

Modification of Deproteinised Natural Rubber by Graft-copolymerisation of Methyl Methacrylate

NURUL HAYATI YUSOF^{*#}, SEIICHI KAWAHARA^{**} AND MA'ZAM MD. SAID^{*}

Natural Rubber (NR) latex was deproteinised by incubation with urea in the presence of sodium dodecyl sulfate (SDS). Urea deproteinised natural rubber (U-DPNR) latex was graft-copolymerised with Methyl Methacrylate (MMA) at a monomer feed of 5, 10, 15 and 20 wt % on rubber. The monomer content, monomer conversion and grafting efficiency of the copolymerisation reaction were determined. The resulting graft copolymers were characterised by FT-IR spectroscopy and morphology observed using a transmission electron microscope (TEM). The monomer content, conversion and grafting efficiency of NR-graft-PMMA, U-DPNR-graft-PMMA and E-DPNR-graft-PMMA were compared as well. The results showed that, MMA feed of 15 wt % on rubber, initiator concentration of 6.6×10^{-5} mol/g-rubber and reaction temperature at 30°C were found to be suitable conditions to obtain high MMA content, high conversion and high grafting efficiency. The highest grafting efficiency was about 80% at 15 wt % on rubber feed of MMA for U-DPNR-graft-PMMA and E-DPNR-graft-PMMA.

Key words: Deproteinisation; urea; sodium dodecyl sulfate (SDS); U-DPNR latex; graft-copolymerisation; methyl methacrylate

Urea-deproteinised NR grafted with poly-methyl methacrylate (PMMA) may have a potential to improve some of the inferior properties of NR such as oil and weather resistance. This could arise from a structure composed of a matrix of PMMA between the rubber dispersoids. Since PMMA is a glassy polymer, it is unlikely that it would form a continuous phase in U-DPNR-graft-PMMA but more likely to form a disperse phase in a matrix of NR¹. Recent work on nano-matrix-dispersed NR prepared from graft-copolymerisation of U-DPNR latex and styrene showed that the outstanding mechanical properties of the

copolymer obtained were probably attributed to the formation of a nano-matrix structure².

In the previous work³⁻⁴, graft-copolymerisation of NR with MMA was carried out after swelling NR rubber particles in the latex with the monomers followed by adding radical initiators. However, the conversion and grafting efficiency of MMA were quite low. To increase conversion and grafting efficiency of the monomer, the initiator and monomer were mixed followed by mixing with the latex⁵. The graft-copolymerisation was also carried out at high dry rubber content, high reaction

^{*}Rubber Research Institute of Malaysia, Malaysian Rubber Board, P.O Box 10150, 50908 Kuala Lumpur, Malaysia

^{**}Department of Materials Science and Technology, Faculty of Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

[#] Corresponding author (e-mail: hayati@lgm.gov.my)

temperatures (50°C–70°C) and a long reaction period of 8 to 16 hours³⁻⁵.

Results obtained from the previous work showed that a high concentration of initiator increased conversion of the monomer. However, high monomer concentration, initiator concentration and conversion gave low grafting efficiency⁶. The results also showed that the PMMA layer over the rubber particles became thicker with a longer period of reaction time⁷.

In the last two decades⁸⁻⁹, highly ammoniated natural rubber latex concentrate (NR) was used as a starting material for graft-copolymerisation with MMA. Later, researchers discovered that proteins that were attached to the rubber particles decreased the grafting efficiency. Proteins may interfere with the graft-copolymerisation since the radical will react with proteins during the reaction⁹. To prevent the side reaction of the proteins, graft-copolymerisation using deproteinised NR latex, prepared with proteolytic enzyme in the presence of a surfactant, was studied¹⁰. The use of enzymatic-deproteinised NR (E-DPNR) latex resulted in a higher grafting efficiency compared to NR¹¹. However, E-DPNR appeared to have a drawback with regards to its preparation requiring a fairly long incubation time of 12 hours at 40°C.

Recently, urea was found to be a suitable denaturant to remove the proteins from NR¹². Previous work reported that the U-DPNR treatment decreased the nitrogen content from 0.38% to 0.02%, which was similar to that obtained by the E-DPNR treatment¹³. Furthermore, the conversion and grafting efficiency obtained for both types of deproteinised NR latices with styrene were found to be quite similar¹⁴.

In this study, graft-copolymerisation of U-DPNR latex with MMA using a redox

initiator comprising *tert*-Butylhydroperoxide (tBHP) and tetraethylenepentamine (TEPA) was carried out in order to investigate the conditions for the graft-copolymerisation that give high conversion and high grafting efficiency. The reactivity of different types of latices was also compared with regards to the MMA content, conversion and grafting efficiency. Characterisation of materials was carried out using Fourier Transform IR (FT-IR) spectroscopy and observation of surface morphology *via* Transmission Electron Microscopy (TEM).

EXPERIMENTAL

High ammoniated (HA) latex was used in the present study. HA Latex with a dry rubber content (DRC) of about 60% was diluted with 1wt% Sodium Dodecyl Sulfate (SDS) solution to 30% DRC latex. U-DPNR latex was prepared by incubating the latex with 0.1wt% urea and 1wt% of SDS for 1 hour at room temperature. E-DPNR latex was prepared by incubating the latex with 0.04 wt% proteolytic enzyme and 1wt% SDS for 12 hours at 40°C.

After incubation, the respective urea and enzyme treated HA latices were centrifuged twice. The cream fraction was re-dispersed in 1wt% SDS solution to make 30% DRC latex after the first and second centrifugations. Conditions of deproteinisation are shown in Table 1. For Nitrogen content determination, cream fractions were coagulated with methanol and dried under reduced pressure at an ambient temperature. Nitrogen content of the respective samples was determined by the Kjeldahl method.

Total solids content (TSC) of NR, U-DPNR and E-DPNR latices was adjusted to 30% before graft-copolymerisation. The NR, U-DPNR and E-DPNR latices were flushed with Nitrogen (N₂) gas for 1 hour at 30°C, copolymerised

with MMA using a redox initiator system comprising tBHP and TEPA. The reaction was performed for 2 hours within a temperature range of 10°C – 50°C with continuous stirring at 400 r.p.m. under N₂ atmosphere. Conditions for graft-copolymerisation are shown in Table 2. The unreacted monomer was removed with a rotary evaporator under reduced pressure. The prepared gross polymer was coagulated with methanol and dried under

reduced pressure at an ambient temperature for a week. The gross polymer was then extracted with acetone/2-butanone 3:1 by means of Soxhlet extraction for 24 hours in a nitrogen atmosphere in the dark and dried under reduced pressure for a week.

Percentage of monomer content, conversion and grafting efficiency were calculated as follows;

$$\text{Monomer Unit, \%} = \frac{\text{Weight of NR after grafting} - \text{Weight of NR before grafting} \times 100}{\text{Weight of NR after grafting}} \quad \dots 1$$

$$\text{Conversion, \%} = \frac{\text{Weight of NR after grafting} - \text{Weight of NR before grafting} \times 100}{\text{Feed of monomer}} \quad \dots 2$$

$$\text{Grafting Efficiency, \%} = \frac{\text{Produced Polymer} - \text{Extracted Polymer} \times 100}{\text{Produced Polymer}} \quad \dots 3$$

TABLE 1. DEPROTEINISATION PROCESS PARAMETERS AND NITROGEN CONTENT OF THE LATTICES

Process parameters	HA latex (NR)	E-DPNR latex	U-DPNR latex
DRC, wt%	30	30	30
Proteolytic enzyme (wt% on latex)	–	0.04	–
Urea (wt% on latex)	–	–	0.1
SDS (wt% on latex)	1	1	1
Incubation period, hr	–	12	1
Incubation temp, °C	–	40	RT
Nitrogen Content, %	0.4	0.02	0.02

The gel content of the grafted rubbers was determined by treating 1 g of sample in dried toluene without stirring, kept in the dark at an ambient temperature for a week. The mixture was then centrifuged and the gel fraction was collected at the bottom. The collected gel fraction was dried under reduced pressure for a week. The dried gel was weighed and the gel content was estimated based on the overall weight of sample.

The nitrogen content of the rubbers was determined by the Kjeldahl method as described in the RRIM Test Method, Method B7¹⁵. Rubber samples, mixed with a catalyst mixture, *i.e.* potassium sulphate : copper sulphate : selenium in the weight ratio of 15:2:1, were digested with concentrated H₂SO₄. The resulting solution was distilled, and distillates were titrated with 0.005 M H₂SO₄ using methyl red as an indicator.

TABLE 2. CONDITIONS FOR GRAFT-COPOLYMERISATION

Ingredients and conditions of reaction	HA latex (NR)	E-DPNR latex	U-DPNR latex
Latex Weight, g	200	200	200
Monomer Feed (wt% on rubber)	5, 10, 15, 20	5, 10, 15, 20	5, 10, 15, 20
Initiator system, mol/g-rubber (%) tBHP : TEPA 1 : 1	6.6×10^{-5}	6.6×10^{-5}	3.3×10^{-5} 6.6×10^{-5}
Reaction period, hr	2	2	2
Reaction temperature, °C	30	30	10, 20, 30, 40, 50

The grafted rubbers were characterised by Fourier-Transform Infra-Red (FT-IR) spectroscopy. Film specimens were prepared by casting the grafted rubbers in 1 wt % chloroform solution onto a potassium bromide (KBr) plate under nitrogen atmosphere. The FT-IR measurement was carried out using a JASCO FT-IR 410 spectrometer with a resolution of 4 cm^{-1} .

Observation of morphology for the graft-copolymer was made using transmission electron microscopy (TEM), Hitachi H-800, at an accelerating voltage of 120kV. The ultra thin sections of the graft-copolymer were prepared by a Sovall Instruments MT6000 Ultra-microtome, at a temperature lower than the glass-transition temperature (T_g) of NR. The thin sections were stained by osmium tetroxide (OsO_4) after annealing the blends at 80°C for 30 minutes.

RESULTS AND DISCUSSION

Initiator Dependency

Figure 1 shows a plot of MMA content in the product of U-DPNR-graft-PMMA against feed of MMA. The reacted MMA unit content increased with increasing feed of MMA at

$3.3 \times 10^{-5} \text{ mol/g-rubber}$ and $6.6 \times 10^{-5} \text{ mol/g-rubber}$ initiator concentrations. The results also showed that the MMA content was higher at higher initiator concentration over a certain range of the MMA feed.

Figure 2 shows the relationship between monomer conversion and feed of MMA. When using $3.3 \times 10^{-5} \text{ mol/g-rubber}$ of initiator system, the conversion increased with increasing feed of MMA. However, the conversion was less than 80%, even at 20 wt % feed of MMA. When the initiator system concentration was increased to $6.6 \times 10^{-5} \text{ mol/g-rubber}$, the conversion increased to more than 90%. This indicates that a fairly large amount of initiator is required for the graft-copolymerisation of MMA in U-DPNR latex in order to obtain a high percentage of monomer conversion.

Figure 3 shows the relationship between grafting efficiency and feed of MMA. The grafting efficiency was significantly dependent on the feed of MMA for both concentrations of initiator system studied. The grafting efficiency increased with feed of MMA up to 15 wt %. Higher grafting efficiency was also observed when a higher level of initiator system concentration, $6.6 \times 10^{-5} \text{ mol/g-rubber}$ was used. In the subsequent experiments, the

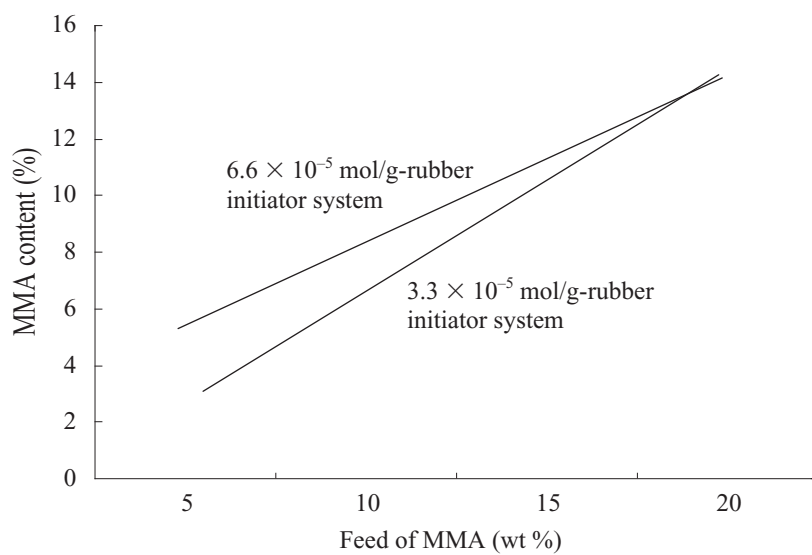


Figure 1. MMA Content (%) vs. feed of MMA (wt %).

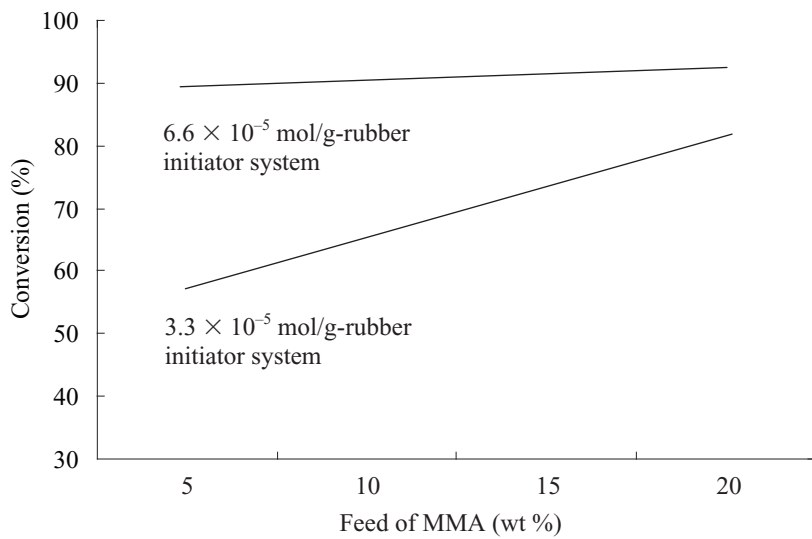


Figure 2. Conversion (%) of I and 2I vs. feed of MMA (wt %).

graft-copolymerisation was carried out with the 6.6×10^{-5} mol/g rubber initiator system.

FT-IR analysis

The resulting U-DPNR-graft-PMMA was characterised by FT-IR measurements. *Figure 4* shows the FT-IR spectra for U-DPNR-graft-PMMA prepared with 5, 10, 15 and 20 wt % feed of MMA. In the spectrum (a), an absorbance band at 1664 cm^{-1} was identified as C=C stretching vibration of *cis* 1, 4 -isoprene units. After graft-copolymerisation (b, c, d, e), the intensity of the absorbance band at 1740 cm^{-1} , identified as the C=O stretching vibration of the ester group of MMA, increased with increasing feed of MMA. The MMA content of the graft-copolymers was estimated from a calibration curve of absorbance ratio of the peak intensity at 1740 to 1664 cm^{-1} versus PMMA concentration with $R^2 = 0.99$. The estimated MMA content is shown in *Figure 5*, together with that estimated by gravimetry.

Figure 5 shows that the MMA content increased with increasing feed of MMA over the range of monomer feed studied. The increase in the MMA content as measured with FT-IR was almost similar to that estimated by gravimetry. Thus, the FT-IR measurement, as well as the gravimetric measurement, was considered to be a suitable method to determine the MMA content of U-DPNR-graft-PMMA.

Temperature Dependency

The temperature dependence of the graft-copolymerisation of MMA was investigated at the feed of MMA of 15 wt % on rubber between 10°C and 50°C . *Figure 6* shows a plot of the MMA content and conversion for U-DPNR-graft-PMMA versus temperature. The MMA content and conversion were dependant on temperature. The maximum values for the MMA content and conversion were 12% and 90%, respectively obtained at 30°C .

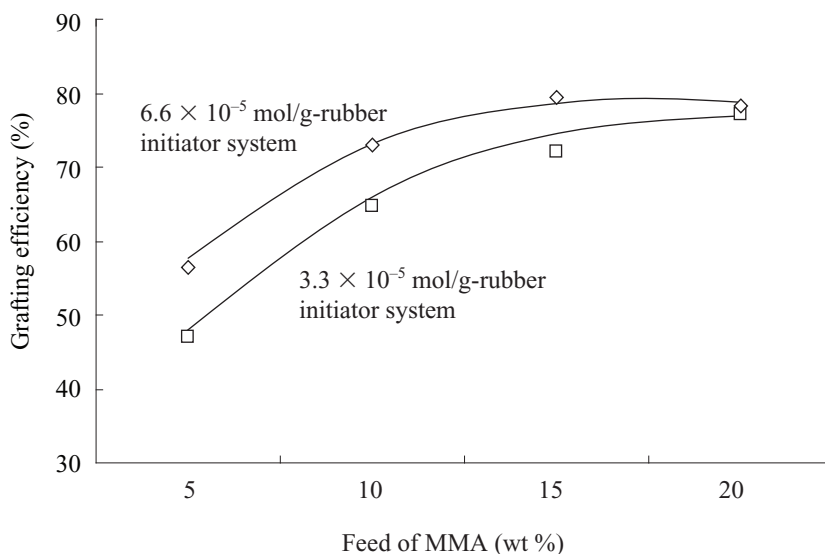


Figure 3: Grafting Efficiency (%) vs. feed of MMA (wt %).

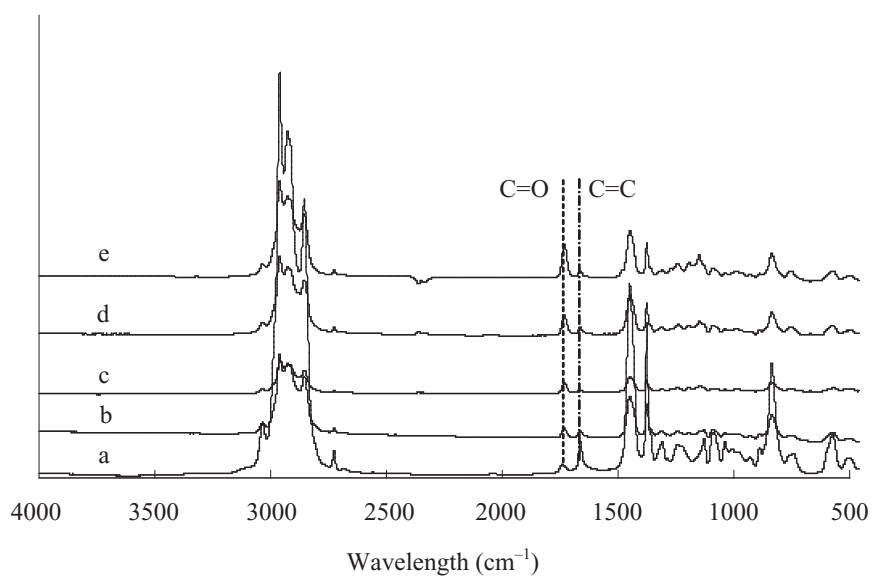


Figure 4. FT-IR spectra of U-DPNR-graft-PMMA. (a) U-DPNR (b) 5 wt % (c) 10 wt % (d) 15 wt % (e) 20 wt % feed of MMA.

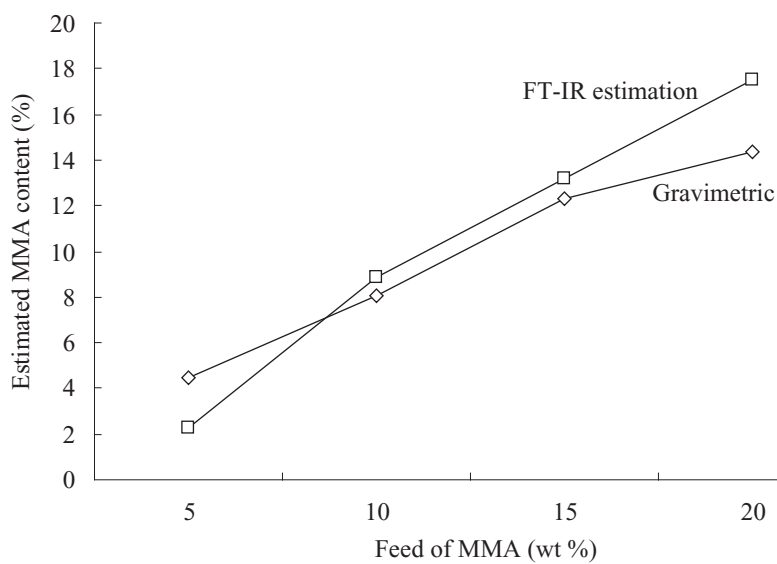


Figure 5. Estimated MMA content (%) vs. feed of MMA (wt %) by FT-IR estimation and gravimetric.

Figure 7 shows a plot of the grafting efficiency *versus* reaction temperature. The grafting efficiency was dependent on temperature and a maximum value of about 80% was obtained at 30°C. The results from Figure 6 and 7 indicate that 30°C is an ideal temperature for graft-copolymerisation of MMA in U-DPNR latex.

Morphology of U-DPNR-graft-PMMA

Figure 8 shows the morphology of U-DPNR-graft-PMMA films. The bright areas represent the rubber particle phase whilst the dark and light-grey areas that surround the rubber particles represent the PMMA phase. At 5 wt % feed of MMA, the PMMA formed was able to cover the entire surface of the rubber particles and was unevenly scattered

over the surface. At 10 wt % and 15 wt % feed of MMA, the light grey area on the rubber surface increased. At 20 wt % feed of MMA, even though the dark areas did not show an apparent difference from 10 wt % and 15 wt % nevertheless, the light grey coverage could be observed all over the rubber particles.

At a lower feed of MMA, the latex particles of grafted PMMA can be clearly seen. However, as the feed of MMA increased, the latex particulate structure becomes less distinct due to the presence of higher concentrations of PMMA. The changing of film morphology is probably indirectly related to the changes in the grafting efficiency with the feed of MMA as discussed earlier. Therefore, the feed of MMA plays an important role in the formation of the PMMA shell onto the rubber particles.

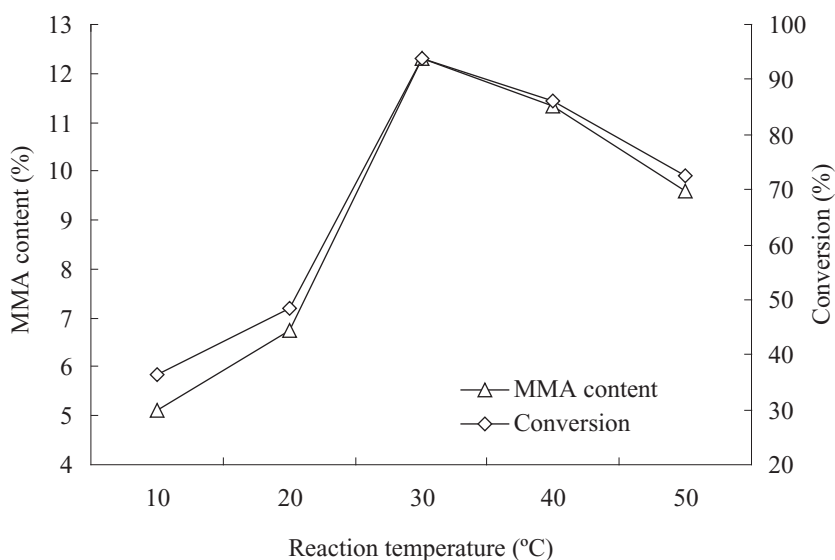


Figure 6. MMA content (%) and Conversion (%) at 15 wt % on rubber feed of MMA vs. reaction temperature.

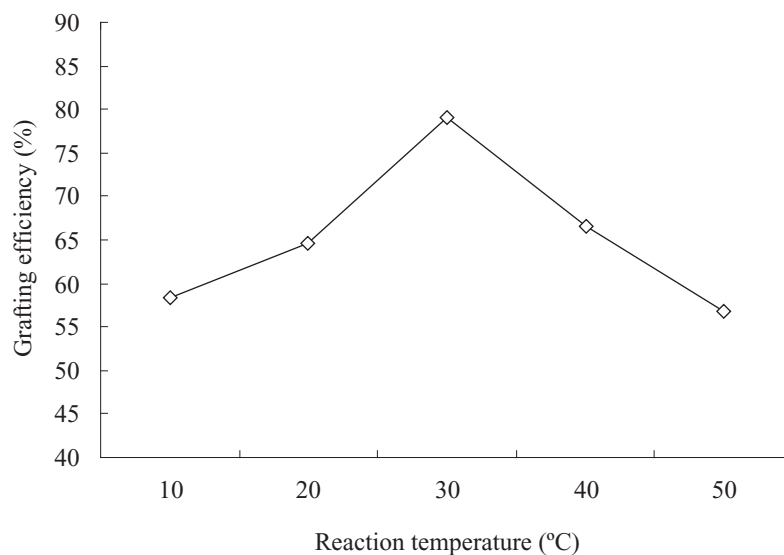


Figure 7. Grafting Efficiency (%) at 15 wt % on rubber feed of MMA vs. reaction temperature.

Comparisons of U-DPNR-graft-PMMA with E-DPNR-graft-PMMA and NR-graft-PMMA

Gel Content. The gel content results for U-DPNR-graft-PMMA, E-DPNR-graft-PMMA and NR-graft-PMMA are shown in Table 3. The gel contents of the control samples, *i.e.* U-DPNR, E-DPNR and NR, were lower than those of U-DPNR-graft-PMMA, E-DPNR-graft-PMMA and NR-graft-PMMA, which were about 90%. The increase in gel content may be explained to be due to the formation of a three dimensional network of rubber molecules during the graft-copolymerisation. It was also found that the gel content of NR was higher compared to U-DPNR and E-DPNR. This probably indicates that the deproteinisation process reduced the number of natural crosslinks formed in the HA latex.

MMA Content, Conversion and Grafting Efficiency. To study the effect of proteins

present in natural rubber on the graft-copolymerisation, the conversion and MMA content for U-DPNR-graft-PMMA were compared with those for E-DPNR-graft-PMMA and NR-graft-PMMA. Figure 9 shows a plot of MMA content *versus* feed of MMA for U-DPNR-graft-PMMA, E-DPNR-graft-PMMA and NR-graft-PMMA. The MMA content of U-DPNR-graft-PMMA was similar to that of E-DPNR-graft-PMMA, but not to that of NR-graft-PMMA. The lower gel content of NR-graft-PMMA may be explained to be due to the effect of the proteins present in NR, resulting in a lower conversion of MMA.

The conversion of MMA was also estimated for U-DPNR-graft-PMMA, E-DPNR-graft-PMMA and NR-graft-PMMA. The estimated conversion is shown in Figure 10. It can be clearly seen that the conversion of U-DPNR-graft-PMMA and E-DPNR-graft-PMMA was about 95%, much higher than the conversion of NR-graft-PMMA. Perhaps, the removal

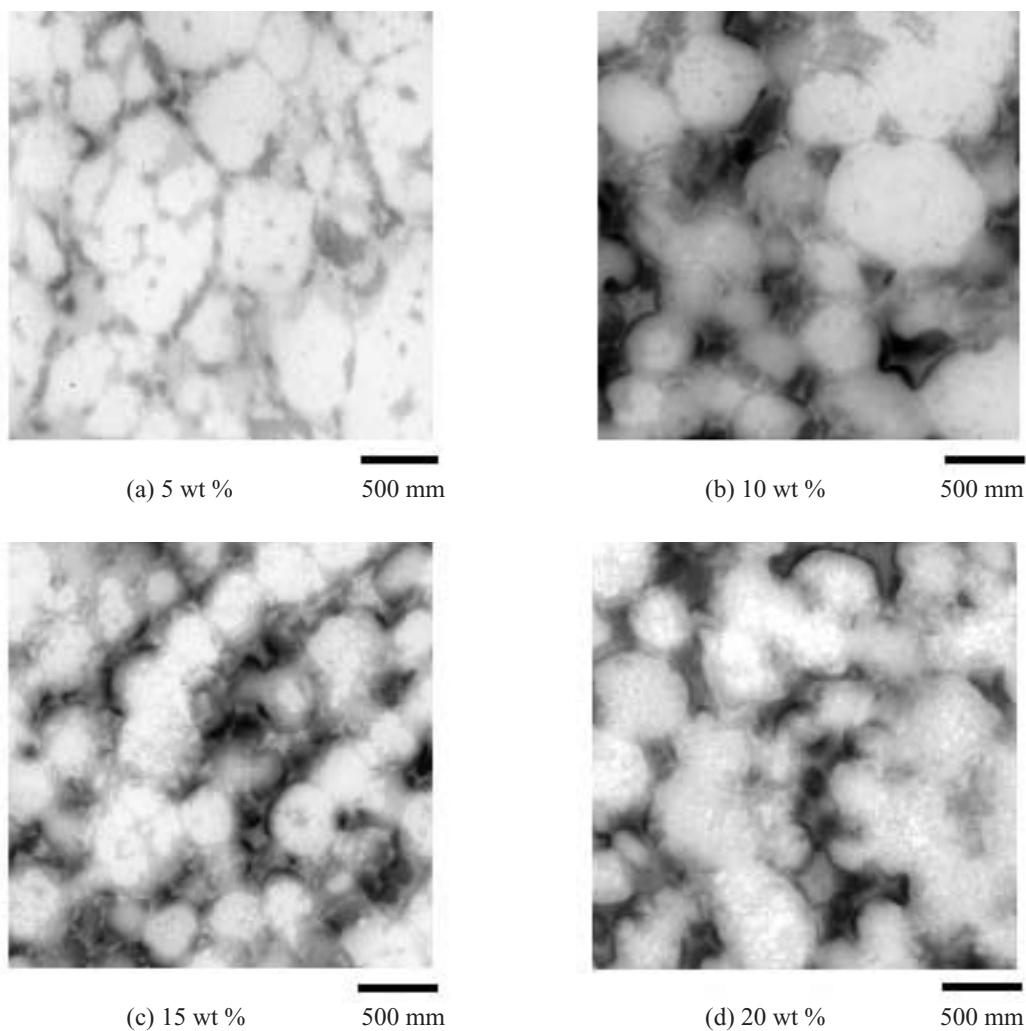


Figure 8. TEM micrographs of U-DPNR-graft-PMMA for (a) 5 wt %, (b) 10 wt %, (c) 15 wt % and (d) 20 wt % on rubber feed of MMA.

of proteins enhanced the interaction of the relevant free radicals with the rubber molecules and reduced the number of side reactions.

A plot of grafting efficiency *versus* feed of MMA is shown in Figure 11. The grafting efficiency of MMA for U-DPNR-graft-PMMA and E-DPNR-graft-PMMA was dependent

on the feed of MMA, whereas it was almost independent of the feed of MMA for NR-graft-PMMA. The highest grafting efficiency for E-DPNR-graft-PMMA and U-DPNR-graft-PMMA was about 80% at 15 wt % on rubber feed of MMA. In contrast, the grafting efficiency of NR-graft-PMMA was the lowest among the copolymers. Similarly,

TABLE 3. GEL CONTENT (%) OF U-DPNR-GRAFT-PMMA, E-DPNR-*GRAFT*-PMMA AND NR-*GRAFT*-PMMA

Samples	Feed of MMA (wt %)	Gel content (%)
U-DPNR	—	19
	5	91
	10	87
	15	89
	20	89
E-DPNR	—	19
	5	90
	10	89
	15	91
	20	88
NR	—	64
	5	90
	10	90
	15	87
	20	84

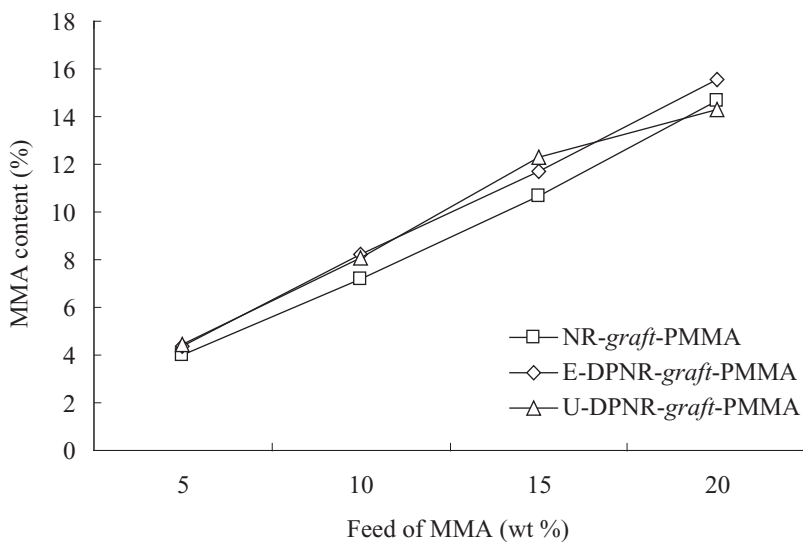


Figure 9. MMA content (%) of U-DPNR, E-DPNR and NR graft-copolymers vs. feed of MMA (wt %).

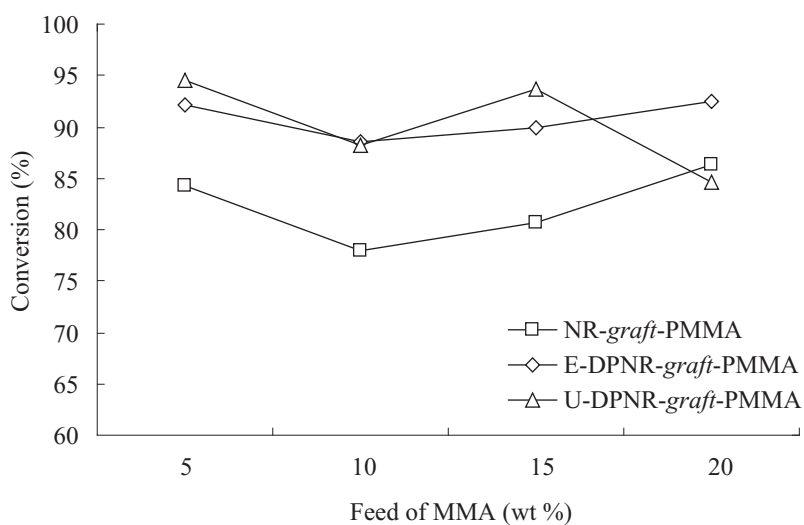


Figure 10. Monomer conversion (%) of U-DPNR, E-DPNR and NR graft-copolymers vs. feed of MMA (wt %).

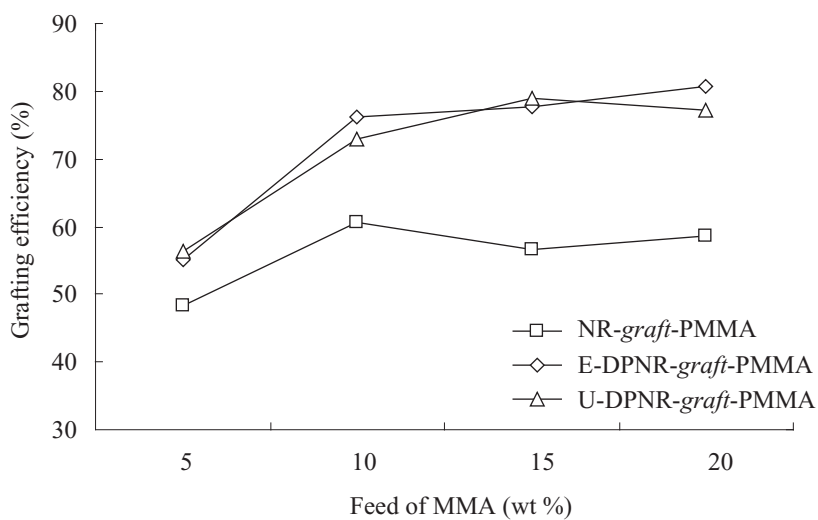


Figure 11. Grafting Efficiency (%) of U-DPNR, E-DPNR and NR graft-copolymers and vs. feed of MMA (wt %).

the removal of the proteins promotes graft-copolymerisation of MMA onto natural rubber. Given the highest conversion and grafting efficiency for U-DPNR-*graft*-PMMA was at 15 wt % on rubber feed of MMA, therefore, this was chosen as a suitable monomer concentration.

CONCLUSIONS

Graft-copolymerisation of MMA onto NR, E-DPNR and U-DPNR latices had shown that high monomer conversion and high grafting efficiency were achieved when deproteinised NR latices were used. A suitable concentration of the redox initiator system and temperature for copolymerisation were found to be 6.6×10^{-5} mol/g-rubber and 30°C, respectively. The highest monomer conversion (90%) and grafting efficiency (80%) were obtained at 15 wt % on rubber feed of MMA for U-DPNR-*graft*-PMMA. The morphology of U-DPNR-*graft*-PMMA, observed by TEM, was dependent on the feed of MMA and hence on the PMMA formed.

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REFERENCES

1. DOUG-YOUN LEE, NADARAJA SUBRAMANIAM, CHRISTOPHER M. FELLOWS AND ROBERT G. GILBERT (2002) Structure Property Relationships in Modified Natural Rubber latexes grafted with Methyl Methacrylate and Vinyl Neodecanoate. *J Polym Sci A: Polym Chem*, **40**, 809–822.
2. SEIICHI KAWAHARA, TETSUJI KAWAZURA, TAKUMI SAWADA, AND YOSHINOBU ISONO (2003) Preparation and Characterization of Natural Rubber Dispersed in Nano-matrix. *Polymer*, **44**, 4527.
3. THIRAPHATTARAPHUN, L., KIATKAM-JORNWONG, S., PRASASSARAKICH, P. AND DAMRONGLERD. S. (2001) Natural Rubber-g-Methyl Methacrylate/Poly(methyl Methacrylate) Blends. *J. Appl. Polym. Sci.*, **81**, 428.
4. LEHRLE, R.S. AND WILLIS, S.L. (1997) Modification of Natural Rubber: A study to Assess the Effect of Vinyl Acetate on the Efficiency of Grafting methyl methacrylate on Rubber in Latex Form, in the presence of azo-bis-isobutyronitrile. *Polymer*, **38**, 5937.
5. ARAYAPRANEE, W. AND REMPEL, G.L. (2004) Factorial Experimental Design for Grafting Vinyl Monomers onto Natural Rubber Latex. *J. Appl. Polym. Sci.*, **93**, 455.
6. ARAYAPRANEE, W., PRASASSARAKICH, P. AND REMPEL, G.L. (2002) Synthesis of Graft Copolymers from Natural Rubber Using Cumene Hydroperoxide Redox Initiator. *J. Appl. Polym. Sci.*, **83**, 2993.
7. VAZQUEZ, F. AND SCHNEIDER, M. (1996) Tha Pith and Morand Lambla. Effect of the Composition of Structured Rubber Particles on the Toughness of Poly(methyl Methacrylate). *Polymer International*, **41**, 1.
8. LENKA, S., NAYAK, P.L., DAS, P.A. AND MISHRA, N.S. (1985) Grafting of Vinyl

- Monomers onto Natural Rubber. I. Graft Copolymerisation of Methyl Methacrylate onto Natural Rubber Using Quinquevalent Vanadium Ion as the Initiator. *J. Appl. Polym. Sci.*, **30**, 429.
9. NAYAK, P.L. AND BASAK, A. (1986) Graft Copolymerization onto Natural Rubber. XV. Graft Copolymerisation of Methyl Methacrylate onto Natural Rubber Using a Potassium Permanganate-Ascorbic Acid Redox System. *J. Appl. Polym. Sci.*, **32**, 4271.
10. FUKUSHIMA, Y., KAWAHARA, S. AND TANAKA, Y. (1998) Synthesis of Graft Copolymers from Highly Deproteinised Natural Rubber. *J. Rubb. Res.*, **1(3)**, 154–166.
11. NAKASON, C., KAESAMAN, A. AND YIMWAN, N. (2003) Preparation of Graft Copolymers from Deproteinised and High Ammonia Concentrated Natural Rubber Latices with Methyl Methacrylate. *J. Appl. Polym. Sci.*, **87**, 68.
12. KAWAHARA, S., KLINKLAI, W., KURODA, H. AND ISONO, Y. (2004) Removal of Proteins from Natural Rubber with Urea. *Polym. Adv. Technol.*, **15**, 181.
13. KLINKLAI, W., SAITO, T., KAWAHARA, S., KEI, T., SUZUKI, Y., SAKDAPIPANICH, J.T. AND ISONO, Y. (2004) Hyper-deproteinised Natural Rubber Prepared with Urea. *J. Appl. Polym. Sci.*, **93**, 555.
14. TOSHIKI KITAI, SEIICHI KAWAHARA AND TAKUMI SAWADA (2006) Nano-matrix formed in Natural Rubber-graft-Polystyrene. *The 6th International Symposium Proceedings, Nagaoka, Japan*, 26–27 January 2006.
15. R.R.I.M TEST METHODS (1973) *SMR Bulletin* No 17, pg 15–16.