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# *Preliminary Study on the Preparation of Latex Foam Rubber from Graft Copolymer of Deproteinised Natural Rubber and Methyl Methacrylate*

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*Deproteinised natural rubber (DPNR) latex was prepared by incubation of fresh field natural rubber latex with a proteolytic enzyme in the presence of an emulsifier. The nitrogen content was decreased from 0.9% (in the fresh field natural rubber latex) to 0.07% (in the DPNR). A graft copolymer of the deproteinised natural rubber latex and poly(methyl methacrylate) (PMMA) was then synthesised using tert. butylhydroperoxide and tetraethylene pentamine as a redox initiator. The presence of grafted PMMA in the natural rubber molecules was confirmed using FTIR. Intense absorption peaks at 1732 $cm^{-1}$ (-C=O stretch) and 1140 $cm^{-1}$ (-C-O stretch) were observed. It was also found that the quantity of grafted PMMA increased with the increase in the level of MMA used in the grafting reaction. The graft copolymer latex was later compounded and processed into a latex foam rubber. Results showed that the latex of graft copolymer blended with high ammonia concentrated latices provided high quality latex foam rubber. This included surface appearance and physical properties, such as hardness, compression set and density. It was also found that hardness, compression set and density of the latex foam rubber increased with the increase in the level of graft copolymer in compounding formulation. Furthermore, at the same blend ratio, the properties increased with the increase in the level of methyl methacrylate used in the grafting reaction.*

**Key words:** Deproteinised natural rubber; graft copolymer; methyl methacrylate; latex foam rubber. FTIR

Natural rubber has been modified for commercial use by copolymerisation with synthetic polymers. The main purpose is to improve properties and extend its use. Graft copolymerisation has been used as one of the main methods of modifying NR in both latex form[1–10] and solution[11–15]. Latex modification has been proved to be the most economical[15]. Initiator systems employed include benzoyl peroxide[1,13–15], redox initiator[7,9–10], AIBN[3,12], vanadium ion[11] and gamma irradiation[6]. The graft copolymer of NR and methyl methacrylate has been the one of main interest. This type of graft copolymer was found useful as a shoe

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adhesive under the trade name of Heveaplus MG® or MG rubber. The method of preparation of Heveaplus MG® has been discussed by Pendle[2]. This was carried out by dissolving graft copolymer, which contained little PMMA homopolymer and ungrafted natural rubber, in a solvent mixture of MEK/ toluene. Furthermore, the MG rubber could be used as a reinforcing agent[16].

Latex foam rubbers, prepared from natural rubber latex, are cellular rubbers produced by the *in situ* generation of gas in the polymer. They have been well known for the manufacturing of cushioning material. The major applications are in the furniture, bedding and automotive industries. Improvement of foam hardness and other important physical properties are generally achieved by adding a certain amount of mineral fillers, such as clay and calcium carbonate. In spite of lowering the cost and improving some properties, high loading of mineral fillers affects the body weight of foamed products. That is, they are sometimes too heavy to handle in some applications, such as in mattresses. Latex foam rubber prepared from modified natural rubber, such as graft copolymer of natural rubber and poly(methyl methacrylate), may provide a certain degree of reinforcement. This will improve foam hardness and other important physical properties. Therefore, special latex foam rubber with a low level or without using mineral fillers can be prepared[17]. The body weight of these foam articles is therefore much lower than those of ones produced using conventional methods. The main aim of this research is to improve the latex foam properties using graft copolymer of deproteinised natural rubber and PMMA. A Dunlop process as described by Fallows[18] and Blackley[19] and Nakason *et al.*[17] was used to produce latex foam rubber. Deproteinised natural rubber was chosen since it provided a higher rate of grafting and grafting efficiency[5,7]. The latex foam product would also provide a lower risk of allergic reactions caused by proteinaceous matter present in the natural rubber latex.

## MATERIALS AND METHODS

### Materials

Fresh field NR latex (collected from the rubber plantation in Kokpoo District, Pattani Province, Thailand) was used to produce the deproteinised natural rubber latex. High ammonia concentrated latex (produced by Pattani Industrial Co. Ltd., Thailand) was used as a blending ingredient for the preparation of latex foam rubber. The Opticlean enzyme (purchased from Cinnamon Co. Ltd., Thailand) was used to hydrolyse the proteins in NR latex. The monomer used in the graft copolymerisation was methyl methacrylate (produced by Merck, Germany). The redox initiators were tert-butylhydroperoxide solution (produced by Fluka, Switzerland) and tetraethylene pentamine (produced by Fluka, Switzerland). The emulsifier used to stabilise DPNR latex was potassium laurate, prepared using potassium hydroxide (produced by Carlo Erba, Italy) and lauric acid (produced by Merck, Germany). The free PMMA and free natural rubber presence in the graft copolymer were extracted using acetone (produced by Lab-Scan, Ireland) and petroleum ether (produced by Lab-Scan, Ireland), respectively. The emulsifier used in the latex foam formulation was potassium oleate, prepared using potassium and oleic acid (produced by Merck, Germany). The vulcanising agent (50% dispersion) was prepared by ball milling sulphur (purchased from Petthai Chemical Co. Ltd., Thailand), zinc diethyldithio-carbamate (purchased from Petthai Chemical Co. Ltd., Thailand), zinc mercaptobenzothiazole (purchased from Petthai Chemical Co. Ltd.,

Thailand), Vultamol (dispersing agent) and water for 48 h. The 50% dispersion of zinc oxide (produced by G.H. Chemicals Ltd., Canada) used as an activator was prepared by ball milling zinc oxide, Betonite, Vultamol and distillated water for 48 h. The gelling agent and secondary gelling agent used in the preparation of the latex foam were 20% dispersion of sodium silicofluoride (purchased from Pattani Industy Co. Ltd., Thailand) and 50% dispersion of Vulcafor EFA® (purchased from Pattani Industry Co. Ltd., Thailand), respectively.

## Preparation of Deproteinised Natural Rubber Latex

Fresh field natural latex was treated with an ammonia solution at a concentration of 0.7% wt. based on the latex weight. Emulsifier (20% potassium laurate) was added at a level of 0.5% wt. of the latex. The Opticlean enzyme, which is a bacterial alkaline protease, was incorporated at approximately 0.03% wt. of the latex. The latex was incubated for 3 days and later centrifuged using a factory scale centrifuge machine, Alfa Laval model 410, at a speed of 800 r.p.m. The ammonia solution was adjusted to the same concentration as in the high ammonia concentrate natural rubber latex (*i.e.* 0.7% wt.). The nitrogen content of DPNR was analysed using the Kjeldahl method, according to *ASTM D3533*, and the average particle size of rubber particles was analysed using a Coulter LS 230 analyser.

## Preparation of Graft Copolymer

A semi-continuous emulsion polymerisation technique was used to prepare the graft copolymer of deproteinised natural rubber and methyl methacrylate (MMA). Tert. butyl hydroperoxide and tetraethylene pentamine were the redox initiator. This permitted the polymerisation to go to completion at 50°C. The latex stability was maintained by an emulsifier, 30% potassium laurate.

Details of process description is as follows. The main reactor (capacity of 2 L), feeding tank, mechanical stirrers, liquid pumping system, nitrogen delivering system and temperature controlled water pump, are shown schematically in *Figure 1*. Graft copolymerisation was started by charging natural rubber latex (~60% DRC), 2.12 gm of 85% wt. tetraethylene pentamine and 87 mL of water into the main reactor. The components were then agitated by means of a mechanical stirrer at 50°C under nitrogen atmosphere. Monomer (MMA), 2.57 gm of 30% wt. tert. butylhydroperoxide, 9 mL. of emulsifier (30% wt. potassium laurate) and 120 mL of water were charged into a feeding tank and thoroughly stirred for 30 min. The chemical mixture in the feeding tank was then pumped into the main reactor using a liquid pumping system at a constant flow rate of 2.7 mm/min. After all chemicals in the feeding tank were transferred into the main reactor, the reaction was continued for 3 h at 50°C. Various mole ratios of natural rubber latex and MMA were each used to carry out the graft copolymerisation, as shown in *Table 1*. The mole ratio of natural rubber latex were calculated based on the molecular weight of the isoprene unit.

TABLE 1. QUANTITY OF NATURAL RUBBER LATEX AND MMA USED

| Latex/MMA (% mole) | Natural rubber latex (60% DRC) (gm) | MMA (gm) |
|---|---|---|
| 95/5 | 321 | 15 |
| 90/10 | 304 | 30 |
| 80/20 | 270 | 60 |
| 70/30 | 236 | 90 |
| 60/40 | 202 | 120 |

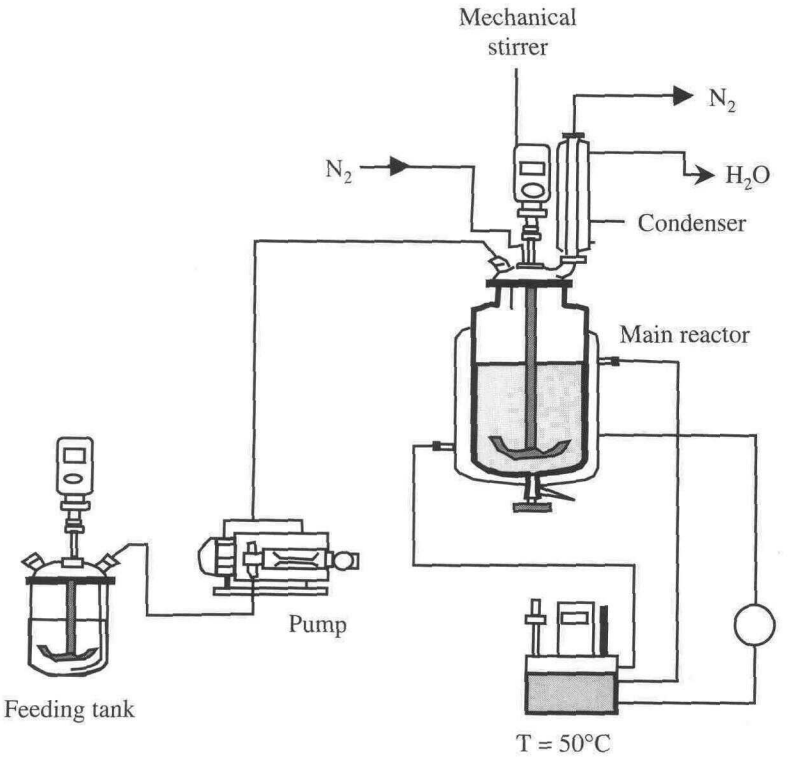



*Figure 1. Apparatus used to prepare graft copolymer from natural rubber and methyl methacrylate*[5].

To study its characteristics, graft copolymer was coagulated. The dried product was purified by means of extraction. The free PMMA and free rubber were removed using acetone and petroleum respectively, as the solvents. The graft copolymer was then characterised using FTIR.

## Preparation of Latex Foam Rubber

The Dunlop process was used to produce latex foam rubber. Details of the compound formulation are shown in *Table 2*. The latex (100 p.h.r.) in the compound formulation was prepared solely using the graft copolymer or the blends of the graft copolymer and high ammonia concentrated latex, at various weight ratios (p.h.r.) of 10:90, 20:80, 30:70, 50:50. The latex was firstly stirred for 5 min in a whisk and bowl type batch mixer. Ammonia, 20% potassium oleate and vulcanising agent were added and mixing continued for 15 min. The froth was made by mechanical agitation. After the level of the froth had been raised to approximately 3 to 4 times higher than that of the initial level, 50% Vulcafor EFA® (a secondary gelling agent) was added and blending continued for 5 min. The 50% ZnO dispersion was then introduced into the mixing chamber and blending continued for 3 min. The final ingredient, 20% sodium silicofluoride

TABLE 2 LATEX FOAM COMPOUND FORMULATION

| Ingredients | Weight (p h r) |
|---|---|
| Latex or blended latex | 100 |
| 20% Potassium oleate | 1 |
| Vulcanising agent | 6 |
| 50% Vulcafor EFA® | 4 |
| 50% ZnO dispersion | 6 |
| 20% Sodium silicofluoride | 3 |

(SSF), a gelling agent, was then added and blended for 1 min The viscous foaming liquid was then delivered into a mould and vulcanised in a steam oven under atmospheric pressure for 20 min The products were finally washed and dried at 50°C for 24 h in a hot air oven The various physical properties of the latex foam rubber were then measured

**Properties of Latex Foam Rubber**

Hardness of the latex foam rubber was characterised using the indentation force deflection test The indentor foot was firstly brought into contact with the test specimen A contact force of 4 5 N was applied and the foam thickness was determined The specimen was allowed to rest for 6 min and was indented at a rate of 0 83 mm/s until 40% of the initial thickness was reached The force in newtons was observed after 1 min

The compression set was tested according to *ASTM D 395* The test specimens were compressed on each side of the spacers for approximately 25% compression The assembled compression device was placed in an oven at 70°C for 72 h The device was then taken out of the oven The specimen was removed immediately and allowed to cool at room temperature for 30 min The percentage compression set was then calculated

RESULTS AND DISCUSSION

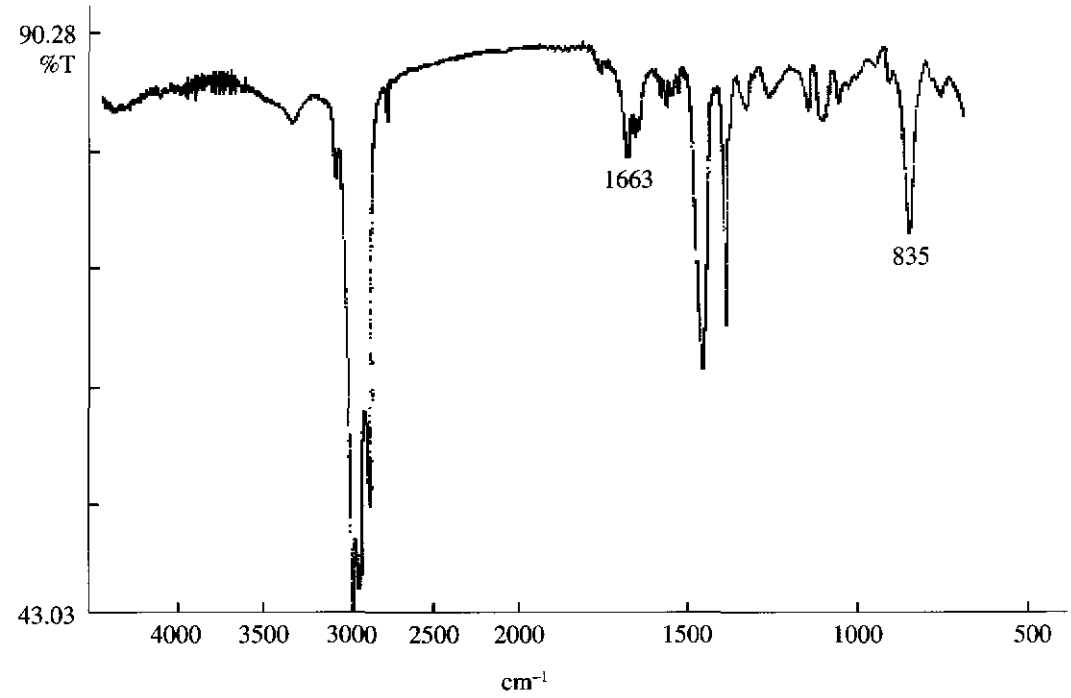
**Properties of Deproteinised Natural Rubber**

The nitrogen content of the DPNR latex was 0 07%, compared with 0 9% in the fresh field natural rubber latex This indicated that the Opticlean enzyme exhibited high capability to hydrolyse the protein's presence in the natural rubber latex The average particle size of rubber particles for the DPNR was 0 862 μm compared with 0 659 μm for the original fresh natural rubber latex Increase of the average particle size may be attributed to the influence of proteolytic enzyme and the centrifuge action Some types of protein normally cover the rubber particles as a shell, which act as an anti-coalescent for the rubber particles[20] Incubation of the latex with the enzyme caused hydrolysis of the proteins The protected shell was therefore destroyed and the particles tend to coalesce upon centrifugation

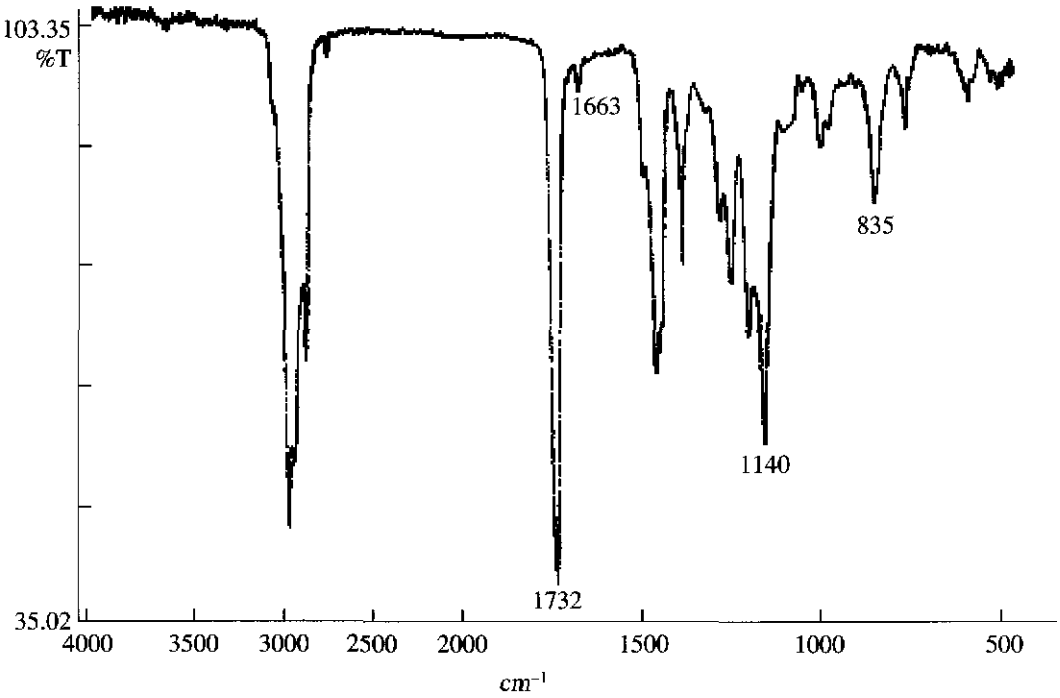
**Characteristics of Graft Copolymer (DPNR-g-PMMA)**

*Figure 2* shows the infrared spectra of natural rubber and graft copolymer It is clear that the infrared spectrum of graft copolymer shows intense absorption peaks at 1732 $cm^{-1}$ and 1140 $cm^{-1}$ This corresponds to -C=O and -C-O groups in the methyl methacrylate chains which have been grafted onto the natural rubber molecules

The quantity of grafted PMMA on the natural rubber molecules could be roughly




(a) Natural rubber




(b) Graft copolymer prepared using mole ratio of natural rubber and MMA = 60/40

*Figure 2. Infrared spectrum of natural rubber and graft copolymer.*

calculated from % free PMMA, % free rubber and % conversion. The results are plotted in *Figure 3*. It was found that the quantity of grafted PMMA increased with increase in the amount of MMA used in the grafting reaction. The results corresponded to the increase in infrared spectrum peak intensity at 1732 $cm^{-1}$ and 1140 $cm^{-1}$.

## Properties of Latex Foam Rubber

Pictures of latex foam products prepared using DPNR-g-PMMA and various blend ratios of DPNR-g-PMMA and the high ammonia concentrated latices, are illustrated in *Figure 4*. It was found that a cracking surface appeared for the compound, prepared solely from DPNR-g-PMMA, especially for the graft copolymer with a high level of grafted PMMA content. However, the graft copolymer with lower grafted PMMA and the blends of the graft copolymer with high ammonia concentrated latex exhibited the better surface appearance. The blended latices were therefore used to study properties of the latex foam rubber throughout this work.

The hardness results are shown in *Figure 5*. It is clear that the indentation force increased with increasing the level of graft copolymer in the compound formulation. Furthermore, at the same blend ratio, the indentation force increased with increase of grafted PMMA content in the graft copolymer molecules. The indentation force reflects hardness of the latex

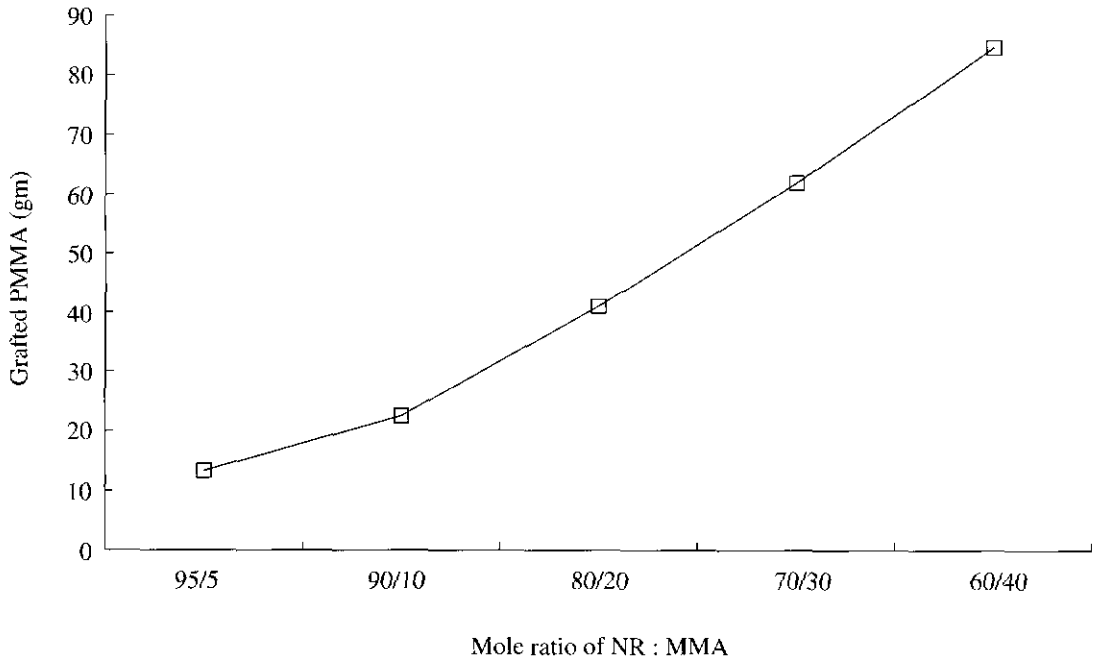
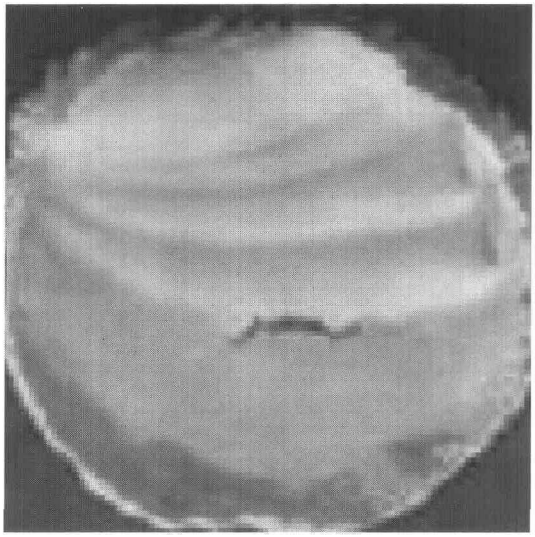
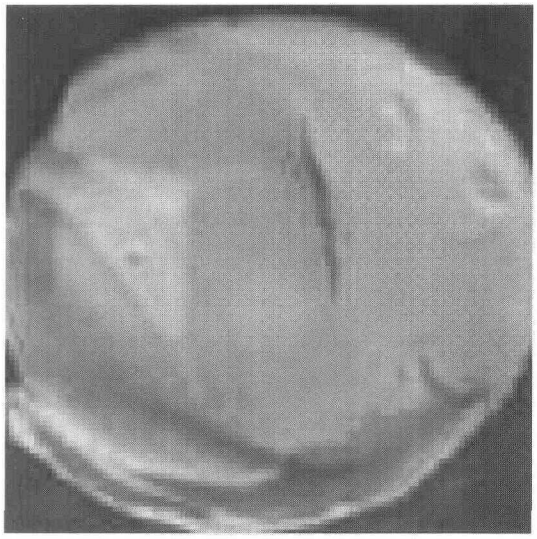


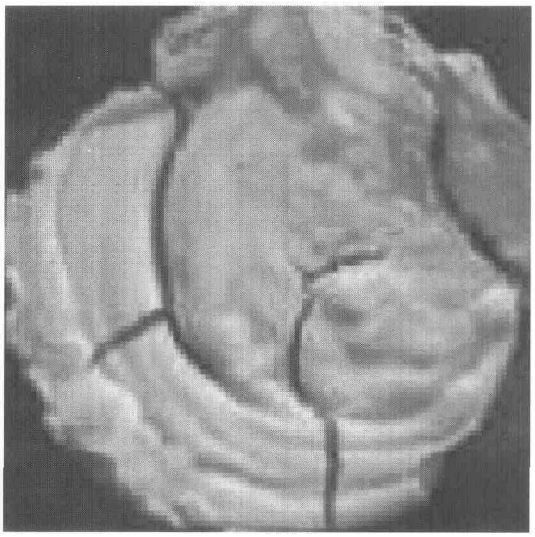

*Figure 3. Quantity of grafted PMMA on NR molecules at various mole ratios of NR and MMA.*



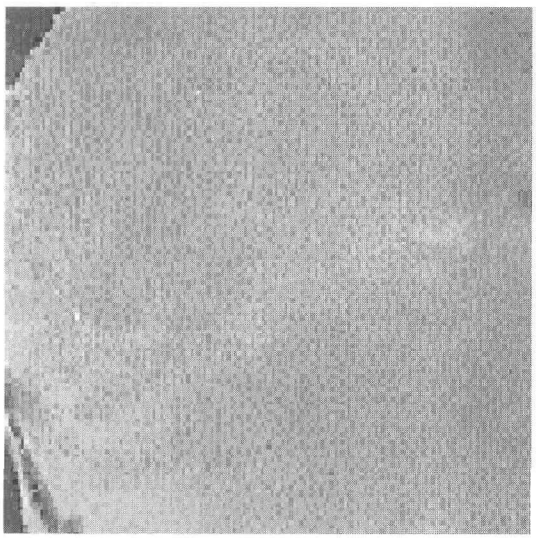
(a) DPNR-g-PMMA prepared using mole ratio of DPNR/MMA = 90/10



(b) DPNR-g-PMMA prepared using mole ratio of DPNR/MMA = 80/20



(c) DPNR-g-PMMA prepared using mole ratio of DPNR/MMA = 70/30



(d) DPNR-g-PMMA prepared using mole ratio of DPNR/MMA = 90/10 blended with the high ammonia concentrated latex at weight ratio of 1:1

*Figure 4. Pictures of latex foam produced from graft copolymer at different levels of PMMA (a, b and c), and blending of graft copolymer with high ammonia natural rubber latex (d).*

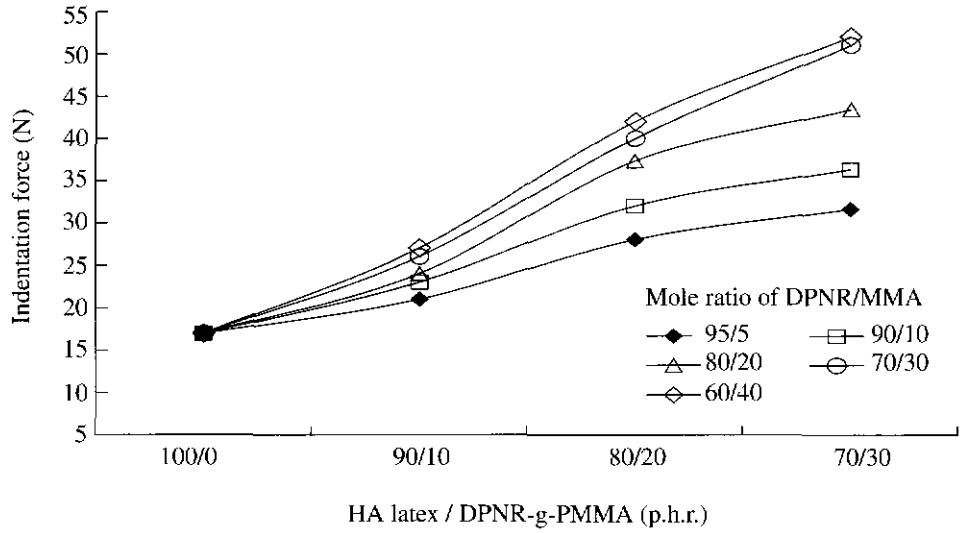



*Figure 5. Indentation force deflection of the latex foams at various blend ratios and levels of MMA used in the graft reaction.*

foam, which depends on both quantities of DPNR-g-PMMA and level of grafted PMMA used in the compound formulation. Therefore, it is concluded that the hardness of foam arises from characteristics of the grafted PMMA present in the compound formulation.

Compression set of the latex foam product is a measure of the tendency of the material to recover from deformation when in use as cushioning material. The compression set results are shown in *Figure 6*. The compression set of the latex foam increased slightly with the level of DPNR-g-PMMA used in the compound formulation. It also increased with increase in the level of grafted PMMA in the graft copolymer. Therefore, the latex foam with the higher PMMA content showed a lower ability to recover from the deformation after a prolonged period of compressive stress.

*Figure 7* shows density of the latex foam product. This was measured based on the mass and volume of the specimen. As in the case of indentation hardness, density of the foam increased with increase in the level of DPNR-g-PMMA and the level of grafted PMMA in the compound formulation.

## CONCLUSIONS

Deproteinised natural rubber was successfully prepared and used to synthesize DPNR-g-PMMA by a semi-continuous emulsion polymerisation technique. A certain level of graft copolymer in the compound formulation can be used to improve latex foam properties. The graft copolymer was blended with high ammonia concentrated latex. To improve the surface appearance, hardness and other significant

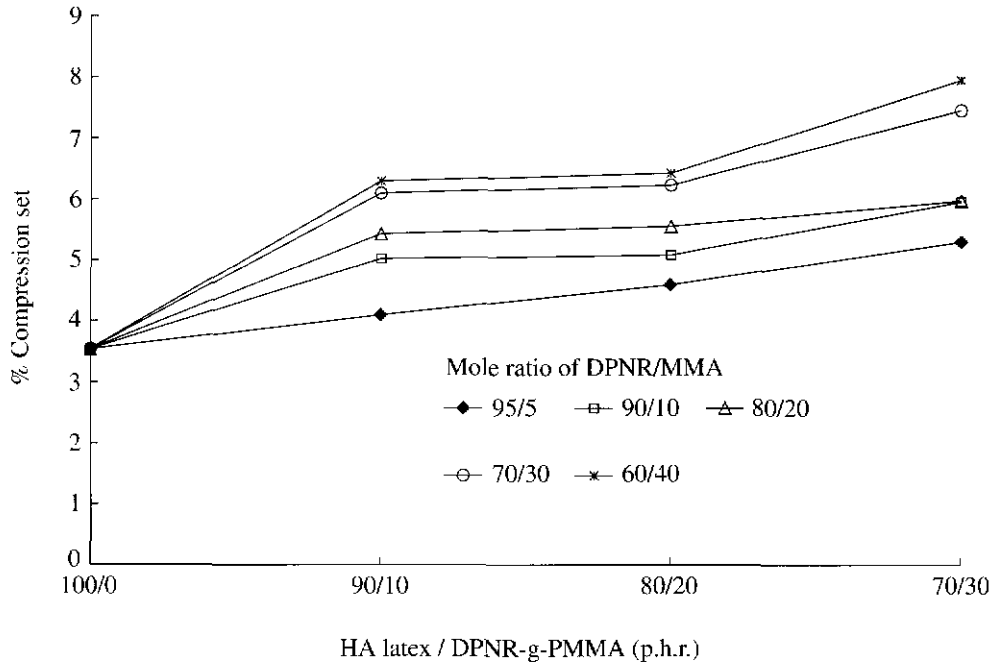



*Figure 6. Compression set of the latex foams at various blend ratios and levels of MMA used in the graft reaction.*

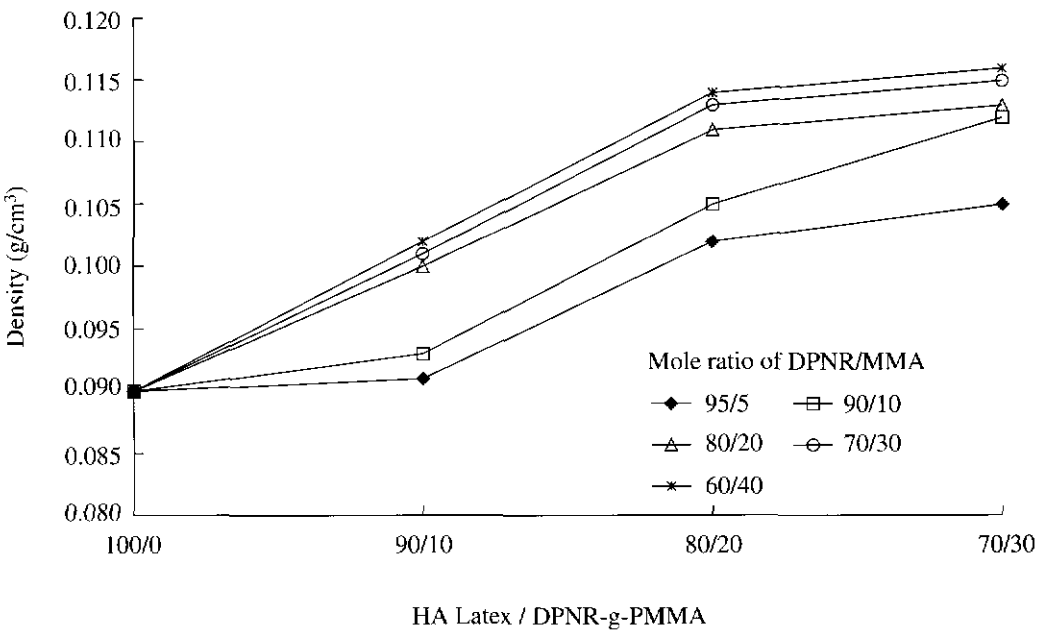



*Figure 7. Density of the latex foams at various blend ratios and levels of MMA used in the graft reaction.*

properties of the latex foam rubber. The indentation hardness, compression set and density of the latex foam increased with increase in the level of PMMA in the graft copolymer and the level of graft copolymer in the compound formulation. The graft copolymer can therefore be used as a reinforcing agent for latex foam rubber manufacturing. However, the ability of the latex foam to recover from the deformation decreased with increase in the level of PMMA in the compounding formulation.

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