuHP at 175 °C is 4.8 h [11], with an advantage of the redox initiation, *t*-BuHP in combination with a reducing agent, i.e., ferrous ion, was applied in this present work. The proposed mechanism of the ferrous ion promotion of the decomposition of *t*-BuHP is as follows [11,12]:

$$\mathrm{Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{\cdot} + OH^{-}} \tag{3}$$

Besides ferrous ion and peroxide initiator, fructose was commonly used for a conventional emulsion polymerisation initiated by redox system [18,19]. The function of fructose was to regenerate or recycle ferrous ion by reducing the ferric ion produced in the decomposition of peroxide.

In order to study the effect of redox initiation system, the swollen NR sheet (dipping in the MMA emulsion for 20 min) was polymerised at 60 °C for 6 h in aqueous solution systems of (i) 10 ppm ferrous ion and 2% fructose at pH 10; (ii) 10 ppm

Table 1
Conversions of MMA polymerised in NR sheets when varying chemicals used in redox system (dipping in MMA emulsion for 20 min and polymerisation at 60 °C for 6 h)

Chemicals used in redox system	MMA conversion (%)
(i) 10 ppm ferrous ion, 2% fructose at pH 10	26.2 ± 2.2
(ii) 10 ppm ferrous ion, 2% fructose at pH 6	1.1 ± 0.1
(iii) 2% fructose at pH 10	12.5 ± 0.7
(iv) 10 ppm ferrous ion at pH 10	−1.7 ± 0.6

ferrous ion and 2% fructose at pH 6; (iii) 2% fructose at pH 10 and (iv) 10 ppm ferrous ion at pH 10. The MMA conversion was gravimetrically determined and the data are shown in Table 1.

It was clearly observed that the relative high percent conversion of MMA (26% with respect to swollen monomer in rubber) was obtained when the polymerisation took place in the presence of ferrous ion and fructose at pH 10 whereas at pH 6 the amount of PMMA was very low. The results agreed well with the explanation that fructose and ferrous ion could form a stable complex under the alkaline condition [20] and effectively activate the decomposition of *t*-BuHP. As previously reported, fructose acted as a powerful reducing sugar in basic medium [20,21]. Fructose could, therefore, regenerate ferrous ion from ferric ion produced in the reaction with *t*-BuHP. This resulted in the rapid initiation and, thus, the high extent of MMA polymerisation. In the absence of fructose at pH 10, the polymerisation of MMA was not observed and the precipitated iron oxide was noticed instead. Due to the oxidised ferrous ion, *t*-BuHP could not be decomposed at this condition. Moreover, the weight loss (−1.7% of MMA conversion) was detected which was possibly caused by the desorption of natural non-rubber components, e.g., water-soluble proteins and lipids [22], from the NR sheet surface. Surprisingly, it was noticed that in the system containing fructose without ferrous ion at pH 10, 12.5% conversion of MMA in NR sheet was obtained. It was believed that a trace of metal ions, e.g., iron and copper ions, typically presented in NR latex [22,23] could activate the redox initiation.

Due to the remarkable effective initiation, the system containing ferrous ion and fructose at pH 10 was subjected to further study. The effect of concentration of ferrous ion when varying fructose from 1% to 4% on the MMA conversion was then examined and results are presented in Fig. 2.

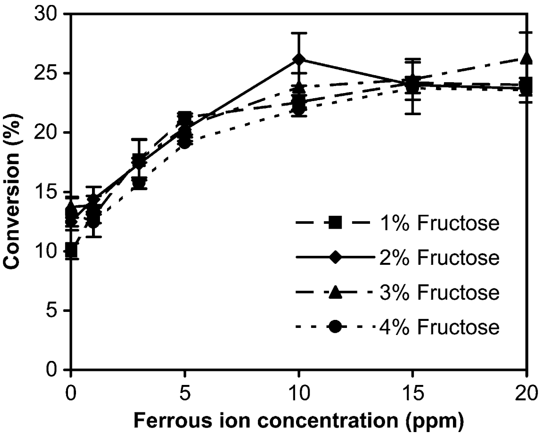


Fig. 2. Effect of concentrations of ferrous ion and fructose on the conversions of MMA polymerised in NR sheet (dipping in MMA emulsion for 20 min and polymerisation at 60 °C for 6 h).

It was observed that the percent MMA conversion increased from 10% to 26% with increasing concentration of ferrous ion up to 10 ppm. This might imply that the higher amount of ferrous ion provided more decomposition of *t*-BuHP which consequently produced more radicals and high content of PMMA. However, the conversion was nearly constant when using the ferrous ion of greater than 10 ppm. It was probably due to the constant amount of MMA (and *t*-BuHP) diffused from the inner part of the swollen NR sheet to its surface where the initiator encountered with ferrous ion. In this case, the influence of fructose concentration used on the percent conversion of MMA was not significantly noticed. It could be explained that the mole ratio of fructose to ferrous ion, aiming to avoid the precipitation of iron oxide, was very high (>155:1). The ferrous ion was, therefore, the rate-determining ingredient. From the results, it was presumed that the polymerisation of MMA could be controlled by simply adjusting the amount of ferrous ion in the redox formula. Since the alkaline aqueous solution containing 10 ppm of ferrous ion and 2% of fructose gave the relative high yield of PMMA, these conditions were selected for use in further experiments.

3.3. Effect of polymerisation temperature and time

Due to the fact that the rates of monomer diffusion and polymerisation depend on temperature, the conversions of MMA in NR sheet at different temperatures were determined and data are presented in Fig. 3.

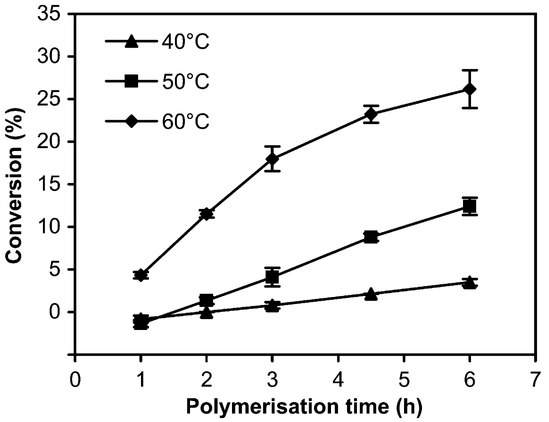


Fig. 3. Conversions of MMA polymerised in NR sheet at various polymerisation temperatures and times (dipping in MMA emulsion for 20 min).

As expected, the percent conversion at a given temperature varied with polymerisation time. When the temperature was raised from 40 to 60 °C, the MMA conversions significantly enhanced and reached the maximum value of about 26%, i.e., equivalent to the calculated amount of PMMA incorporated into NR sheet of 4%. It could be considered that besides the increase in overall rate constant with higher temperature [12], the concentration of MMA and *t*-BuHP at the polymerisation loci near the interface also augmented due to their higher diffusion rates or rapid thermal motion of molecules. For the redox-initiated polymerisation, rate of polymerisation (R_p) is generally given by the following expression [11]:

$$R_p = K[M]([\mathrm{Fe}^{2+}][t\text{-BuHP}])^{1/2} \quad (4)$$

where K is an overall rate constant, $[M]$, $[\mathrm{Fe}^{2+}]$ and $[t\text{-BuHP}]$ are the concentrations of monomer (MMA), ferrous ion and *t*-BuHP, respectively.

From Eq. (4), when increasing the polymerisation temperature, R_p substantially increased due to the increments of K, $[M]$ and $[t\text{-BuHP}]$. The incomplete MMA conversion might be due to MMA leaching out in the aqueous phase during the polymerisation process and also the slow diffusion of MMA and *t*-BuHP to the polymerisation loci. The optimal condition selected for polymerisation of MMA on the NR surface was at 60 °C for 6 h.

The presence of PMMA on the surface of modified NR sheet was then characterised by using ATR-FTIR, a technique well suited for the study of surface chemical species [1], and the spectra are shown in Fig. 4.

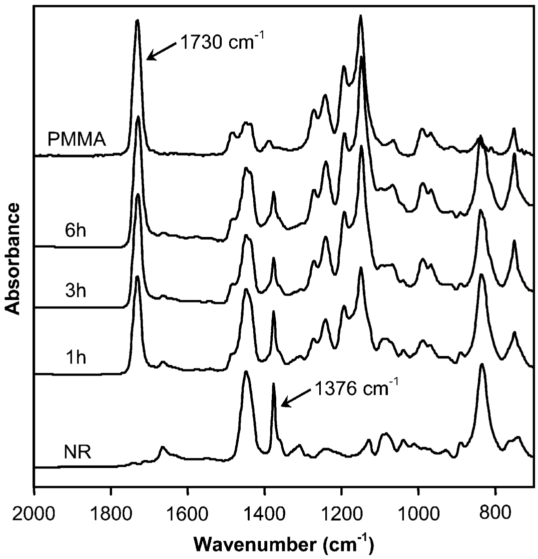


Fig. 4. ATR-FTIR spectra of unmodified and modified NR sheets at various polymerisation times, compared with that of PMMA (dipping in MMA emulsion for 20 min and polymerisation at 60 °C).

The results showed that the ATR-FTIR spectrum of the modified NR sheet was different from that of the unmodified sample. The characteristic absorption peak at 1730 cm^{-1}, corresponding to C=O stretching, was clearly observed in all NR surfaces modified with PMMA which indicated that PMMA was introduced into the sample. Their intensities increased with increase in polymerisation time, concomitantly, the intensity of absorbance peak at 1376 cm^{-1} of NR decreased. It should be considered that under redox initiation of hydroperoxide, PMMA was partially grafted on the rubber by either the transfer of active radicals of growing PMMA chains to polyisoprene or the generation of radicals on NR molecules directly by an initiator [24,25]. In order to evaluate the change in PMMA content in the samples, the ratios of the absorbance at 1730 cm^{-1} of PMMA to that at 1376 cm^{-1} of NR were calculated and plotted versus polymerisation times as shown in Fig. 5.

Results showed that the absorbance ratios of 1730 cm^{-1} to 1376 cm^{-1} of the samples rapidly increased with polymerisation time in the initial period. After 3 h, the absorbance ratios did not significantly change. This indicated that the PMMA content estimated from ATR-FTIR was not correlated well to that calculated by gravimetric method (Fig. 3), which the conversion of MMA increased from 18% to 26% for the polymerisation time of

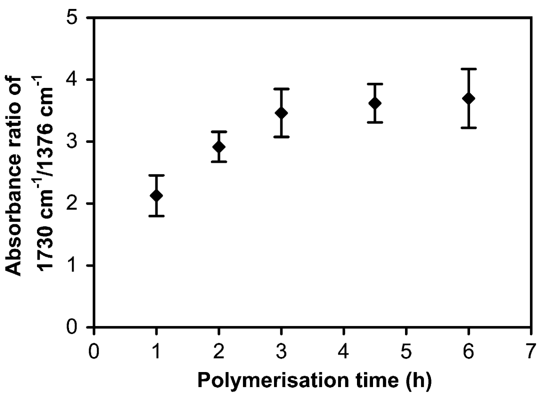
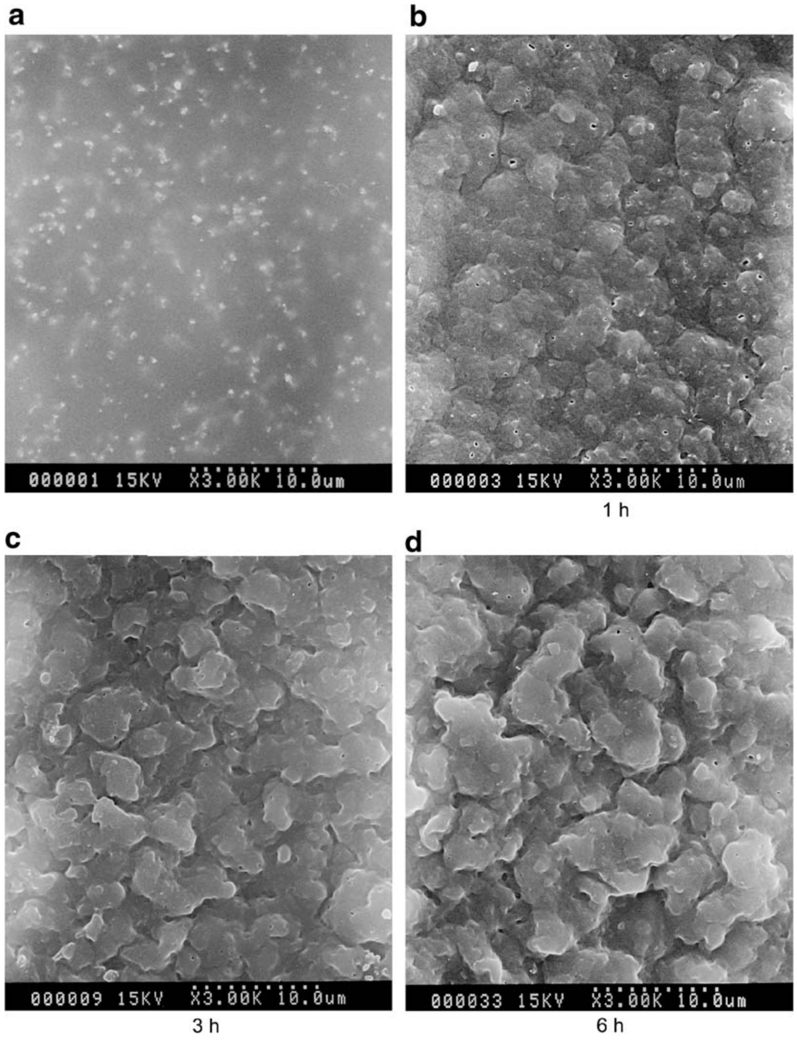


Fig. 5. Absorbance ratios of characteristic absorption peaks of PMMA to that of NR ($1730\,\mathrm{cm}^{-1}/1376\,\mathrm{cm}^{-1}$) of the modified NR surface polymerised at 60 °C for various times.

3 to 6 h. It might be due to the fact that the depth of IR beam penetrating into the sample surface was approximately 1.2 μm (calculated from Eq. (1) at wavenumber of $1730\,\mathrm{cm}^{-1}$). Thus, the presence of PMMA in the whole sample, if existed in the depth greater than 1.2 μm, could not be detected by using the ATR-FTIR.

3.4. Morphology and properties of modified NR surface

The surface morphologies of unmodified NR and NR modified by MMA polymerisation investigated by using SEM and AFM are presented in Figs. 6 and 7, respectively.



1 h

3 h

6 h

Fig. 6. SEM micrographs of (a) untreated NR sheet and (b)–(d) NR sheets modified by MMA polymerisation at 60 °C for various times.

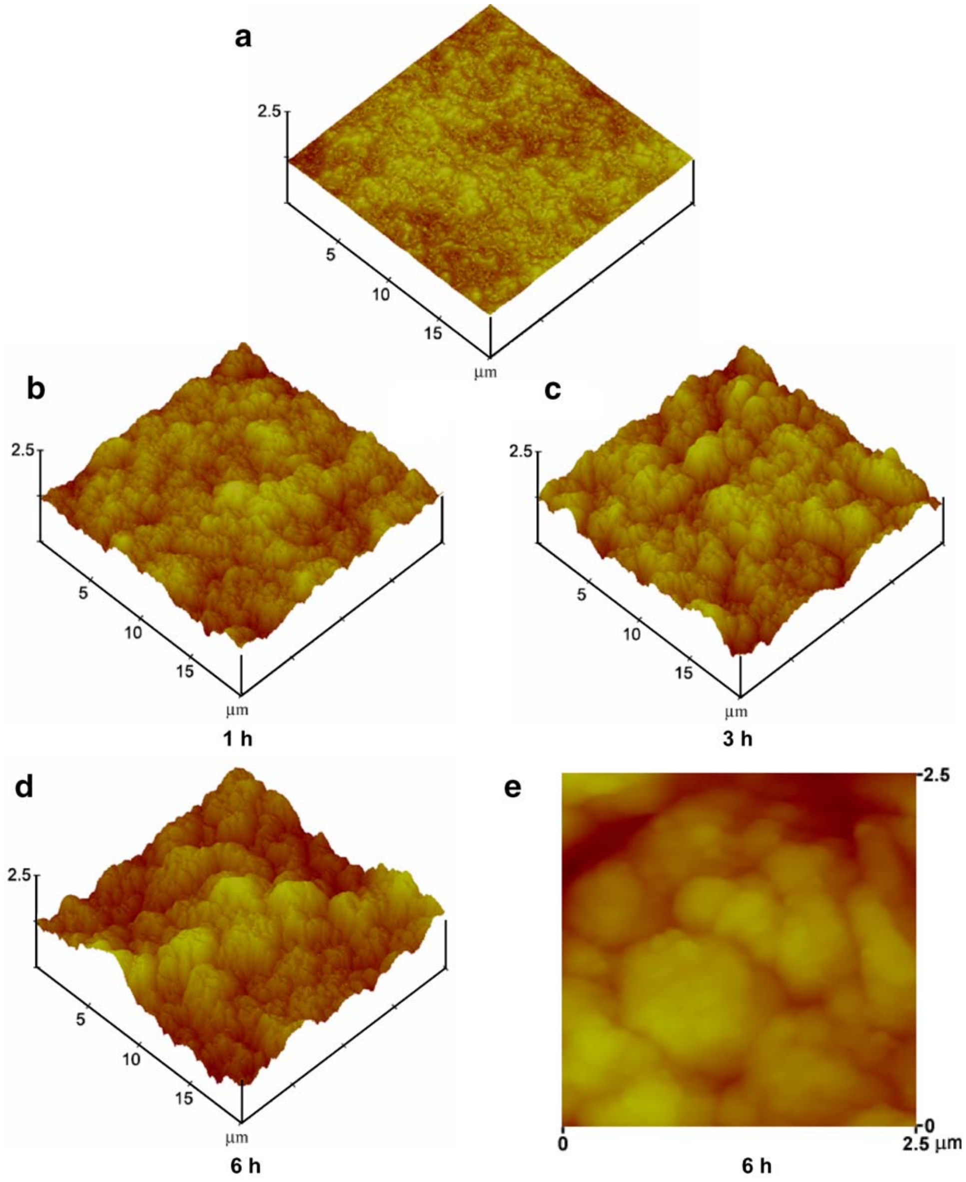


Fig. 7. AFM micrographs of (a) untreated NR sheet and (b)–(e) NR sheets modified by MMA polymerisation at 60 °C for various times.

Both SEM and AFM micrographs in Figs. 6(a) and 7(a) similarly showed the relative flat and smooth surface of the untreated NR. Many nodules in micron-sized range on the rubber surface after polymerisation of MMA for 1, 3 and 6 h were observed in Figs. 6(b)–(d) and 7(b)–(e). Surprisingly, the micrograph in Fig. 7(e) revealed the nano-sized granular substructure (100 nm) which was caused by the phase separation between PMMA formed and NR, in spite of the presence of PMMA partially grafted on the rubber. It was also noticed that the size of nodules increased in proportion with polymerisation time, i.e., increasing PMMA content and PMMA phase size. The formation of PMMA causing the nodular structure would permanently modify the surface of NR sheet because of the molecular interlocking between PMMA molecules penetrated and/or grafted to the rubber chains.

The surface mean roughness (R_a) and hardness (Shore A) of the modified samples were then determined and the data are, respectively, presented in Figs. 8 and 9.

Results indicated that R_a abruptly increased and reached the maximum value of 400 nm within 4.5 h

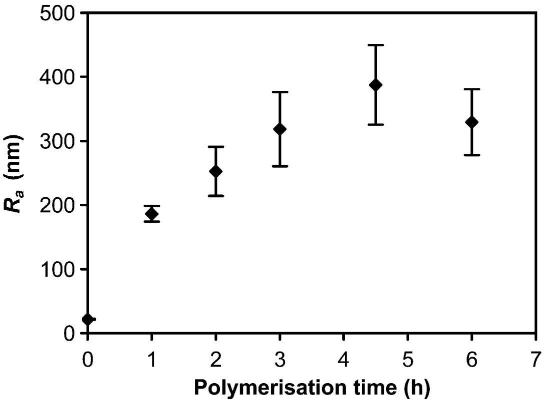


Fig. 8. Surface mean roughness (R_a) of NR sheets modified by MMA polymerisation at 60 °C for various times.

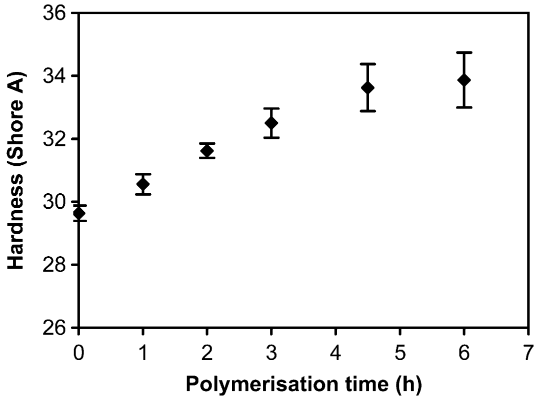


Fig. 9. Hardness (Shore A) of NR sheets modified by MMA polymerisation at 60 °C for various times.

of polymerisation time. With increasing polymerisation time to 6 h, the aggregation of small nodules to become larger lumps, as shown in Fig. 7(e), was the cause of low R_a value. The similar trend was observed in the hardness values (Shore A) in Fig. 9. The consequence of surface roughening and hardening was the reduction in the effective points of contact of the modified NR surface with another substrate which would result in considerable reduction in adhesive or surface friction, as previously demonstrated [1,9,10].

4. Conclusions

MMA polymerised at the NR film surface, in the water-based system, was achieved by using *t*-BuHP-ferrous ion/fructose redox initiation in the alkaline medium. The amount of swollen MMA into NR sheet was proportional to the immersion time. At 60 °C, the percent MMA conversion increased from 10% to 26% with increasing concentration of ferrous ion up to 10 ppm. The low amount of PMMA incorporated in the rubber (4%) was sufficient to modify surface properties of the rubber. The presence of PMMA on the surface of modified NR was indicated by using ATR-FTIR and the ratios of the absorbance at 1730 cm^{-1} of PMMA to that at 1376 cm^{-1} of NR increased with polymerisation time in the initial period. Both SEM and AFM showed the nodular morphology of the modified NR surface. The aggregation of nodules in micron-sized range with a nano-sized granular substructure was clearly apparent under AFM and their size increased in proportion with polymerisation time. The increment of both surface roughness and hardness, leading to a lower adhesive friction against substrate, would potentially reduce the surface friction of the modified NR.

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