PII: S0032-3861(97)00157-2

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

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(Revised 5 February 1997)

On the basis of the proposal that highly reactive vinyl acetate (VAc) radicals could facilitate the grafting of other monomers on to natural rubber (NR), the effect of the presence of small quantities of VAc on the efficiency of grafting methyl methacrylate (MMA) on NR molecules in latex form has been studied. Several VAc concentrations have been examined, and the initiator azo-bis-isobutyronitrile was added to the systems to promote the formation of VAc radicals. There is good evidence for the formation of graft copolymer under the conditions used, but it was found that the grafting is not significantly affected by the presence of VAc. It is proposed that this could be due to the fact that the oil-soluble initiator is not accessible to the relatively large amount of VAc present in the aqueous phase. A higher than expected portion of the products was extractable with petroleum ether, and this may be attributable to the initiator inducing a small amount of degradation in the rubber. Finally, although acetone is not considered a good solvent for NR, it was found to be capable of extracting from the graft copolymers relatively large quantities of material containing the cis-1,4-polyisoprene structure. This observation is consistent with the effect that PMMA grafts on the NR molecules would have on their solubility in this solvent. © 1997 Elsevier Science Ltd.

(Keywords: natural rubber; latex; graft copolymer)

INTRODUCTION

The chemical constitution of natural rubber (NR) is determined entirely by the processes occurring in the rubber tree[1]. Although in principle it might be possible to incorporate co-monomer units into the NR backbone during this biosynthetic process, this has not yet been achieved. In this respect, NR is at a disadvantage compared with its synthetic competitors, whose properties can be varied by incorporating suitable co-monomers during synthesis. When modification of NR is required, it is necessary to rely entirely on the modification of the natural pre-formed polymer.

Currently, there is increasing awareness of environmental issues[2], and this has created a high level of interest in NR and its derivatives. The reason for this is that NR is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non-renewable oil-based resources. NR latex is the form in which rubber is exuded from the *Hevea brasiliensis* tree as an aqueous emulsion, and it would be desirable to modify the NR whilst it is in latex form for several reasons, the most important of these being that the NR not only has a very high molecular weight, but also an appreciable and widely varying gel content. Preparing a complete solution is therefore difficult if not impossible,

and even if a solution can be obtained, its viscosity can be high even at modest concentration[3].

The excellent physical properties of NR include resilience, strength and fatigue resistance, and these, together with the fact that it is a renewable resource, mean that it is a very important elastomeric material. In efforts to extend its use, there have been various methods developed in order to modify its properties. These modifications have not only been directed towards the enhancement of certain properties characteristic of NR, but also to introduce totally new properties not usually associated with NR. Reactions that have been utilized in this way include substitution[4], simple addition[5–9], cyclo-addition[9–14], electrocyclic reactions[15,16] and the 'ene' reaction[17].

Graft copolymerization has been used as a method for modifying NR in both latex form and in solution. Reactions involving free radicals have been the most widely applied in grafting processes, and such reactions have been used with a wide range of polymers and monomers[18]. Free radical initiators may promote grafting in two different ways when added to a monomer/polymer system. These are shown below, and involve transfer reactions in both cases.

Type 1: direct attack by initiator radical

$$RO\cdot + PH \rightarrow ROH + P\cdot$$

$$P\cdot + M \rightarrow \text{Graft copolymer}$$

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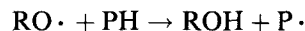
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Here, RO· represents the initiating free radical formed from, e.g. the decomposition of a peroxide, and PH is the polymer chain, containing hydrogen atoms which are sufficiently labile to be abstracted by the initiator radical[18].

Type 2: chain transfer with polymer

$$ROM_x· + PH \rightarrow ROM_xH + P·$$

$$P· + M \rightarrow \text{Graft copolymer}$$
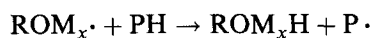
In this case, the growing long chain radical $ROM_x·$ undergoes chain transfer with the polymer, probably by hydrogen abstraction, leading to the initiation of a graft.

In both of these cases, there is also the possibility of formation of homopolymer during the grafting reaction, either by direct initiation of M, or via chain transfer with species other than the polymer backbone (e.g. monomer, solvent or initiator).

Reactions of Type 1 have been applied in order to graft monomers such as styrene (St) or methyl methacrylate (MMA) to NR in latex form[19,20]. In this case, oxy radicals of the RO· type such as result from decomposition of peroxides, were found to be much more active in direct attack on the polymer than radicals such as those obtained from decomposition of azo-compounds, e.g. azo-bis-isobutyronitrile (AIBN)[20].

Of the Type 2 grafting reactions, the MMA and St polymerizing systems are the only two that have been extensively studied and reported in rubber grafting. One reason for the lack of research on other vinyl monomers is that MMA and St are the only two monomers which have so far been shown to produce directly useable rubber latices when polymerized in NR latex under conditions that are expected to give a high degree of grafting[21]. Work with these monomers has resulted in the development of products under the trade name 'Heveaplus', and in particular the graft co-polymer with MMA has been commercialized as 'Heveaplus-MG'. The properties and applications of these materials have been reviewed[22], with particular reference to latex preparation procedures and uses of the modified latex. Interest has also been shown in the synthesis of composite materials prepared by seeded emulsion polymerization of St or MMA in NR latex, and several papers have been published on the subject[23-26].

The present study has involved the second type of graft reaction, i.e. chain transfer between growing polymer radicals and NR molecules. Early work[27] on transfer reactions of this kind used the model polyisoprenic hydrocarbon dihydromyrcene (DHM), in which the α-methylenic groups have a chemical reactivity similar to those of NR. These experiments provided values for the transfer constants C_S (i.e. DHM regarded as the solvent) listed in *Table 1*. These C_S values give the relative reactivities of the DHM molecule and the monomer

molecule towards reaction with the same long chain radical, the latter in each case corresponding to the monomer cited. From these results it can be seen that DHM is much more reactive towards the long chain vinyl acetate (VAc) radical than it is towards the styryl and MMA long chain radicals.

It has been reported[28] that VAc does not readily polymerize in synthetic or NR latices. Thus, although the rubber molecules are expected to transfer readily to the long chain VAc radical, the product radical on the rubber is apparently not particularly reactive towards VAc monomer. The results obtained[28] suggest that propagation of long chain graft copolymer from the radical centre is not occurring even over a wide range of reaction conditions. Thus, although the VAc radical is reactive, the monomer is not sufficiently reactive towards the NR radical.

It was therefore proposed in the present study that if MMA monomer were also added to the VAc/NR system, it may be possible for MMA to propagate from the radical centres readily produced on the NR backbone by VAc radical transfer. This paper describes experiments carried out to modify NR latex to test this approach. The paper also reports on attempts to quantify the level of graft copolymerization. In the study described here, the oil-soluble initiator AIBN was added to the systems to promote the formation of VAc radicals.

EXPERIMENTAL

Materials

The NR vulcanizate and the NR 'LATZ' latex were supplied by TARRC (Malaysian Rubber Producers Research Association), Hertford (UK). The latex had a dry rubber content of 59.5%. Both were used as supplied.

The monomers, acrylonitrile (AN), butyl acrylate (BA), methyl acrylate, MMA, St, VAc and 4-vinylpyridine, were supplied by Aldrich. In the swelling experiments, the monomers were all used as supplied.

For the polymerization reactions, both MMA and VAc were purified further. MMA monomer was de-inhibited prior to polymerization by washing several times with 5% w/v sodium hydroxide solution, followed by distilled water washes until neutral, and then dried using anhydrous magnesium sulfate. The resulting de-inhibited monomer was finally distilled under reduced pressure. VAc monomer was de-inhibited by fractionation under nitrogen at reduced pressure using a 1 m column packed with Fenske helices. The middle fraction was collected and used in the experiments.

All other materials were used as supplied. The AIBN was obtained from BDH, deuterated chloroform was supplied by Fluorochem, and all other solvents were obtained from Fisons Scientific. Sodium chloride was obtained from May and Baker, and anhydrous magnesium sulfate and oleic acid were both obtained from BDH.

Procedure used in swelling experiments

A strip of NR vulcanizate (6 mm × 60 mm) was immersed in the chosen monomer (200 cm³) contained within a crystallizing dish at room temperature. The change in its length due to swelling was followed by projecting a magnified image of the strip on to a vertical screen using an overhead projector. The experiment was

Table 1 Transfer constants (C_s) for DHM in different polymerizing systems[21]

Monomer	Transfer constant (C_s)
Styrene	2×10^{-4}
Methyl methacrylate	7×10^{-4}
Methyl acrylate	4×10^{-3}
Vinyl acetate	4×10^{-2}

complete when no further increase in the strip length was observed. This was taken to be the saturated swelling point for the rubber vulcanizate in that monomer at room temperature, and the percentage increase in length for this situation was calculated. The experiment was repeated using identical rubber strips with the other vinyl monomers.

Polymerization procedure

The 'LATZ' NR latex ($10 cm^3$) was placed in a $30 cm^3$ polypropylene bottle, and the MMA monomer ($1.5 cm^3$) was then added dropwise while stirring. The mixture was then continually stirred for 1 h at room temperature to allow time for the latex particles to attain equilibrium swelling; $10 cm^3$ of the emulsifier (ammonium oleate: 1 g in $40 cm^3$ distilled water) was then added. Distilled water ($2 cm^3$) and the initiator (0.072 g) were then added, and the reaction mixture was thoroughly shaken. The reaction mixture was then purged with nitrogen for approximately 15 min. The reaction was performed by tumbling the bottle for a total of 16 h end over end in a water bath maintained at 65°C. The products were then isolated, and finally dried in a vacuum oven at 40°C for approximately 24 h.

Four reaction mixtures were studied which differed in the amounts of MMA, VAc and distilled water added. (The distilled water was added in order to keep the volume of the reaction mixtures constant for each of the reactions.) *Table 2* lists the reaction mixture formulations used.

Soxhlet extraction procedures

After the products had been isolated, some Soxhlet extraction experiments were carried out to assess the extent to which the products contained insoluble material. In the initial experiments, the extraction of products was by petroleum ether (40/60) and then a further extraction was performed using acetone. The acetone extracts obtained were analysed by gel permeation chromatography (g.p.c.) in order to determine if any degradation of the polymer was occurring during extraction.

The next experimental procedure involved the Soxhlet extraction of each product, first with acetone, followed by petroleum ether, and finally with acetone for a second time.

All the extractions were carried out under nitrogen for a period of 24 h. After each extraction, the percentage of the material extracted was calculated. In addition, the soluble extracts and the insoluble portions were isolated after each extraction and analysed by ^1H and/or ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy (see below).

In addition, a sample of NR sheet cast from the latex

was Soxhlet extracted using various solvent systems as a reference for the extractions described in (*i*) below. A blend of poly(methyl methacrylate) (PMMA) and NR was made by mixing NR latex and a PMMA latex in the appropriate volumes so that the final blend contained 20% w/w PMMA molecules. A sheet cast from this blend was extracted as a reference for the extractions described in (*ii*) below.

n.m.r. spectroscopy

The ^1H and ^{13}C n.m.r. spectroscopy was carried out on samples either dissolved or swollen in deuterated chloroform. A Bruker AC300 series n.m.r. spectrometer was used.

g.p.c.

Molecular weights of the acetone extracts from the reaction products were studied using a Waters Associates liquid chromatography apparatus with a Waters differential refractomer detector R401. A flow rate of $1.5 cm^3$ min^{-1} was used, and tetrahydrofuran was the solvent. Polymer Laboratories supplied the PLgel type Universal Columns. The apparatus was calibrated using monodisperse PMMA calibration standards, also supplied by Polymer Laboratories.

RESULTS AND DISCUSSION

The products obtained when MMA monomer was present in the reactions were all similar in character as tough, rubbery, non-tacky materials. The latices tended to solidify during the reaction if VAc was present in the reaction mixture, but this was not observed with reaction mixtures I and IV, which did not contain VAc. The swelling results were examined with a view to understanding these observations. *Figure 1* shows the results obtained by swelling natural rubber vulcanizate in
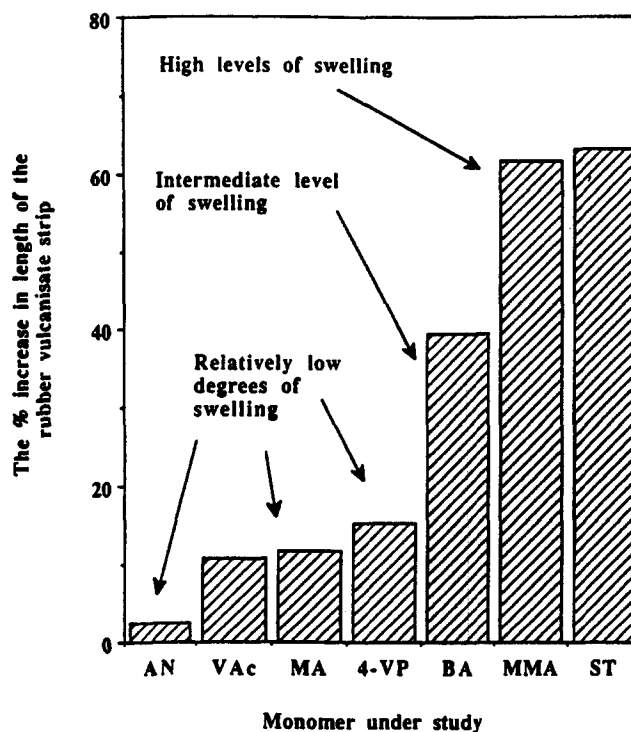

Figure 1 Percentage increase in length of vulcanized NR strips in various vinyl monomers after equilibrium swelling

Table 2 Amount of each variable reactant added to the reaction mixtures

Reactant	Sample I	Sample II	Sample III	Sample IV
NR latex (g)	10	10	10	10
MMA (cm^3)	1.5	1.5	1.5	0
Emulsifier (cm^3)	10	10	10	10
AIBN (g)	0.072	0.072	0.072	0.072
Distilled water (cm^3)	2	1.8	1.6	3.5
VAc (cm^3)	0	0.2	0.4	0

different monomers. St and MMA have previously been shown to be capable of being polymerized in NR latex without causing latex instability[25-27]. It can be seen in *Figure 1* that these two monomers show relatively high compatibility with NR vulcanizate. This was also observed for BA, which also happens to show relatively high compatibility with NR vulcanizate[28]. The other monomers depicted in *Figure 1*, however, were generally found to cause NR latex to cream during polymerization[28]. This was especially true for both VAc and AN. It can be seen that these two monomers swell the NR vulcanizate by the smallest extent, and therefore are the least compatible of the monomers with this material. It could therefore be possible that the low compatibility

of VAc with NR is the reason why the latex tends to coagulate when this monomer is polymerized within it.

(i)   Soxhlet extraction with petroleum ether (40/60) and acetone

Soxhlet extraction of the modified products with petroleum ether (40/60) was carried out as an assumed specific extraction for the linear NR molecules. Acetone extractions were then performed on the remaining solid on the assumption that this solvent would remove the free PMMA from the modified materials. *Table 3* shows the percentage extraction determined for each of the products with petroleum ether (40/60) and acetone. Any PMMA or NR polymer remaining after these extractions was assumed to be in the form of either a crosslinked gel or a grafted copolymer.

An example of a [1]H n.m.r. spectrum obtained for the first acetone extracts is shown in *Figure 2*. In addition, an example of a g.p.c. trace obtained for the acetone extracts is shown in *Figure 3*. A [1]H n.m.r. spectrum of the acetone extract from the NR cast sheet which had previously been extracted with petroleum ether (40/60) is shown in *Figure 4* for comparison. A [13]C n.m.r. spectrum of one of the insoluble portions remaining after extraction with petroleum ether and acetone is shown

Table 3 Percentage extracted from each of the samples

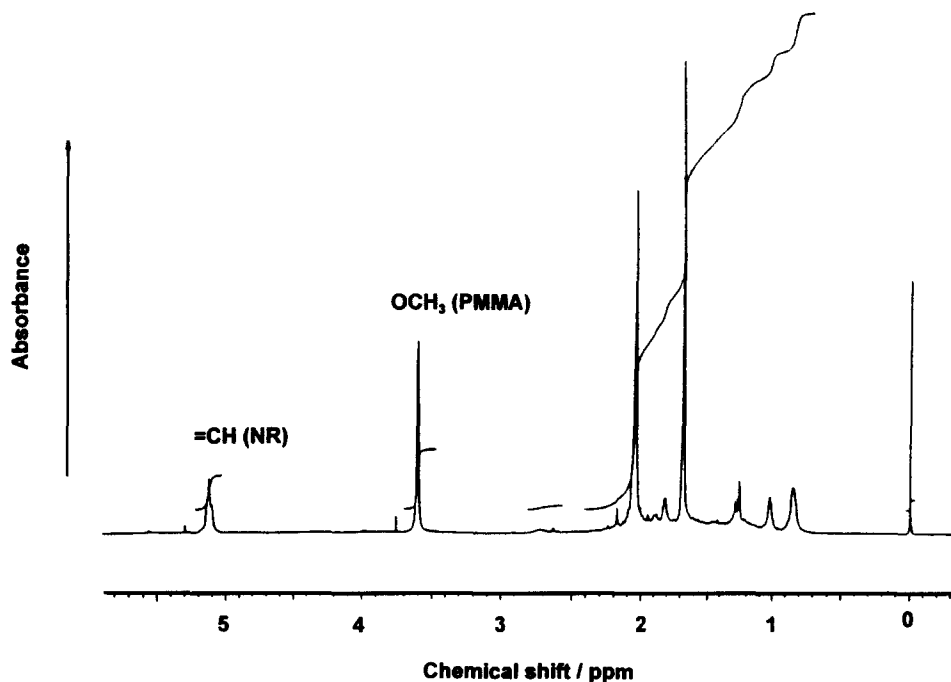| Sample code	Pet. ether extraction	Acetone extraction	Ratio PMMA/NR in acetone extract
I	30.1	31.7	1/0.55
II	23.0	25.8	1/0.36
III	28.0	57.4	1/2.75
IV	57.7	2.5	No NR extracted
NR sheet	10.9	<1.0	No NR extracted

Figure 2 Example of a [1]H n.m.r. spectrum obtained for the acetone extracts. This sample had previously been extracted with petroleum ether (40/60) prior to extraction with acetone
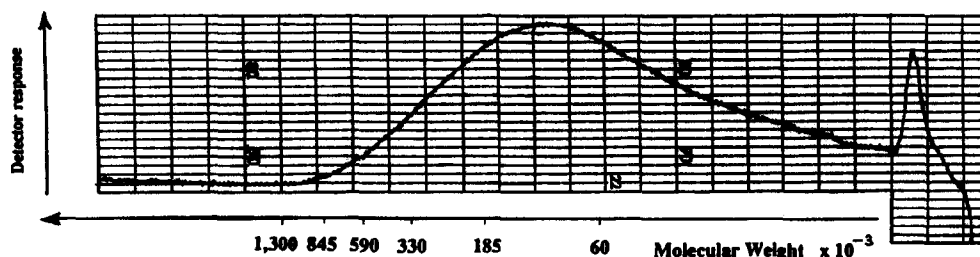

Figure 3 Example of the type of g.p.c. trace obtained for the acetone extracts. This sample had previously been extracted with petroleum ether (40/60) prior to extraction with acetone

in *Figure 5*, together with the corresponding expansion in *Figure 6*. Included for comparison is an ¹H n.m.r. spectrum of the same insoluble portion in *Figure 7*.

From the ¹H n.m.r. spectra of the petroleum ether extracts it was found that only NR molecules were being extracted using this solvent. This was expected because petroleum ether (40/60) is known to be a moderately good solvent for NR and a relatively poor one for PMMA. The amount of material extracted using petroleum ether was found to be in the region 23–30% for samples I–III (see *Table 3*). This suggests that the

amount of linear NR contained in each of the modified materials is rather similar. With sample IV (from the blank reaction containing no added monomer) petroleum ether removed a high proportion (58%), and ¹H n.m.r. spectroscopy showed the extract to be virtually 100% NR. On the other hand, the amount of material extracted from NR sheet was quite small (10%). It therefore appears that the reaction conditions are providing products with a higher proportion extractable by petroleum ether. A plausible explanation of this could be that some degradation of the NR backbone has led to
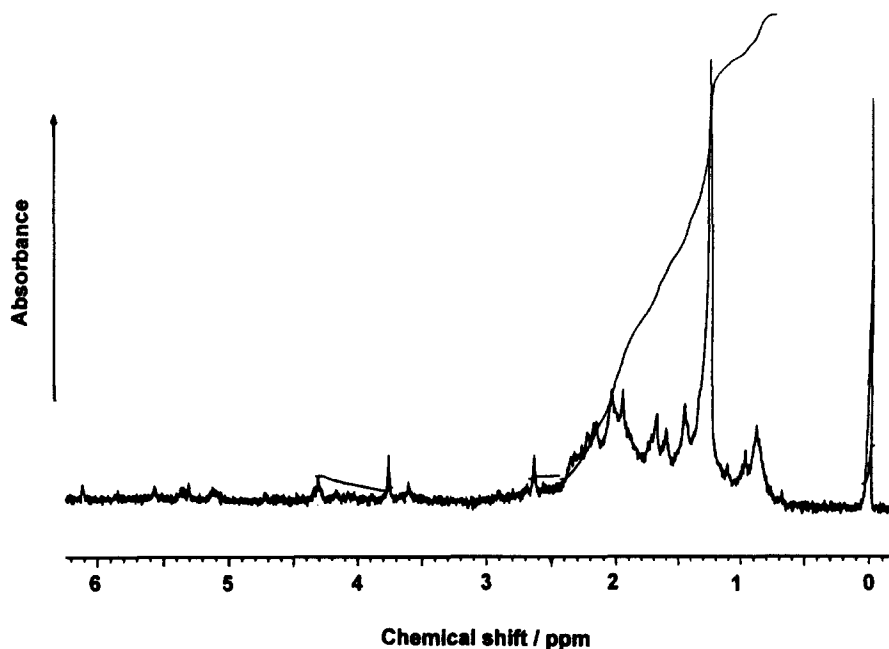

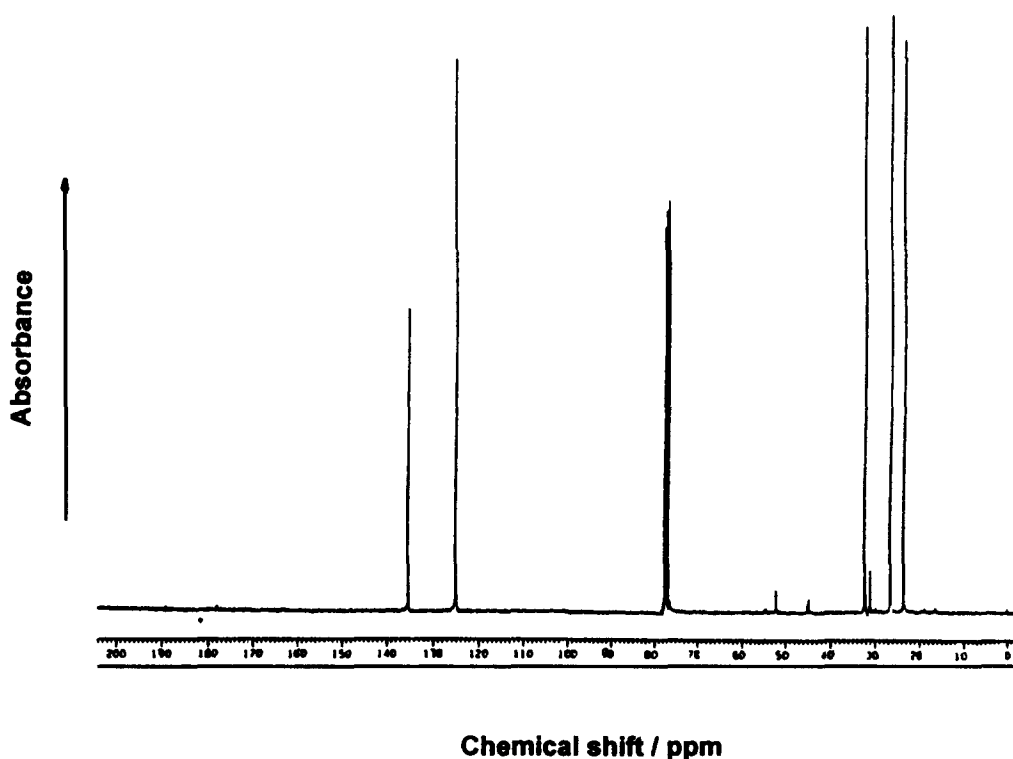**Figure 4** ¹H n.m.r. spectrum for the acetone extract obtained from the NR cast sheet

Figure 5 Example of a ¹³C n.m.r. spectrum obtained for the insoluble portions remaining after extraction with petroleum ether (40/60) and acetone

a reduction in molecular weight of the rubber molecules. Such a reduction in molecular weight would be expected to lead to a higher petroleum ether extractable content. Hourston and Romain[25] have reported degradation of rubber by AIBN initiator. They found that when AIBN was used as the initiator for the polymerization of St in NR latex, the amount of material extracted with petroleum ether was much higher than for compositionally similar compounds produced using an amine-activated hydroperoxide initiating system. They also

found that at polystyrene contents of 10% w/w, the AIBN-induced degradation was not markedly deleterious to the physical properties of the resulting modified materials. This was found to be especially so if a significant amount of crosslinking was present in the sample.

The results for acetone extraction experiments on materials that had previously been extracted with petroleum ether show some interesting features. It can be seen from the ^{1}H n.m.r. spectra obtained for the
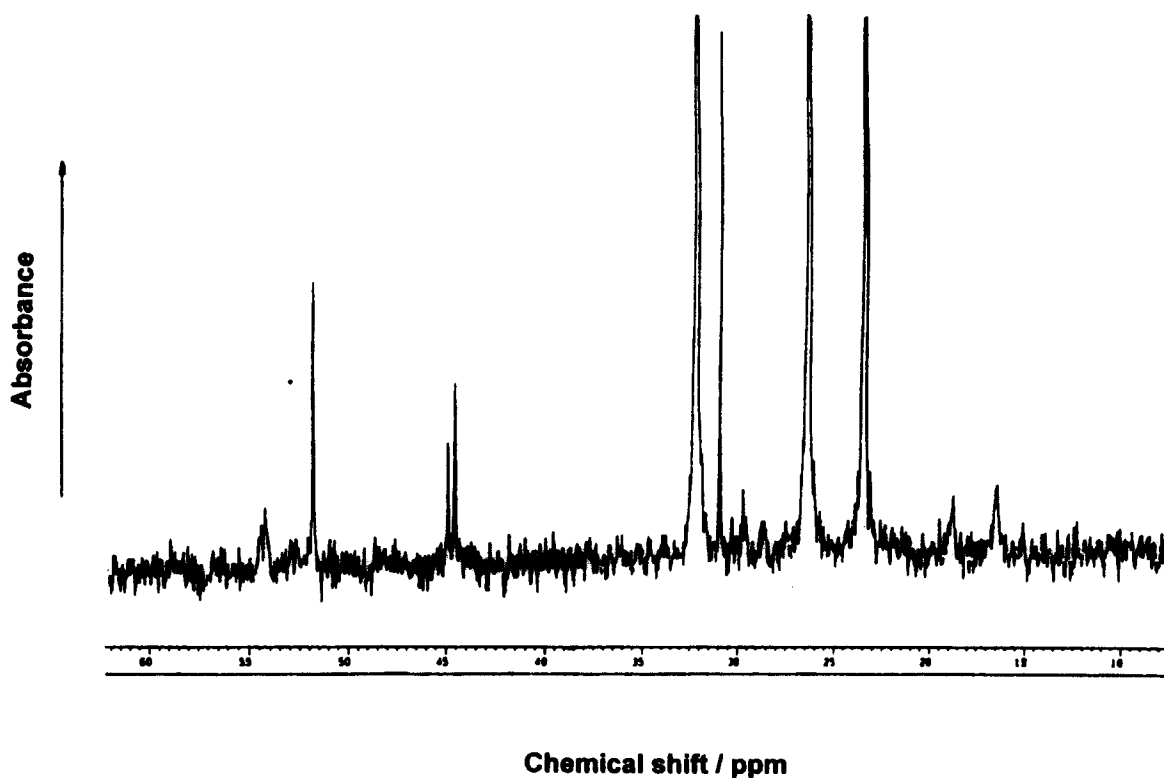

Chemical shift / ppm

Figure 6 Expansion of the ^{13}C n.m.r. spectrum shown in *Figure 5*
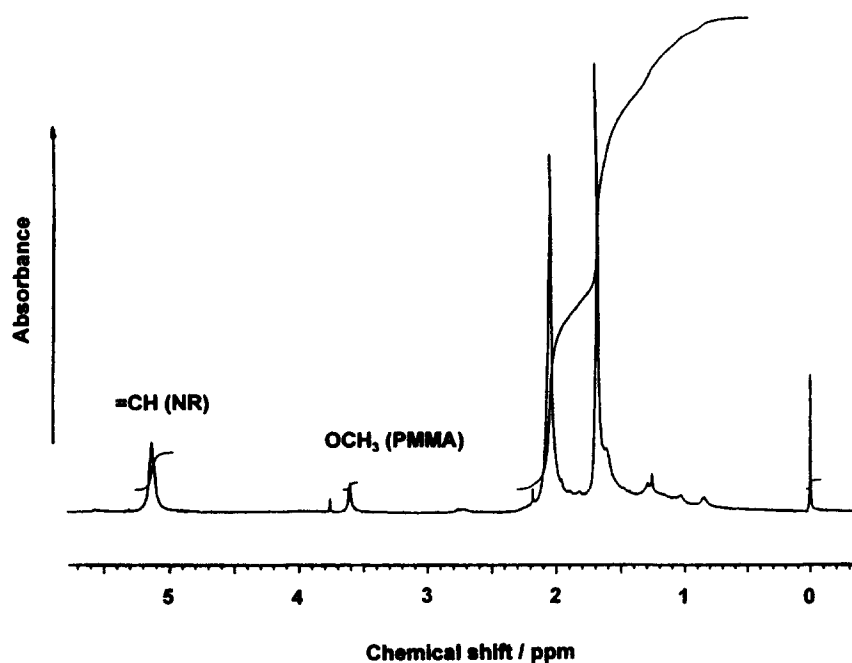

Chemical shift / ppm

Figure 7 Example of a ^{1}H n.m.r. spectrum obtained for the insoluble portions remaining after extraction with petroleum ether and acetone

acetone extracts (e.g. *Figure 2*) that both NR and PMMA structures are present. Also, it is surprising that the amounts of rubber extracted with this solvent are relatively high, in view of the fact that acetone is not regarded as a good solvent for NR. It is therefore probable that the rubber extracted with acetone from these samples is largely grafted to the PMMA chains. The acetone extracts could therefore be a mixture of both PMMA homopolymer and grafted PMMA-*graft*-NR.

The amount of material extracted from the blank (sample IV) using acetone is relatively small compared with the amount extracted from the other reaction products. This is also the case for the amount extracted by acetone from the NR sheet. Analysis of these acetone extracts using ^{1}H n.m.r. spectroscopy (*Figure 4*) showed the presence of little, if any, NR. This provides evidence that the high extractions from the modified samples using acetone is not due to AIBN-induced degradation of the NR backbone, but to the presence of graft copolymers in the modified materials. If AIBN-induced degradation were solely responsible for these high extractions with acetone, then acetone would be expected to have removed a higher proportion of sample IV than was the case.

The g.p.c. traces of the acetone-soluble extracts show wide molecular weight distributions for each of the modified materials. However, only low molecular weight

material was extracted from the NR cast sheet using acetone, and it is thought that this corresponds to artefacts such as emulsifier and protein. The g.p.c. results show that a considerable portion of high molecular weight material can be extracted from the modified materials. It is known that NR contains very high molecular weight *cis*-1,4-polyisoprene[29], but it seems surprising that the very high molecular weight rubber would be extracted using acetone, even if grafted to PMMA molecules.

From the ^{13}C n.m.r. analysis of the materials remaining after extraction with first petroleum ether and then acetone it is obvious that both NR and PMMA structures are present. An example is shown in *Figure 5*, together with the expansion in *Figure 6*. An example of a ^{1}H n.m.r. spectrum obtained for the same material is shown in *Figure 7*. All of these show that both NR and PMMA structures are present. This gives a strong indication that some MMA has graft-copolymerized with the insoluble portion of the NR. This is in addition to the MMA-*co*-NR graft copolymer that was extracted with acetone.

(ii)   Extraction with acetone, petroleum ether (40/60) and acetone

Further extraction experiments were performed with acetone and petroleum ether, with the order of extraction

Table 4 Percentage extracted from each of the samples

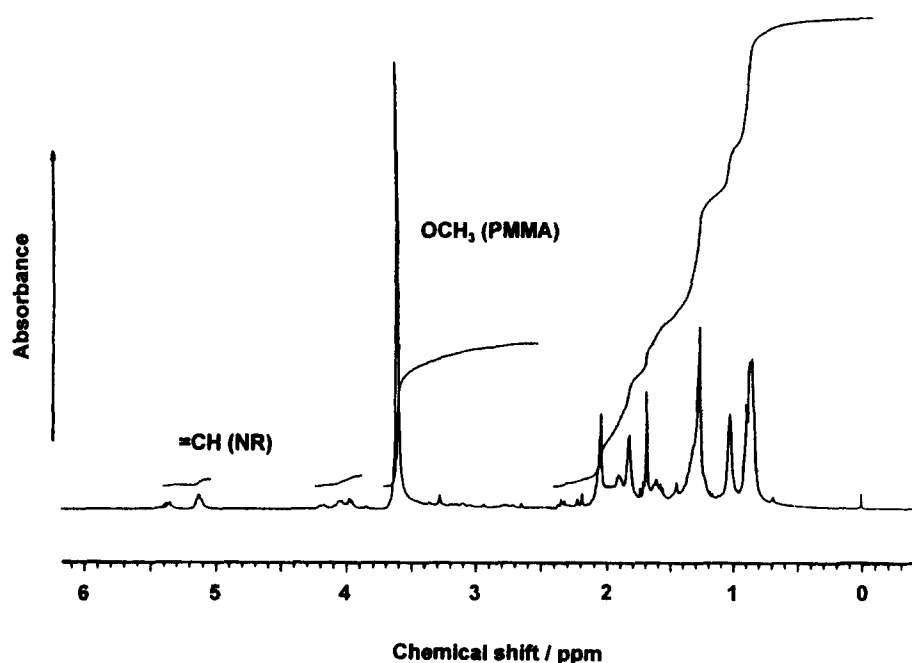| Sample code	1st acetone extraction	Pet. ether extraction	2nd acetone extraction	Ratio PMMA/NR in 1st acetone extract
I	13.2	21.6	1.3	1/0.17
II	10.2	9.4	2.1	1/0.10
III	12.2	15.5	2.4	1/0.08
PMMA/NR blend	19.0	6.09	<1.0	No NR extracted
NR sheet	2–3	NA	NA	No NR extracted

Figure 8   Example of a ^{1}H n.m.r. spectrum obtained for the first acetone extracts from the modified materials

now being changed. This was done in an attempt to determine whether the order of the extraction solvent had any effect on the extractable content of the modified materials. In this work a second acetone extraction was performed after the petroleum ether extraction in order to remove any residual PMMA homopolymer. Because the petroleum ether should have removed the majority of the linear NR molecules, the product would be expected to be relatively rich in PMMA and therefore should swell more readily in acetone; this would make the extraction of PMMA and PMMA-rich material more efficient. *Table 4* shows the percentage extraction determined for each of the products with acetone, petroleum ether (40/60) and acetone, respectively.

An example of the type of ^{1}H n.m.r. spectrum obtained for the first acetone extract of a modified material is shown in *Figure 8*. The ^{1}H n.m.r. spectrum for the acetone-soluble extract of the equivalent NR/PMMA blend prepared from the corresponding latex is shown in *Figure 9*. In addition, an example of the type of ^{1}H n.m.r. spectrum obtained for the insoluble portions after extraction with acetone, petroleum either (40/60) and acetone is shown in *Figure 10*. From *Figure 8*, it can be seen that both NR and PMMA structures are present, and that the NR structures are present at significant concentration. However, no NR of any significance was removed from either the PMMA/NR blend or the NR sheet. This therefore confirms the earlier proposal that
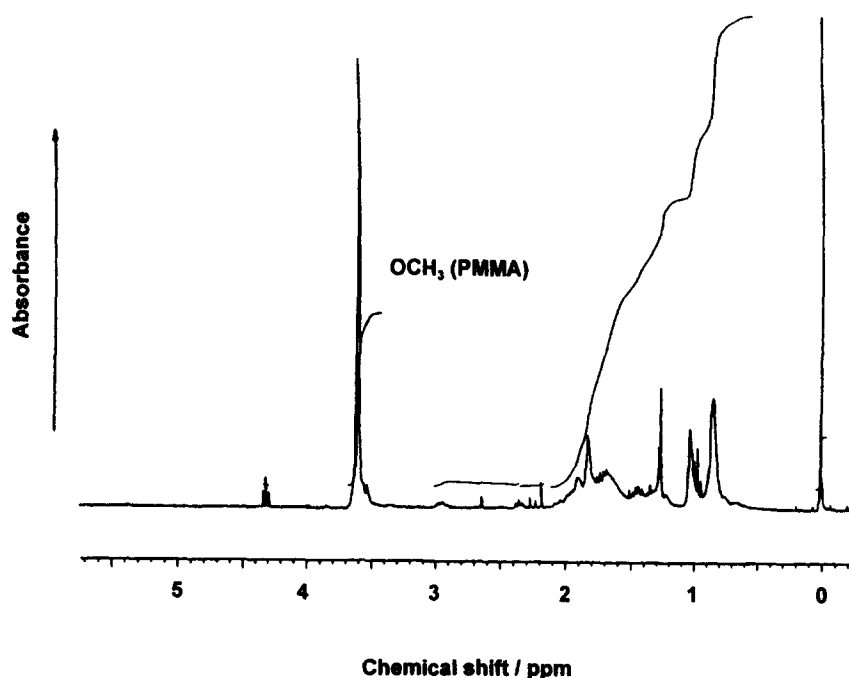

Figure 9 ^{1}H n.m.r. spectrum obtained for the first acetone extract from the NR/PMMA latex blend
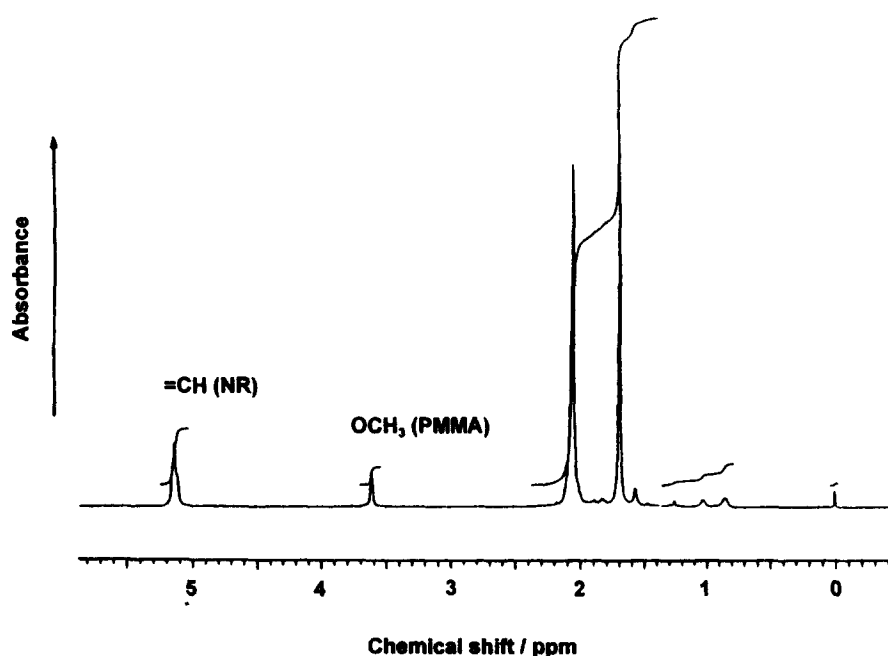

Figure 10 Example of a ^{1}H n.m.r. spectrum obtained for the insoluble portions remaining after extraction with acetone, petroleum ether and acetone

some of the NR molecules extracted with acetone exist as grafts on PMMA molecules.

The amount of NR extracted using acetone as the first extraction solvent is smaller than the amount of this material extracted when acetone was used as an extraction solvent on materials that had previously been extracted using petroleum ether. This is probably due to the fact that by first extracting the modified materials with petroleum ether, a large proportion of the NR molecules have been removed. The material then being Soxhlet extracted with acetone would contain less NR, and this could have various consequences. For example, lower levels of NR should allow the material being extracted to swell more effectively in acetone because the material is relatively richer in PMMA. This would make the extraction process more effective. Also, NR molecules could be expected to interact with the NR-*graft*-PMMA molecules, thus making their removal by Soxhlet extraction with acetone more difficult.

The second acetone extraction removed very little material from the samples, and the extracts again showed a mixture of NR and PMMA structures.

Analysis of the insoluble portion after extraction with acetone, petroleum ether and acetone by ^{1}H n.m.r. spectroscopy showed the presence of PMMA in all the modified samples produced. This gives further evidence that PMMA molecules are grafted on to NR molecules remaining in the insoluble portion.

The objective underlying the addition of VAc to the reaction mixtures were explained at the start of this paper. If we assume that the PMMA remaining in the modified materials after the first and second acetone extractions is graft copolymer, then it seems that the addition of VAc to the reaction mixture does not have any significant effect on the resulting graft copolymer content under the conditions used, and we must therefore conclude that the objectives have not been fulfilled. On the basis that VAc monomer does show a small, but significant degree of compatibility with NR molecules according to the swelling experiments, it would be expected to migrate at least to some degree into the NR latex particles where reaction with primary radicals might have been expected. However, it must be borne in mind that VAc monomer is quite water-soluble and in this phase it would not have ready access to the initiator fragments which are generated by this oil-soluble initiator in the NR latex particles and in the monomer droplets.

CONCLUSIONS

The following conclusions can be summarized as arising from the present study.

(a) When VAc is present in the graft copolymerization of MMA in NR latex, there is graft copolymer formed under the conditions employed, but the level of grafting does not seem to have been affected significantly by the presence of the VAc. Thus, the initial proposal that the presence of VAc would facilitate the grafting has not been fulfilled. The fact that a high proportion of the VAc is present in the water phase, and that the initiator is oil soluble, is offered as a possible explanation of the failure of the VAc to influence the grafting.

(b) A higher than expected petroleum ether extractable content in the reaction mixtures may be associated with the use of AIBN in the reaction mixtures. It has been proposed that the initiator could be inducing some degradation of the rubber backbone, but this is not an important factor.

(c) It has been found that although acetone is not considered a solvent for NR, it was capable of extracting relatively large quantities of *cis*-1,4-polyisoprene from the modified materials. This supports the conclusion that PMMA-*graft*-NR formation has occurred. A further consequence of this is that the estimation of the level of graft copolymer is more complicated than can be achieved by simply assuming that unextracted material is the only graft copolymer contained in the reaction products. The present study has shown such an assumption to be invalid.

In the light of conclusion (a) above, a study of the grafting in the presence of water-soluble initiators is in progress, and the results will be reported in due course.

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