

Graft Copolymerisation of Some Hydrophilic Vinyl Monomers in Natural Rubber

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Attempts have been made to graft hydrophilic vinyl monomers such as 2-hydroxyethyl methacrylate, n-vinyl pyrrolidone and methacrylic acid onto natural rubber (NR) using procedures similar to those for grafting methyl methacrylate monomer onto NR latex in order to use the copolymers as a contact lens material. However, these hydrophilic monomers could not be grafted with hydroperoxide-polyamine and ammonium persulphate-sodium meta bisulphite initiator systems due to their high solubilities in the water phase of NR latex.

The monomer, 2-hydroxyethyl methacrylate could not be grafted onto dry NR in benzene solution because of its high self propagation tendency. A blend of homopolymers was produced.

The reduction of the pendant methacrylate groups on NR-methyl methacrylate graft copolymer with LiAlH_4 in tetrahydrofuran solution introduced hydroxyl groups and hydrophilicity, and reduced the transparency of the reaction product.

Polymers for contact lens applications are often required to possess a spectrum of properties which are not generally found in any one polymer. The five major requirements of a contact lens are transparency, high oxygen permeability, sufficient mechanical properties to resist the deforming force of the eyelid during the blink cycle, wettability by the tear fluid and low protein absorbance¹. A continuous-wear contact lens can be worn in the eye for successive day and night periods without causing any adverse effect on the eye and it must possess an oxygen permeability coefficient sufficiently high to meet the oxygen consumption rate of the cornea.

Since the copolymerisation provides a balance of the properties of the corresponding homopolymers, the graft copolymerisation would effectively combine the desirable properties of an oxygen-permeable polymer with a hydrophilic monomer in order to produce a contact lens material.

Natural rubber (NR) is chosen for the backbone polymer because of its high oxygen per-

meability coefficient² [238×10^{-10} cc (STP), mm, cm^{-2} , s^{-1} , cmHg^{-1}] and its appropriate mechanical properties. 2-hydroxyethyl methacrylate (HEMA), n-vinyl pyrrolidone (NVP) and methacrylic acid are chosen as hydrophilic monomers to graft onto the polyisoprene backbone chain.

HEMA is a suitable monomer for contact lens applications due to its hydrophilicity³ and polyHEMA hydrogels have been used in biomedical applications since 1960. HEMA monomer has been grafted onto ethylene-vinyl acetate copolymer⁴, cellulose⁵, silk and wool⁶. PolyNVP has been used as a contact lens material, blood plasma extender and is widely used as a co-monomer for modifying less expensive monomers by enhancing hydrophilicity, improving adhesion properties and increasing softening points of the copolymers. Grafting NVP has been performed by pre-radiation techniques followed by treatment with monomer, whereas other methods involved direct grafting in the presence of azo or peroxide catalysts. NVP has been grafted onto polyacrylonitrile⁷, cellulose⁸ and nylon⁹.

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Grafting methacrylic acid esters, styrene and some other vinyl monomers onto NR has been the subject of a large number of investigations¹⁰⁻¹⁴. Methyl methacrylate (MMA) grafted NR is a commercial product known as 'Hevea-plus MG' and it is used in solvent adhesives and flexible hard mouldings¹⁵.

This paper discusses the unsatisfactory results¹⁶ of some attempts to graft hydrophilic monomers such as HEMA, NVP and methacrylic acid (MA) onto NR. In addition, grafting MMA monomer onto NR and reducing the grafted methacrylate group by LiAlH_4 -tetrahydrofuran solution was attempted to enhance the hydrophilicity to the copolymer.

MATERIALS

NR latex containing 62.5% NR was the product of W.M. Symington and Sons Ltd. and it was used as received. MMA, HEMA and NVP monomers were the products of BDH Chemicals Ltd. and they were distilled prior to use. Tert-butyl hydroperoxide, 10% tetraethylene pentamine and MA monomer were the products of Koch-Light Labs. Ltd. and they were used as received.

METHODS

Grafting vinyl monomers onto NR latex with polyamine activated hydroperoxide initiators.

In a typical procedure, 30 parts of 2% aqueous NH_3 solution was added to 100 parts of NR latex and the mixture was stirred mechanically in a split resin flask at 20°C. 5-30 parts monomer was mixed with 0.18 parts tert-butyl hydroperoxide and 0.3 parts oleic acid and these were added to the NR latex solution with moderately vigorous stirring and the mixture was agitated for 15 min. 0.8 parts 10% tetraethylene pentamine solution was then added to the mixture and stirring continued for a further 10 min. The mixture was left for at least 18 h to permit completion of polymerisation. The product was then isolated by running the latex into at least three times its volume of boiling water containing 0.5% formic acid, the resulting crumb was filtered, washed and dried.

Grafting vinyl monomers onto NR latex with ammonium persulphate-sodium meta bisulphite initiators. 10 parts monomer was added to 100 parts NR latex and the mixture was stirred in a split resin flask for 15 min. 1 part of 12% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 1 part of 6% $\text{Na}_2\text{S}_2\text{O}_5$ (in water) solutions were added to the mixture and stirring continued for a further 15 min. The mixture was then left for at least 12 h to permit the completion of polymerisation.

Grafting vinyl monomers onto NR in benzene solution with benzoyl peroxide initiator.

10 parts monomer solution containing 1% benzoyl peroxide was added to 200 parts 10% NR in benzene solution at 20°C and the mixture was agitated for 15 min. The mixture was then heated to 60°C in 30 min and was kept at this temperature for 8 h.

Reduction of NR-MMA graft copolymer.

5% solution of NR-MMA graft copolymer in tetrahydrofuran was added slowly with vigorous stirring to the 7% solution of LiAlH_4 in dry tetrahydrofuran. The copolymer converted into a jelly and was heated at 66°C under reflux for two days. It was then cooled to 0°C by pouring into a mixture of dilute HCl and ice. Sufficient methanol was added until the polymer precipitated and the solution was centrifuged¹⁷. The insoluble part was separated and dried.

Compression mouldings of the copolymerisation products.

The copolymerisation products were mixed with 2% dicumyl peroxide on a two-roll mill. The samples were then compression moulded at 180°C, under 1.4 MPa pressure for 45 min using polished metal plates. Cylindrical thin mouldings were formed.

Fractional precipitation of the copolymerisation products.

Fractional precipitation was used to determine the unreacted natural rubber content in the copolymerisation products¹⁸. Benzene-petroleum ether, 50/50 (60°C-80°C) solution was used to dissolve the products. 1 g of reaction product was left overnight in 200 ml of this solution; it was then stirred at 40°C for 30 min. The undissolved solid content was centrifuged and separated. 20% methanol

(containing 0.01% CaCl_2) was added to the remaining solution. The unreacted polyisoprene was precipitated, dried under vacuum and weighed. Percentages of unreacted and reacted NR were calculated. The unreacted polyisoprene film was formed on the cell from CHCl_3 solution and the structure of the polymer was identified by IR spectrophotometric analysis using Perkin Elmer Model 457 instrument in order to determine the presence of grafted polymer. The presence of the ester group peak at 1740 cm^{-1} was detected. For MMA grafts, the peaks at 1160 cm^{-1} , 1200 cm^{-1} and 1260 cm^{-1} were also considered.

Contact angle measurements. The contact angle is the angle between the liquid-vapour and liquid-solid interfaces of a drop of the liquid on a solid surface. The contact angle is determined by constructing a tangent to the profile of the drop at the point of contact with the solid surface. Since the tendency for a drop of liquid to spread over a plane surface increases as the contact angle decreases, the contact angle provides a useful inverse measure of hydrophilicity.

Prior to contact angle measurements, the polymer surfaces were cleaned by washing with a detergent solution followed by a thorough rinsing with distilled water and dried. The sessile drop of distilled water was formed on the surface of the polymer through a hypodermic needle. The contact angles were determined directly by using a special low-power microscope as the average of three measurements and reported within a range of $\pm 1^\circ$.

RESULTS AND DISCUSSION

Graft Copolymerisations

The results of graft copolymerisations of vinyl monomers onto NR latex with polyamine activated tert-butyl hydroperoxide initiator and with ammonium persulphate, sodium meta bisulphite initiators are given in *Tables 1* and *2* respectively. The results of the graft copolymerisations of MMA and HEMA monomers onto dry NR in benzene solution with benzoyl peroxide initiator are given in *Table 3*.

In the graft copolymerisation of NR latex, it is necessary that the monomer is absorbed by the rubber particles and the polymerisation takes place within the swollen globules. When MMA monomer was stirred into latex, it first separated into an upper layer, but fairly rapidly, disappeared as a separate liquid phase and soon afterwards no visible separation of monomer occurred on standing. This was due to the slight solubility of MMA in the water phase of latex. However, HEMA monomer has a high water solubility, NVP and MA monomers are also much more water-soluble than MMA and during the course of the copolymerisation, these monomers were homopolymerised in the water phase of the NR latex.

Consequently, as seen from *Tables 1-3*, only MMA-NR graft copolymer was produced in these reactions with used initiator systems. Blends of homopolymers were formed with other vinyl monomer graft copolymerisation attempts. The blends were unsatisfactory for the control of the elastic and hydrophilicity properties of the product.

Ammonium persulphate-sodium meta bisulphite initiator system has lower initiating efficiency than hydroperoxide system and was used for this reason. However, HEMA monomer homopolymerised with this system too. A powerful stabilising system in latex is required, which prevents HEMA monomer dissolving in the water phase of NR latex and which forces HEMA to be absorbed in NR particles. The formation of magnesium hydroxide gel in the water phase of latex may be suggested as a suitable stabilising system for HEMA monomer¹⁹. On the other hand, the use of the water-insoluble initiator systems may force the monomers to polymerise on the surface of the latex particles.

It was not possible to graft HEMA onto dry NR in benzene solution (*Table 3*) due to the higher rate and the preference of the reaction between HEMA monomer and propagating polyHEMA chain rather than the reaction between HEMA monomer and active species on the NR backbone.

TABLE 1. GRAFT COPOLYMERISATIONS OF VINYL MONOMERS IN NR LATEX WITH
POLYAMINE ACTIVATED HYDROPEROXIDE INITIATOR

Copolymer No.	NR latex	Parts by weight				Reacted NR (%)	Colour and transparency	Water contact angle (°)	Comments
		MMA	HEMA	NVP	MA				
1	100	10	—	—	—	7	Light yellow, transparent	82 ± 1	NR-MMA graft copolymer
2	100	28	—	—	—	19	Light yellow, transparent	77 ± 1	NR-MMA graft copolymer
3	100	15	5	—	—	11	Brown, translucent	79 ± 1	NR-MMA graft copolymer and polyHEMA blend
4	100	—	30	—	—	0	Brown, transparent	74 ± 1	Blend of NR and polyHEMA homopolymers
5	100	—	5	—	—	0	Brown, transparent	76 ± 1	Blend of NR and polyHEMA homopolymers
6	100	—	—	25	—	0	Brown, transparent	78 ± 1	Blend of NR and polyNVP homopolymers
7	100	20	—	—	5	13	Light yellow, transparent	82 ± 1	NR-MMA graft copolymer and polyMA blend

TABLE 2. GRAFT COPOLYMERISATIONS OF MMA AND HEMA MONOMERS IN NR LATEX WITH AMMONIUM PERSULPHATE, SODIUM METABISULFITE INITIATORS

Copolymer No.	Parts by weight			Reacted NR (%)	Colour and transparency	Water contact angle (°)	Comments
	NR latex	MMA	HEMA				
1	100	10	—	8	Light yellow, transparent	78 ± 1	NR-MMA graft copolymer
2	100	—	10	0	Brown, transparent	76 ± 1	Blend of NR and polyHEMA homopolymers

TABLE 3. GRAFT COPOLYMERISATIONS OF MMA AND HEMA MONOMERS ONTO DRY NR IN BENZENE SOLUTION WITH BENZOYL PEROXIDE INITIATOR

Copolymer No.	Parts by weight			Reacted NR (%)	Colour and transparency	Water contact angle (°)	Comments
	NR latex	MMA	HEMA				
1	20	10	—	28	Light yellow, opaque	73 ± 1	NR-MMA graft copolymer
2	20	—	10	0	Brown, opaque	79 ± 1	Blend of NR and polyHEMA homopolymers

TABLE 4. REDUCED NR-MMA GRAFT COPOLYMERS BY LiAlH_4 IN TETRAHYDROFURAN SOLUTION

Reaction No.	Reduced copolymer	Colour and transparency	Water contact angle (°)
1	Table 1, No: 1	Dark yellow, opaque	76 ± 1
2	Table 1, No: 2	Brown, opaque	73 ± 1
3	Table 2, No: 1	Dark yellow, opaque	75 ± 1
4	Table 3, No: 1	Brown, opaque	71 ± 1

The transparency and colour of the moulded discs depended upon the structure of the copolymerisation products. NR-MMA graft copolymer discs were pale yellow in colour and their transparency decreased with the increase of the MMA content in graft copolymer. The transparency of NR-MMA graft copolymer was a result of both the similarity in the refractive indices ($\text{NR} = 1.52$, $\text{PMMA} \approx 1.49$) and possible good phase-separation of the long-chain

PMMA from the main chain of polyisoprene. The rigidity of the discs increased with the increase in the MMA content.

The water contact angle measurements of the discs showed that there was an increase in wettability of both NR-MMA graft and NR-homopolymer blend products compared with pure NR itself. (The water contact angle of pure NR was 82°). However these products were

found to be too hydrophobic for contact lens applications since the water contact angles of commercial lenses²⁰ are between 60° and 70°.

Reduction of NR-MMA Graft Copolymer

The results of the reduction of the NR-MMA graft copolymer products by LiAlH_4 in tetrahydrofuran solution are given in Table 4. The hydrophilicity was increased by the substitution of hydroxyl groups with methacrylate groups as seen in water contact angle results of the graft copolymer discs and confirmed with IR spectroscopy. However the material did not seem to be suitable for contact lens applications since the reduction reaction decreased the transparency of the copolymer. This was due to the fact that, with the reduction of ester group into hydroxyl group, the chemical environment prevented a good phase-separation and since the refractive indices were different from each other, the opaqueness was usual.

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