

# Modification of Natural Rubber Latex. II. Natural Rubber Poly(methyl Methacrylate) Composite Latexes Synthesized Using an Amine-Activated Hydroperoxide

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## Synopsis

Composite latex particles based on natural rubber latex have been synthesized to yield materials which may be formally regarded as interpenetrating polymer networks and semiinterpenetrating polymer networks. Methyl methacrylate was added to a carefully stabilized natural rubber latex and polymerized *in situ* using an amine-activated initiator, *tert*-butyl hydroperoxide. The resulting materials were cast to yield solid sheets. The morphology of the materials was determined both by transmission electron microscopy and by dynamic mechanical analysis. In addition the stress-strain behavior was studied.

## INTRODUCTION

Natural rubber (NR) has the advantage of renewability conferred on it by its biological origin. In addition, it has an attractive range of properties which allows it to compete successfully with synthetic rubbers.

The backbone unsaturation in NR, *cis*-polyisoprene, facilitates certain types of chemical modification to yield a range of modified NR polymers. In NR the all-*cis*, trialkyl-substituted double bond is electron-rich via both hyperconjugative and inductive effects, but is also somewhat sterically hindered. Chemical reactions directly on NR latex or on dry rubber can be influenced by the presence of nonrubber contaminants such as proteins. These contaminants, for example, can act as catalyst inhibitors and can influence the course of free-radical reactions.<sup>1</sup> The modification of NR may conveniently be divided into two classes: low-level and high-level modifications. In the former class, modification is often around 1 mol %<sup>2</sup> while in the latter it may be in the 20–100 mol %<sup>2</sup> range to endow NR with new chemical and physical properties which effectively upgrade it into new materials.

The modification of NR while still in the latex form is clearly more challenging than in the dry state. The work to be reported in this series of papers<sup>3</sup> is concerned with such a modification and is a logical extension of earlier studies<sup>4</sup> in which NR latex particles were swollen with a monomer, methyl methacrylate (MMA), which was then polymerized. This was an attempt to produce PMMA-grafted NR. In fact, the level of grafting obtained was quite low, but such materials, despite some obvious drawbacks such as cracking on casting, have become commercial products known as Hevea Plus.<sup>4–6</sup> Because in such a process the free-radical initiator can lead to some

crosslinking of the original NR latex particles, such materials could be classified as latex semi-IPNs. An IPN is formed when a pair of networks are synthesized in such a manner that at least one of the networks has been formed and/or crosslinked in intimate juxtaposition with the other. IPNs are classified<sup>7</sup> into a number of categories including latex IPNs in which, ideally, every latex particle is an IPN in microcosm. Semi-IPNs are formed when only one of the component polymers is crosslinked. Normally latex IPNs are made in two stages. The first crosslinked latex is formed and then the second monomer is added and polymerized in or on the first-formed particles. Care has to be taken of this stage to avoid the formation of a new generation of particles consisting of just the second-formed polymer. Careful control of the level of surfactant in the system is vital, and, consequently, no new surfactant is added with the second monomer.

Quite an extensive literature now exists<sup>7-11</sup> on latex IPNs and latex semi-IPNs. Such materials can, of course, be prepared without the crosslinking of either polymer. It is convenient to consider such uncrosslinked materials, plus latex IPNs and latex semi-IPNs, as constituting a group of materials referred to as composite latex particles. There is currently a considerable amount of interest in such materials with work being reported on the morphologies of such particles,<sup>3,7-9</sup> the factors which influence these morphologies<sup>7,8</sup> and the properties of such materials.<sup>8-11</sup> Broadly, the possible range of morphologies varies from a core-shell structure,<sup>7</sup> on the one hand, in which the constituent polymers are present as a pure core of one polymer, and an outer sheath, the shell, on the other, to the situation where one of the polymers forms a continuous phase in which is embedded microphases of the other material.

In this paper the synthesis, characterization, and properties of materials which may be classified as semi-IPNs or full IPNs is presented. In these the second component, PMMA, is either linear or crosslinked, respectively.

## EXPERIMENTAL

### Materials

The natural rubber latex which had a solids content of ca. 60% was kindly donated by Revertex Ltd. Its average particle size and its long-term stability were measured with a Malvern Instruments Autosizer-II.

Methyl methacrylate (BDH Ltd.) and the crosslinker, divinyl benzene, were destabilized as previously reported.<sup>3</sup> The *tert*-butylhydroperoxide (Fluorochem) and the tetraethylene pentamine were used as supplied as was the stabilizer, oleic acid (BDH Ltd.).

### Polymerization

The NR latex (250 g) was charged to a polymer reactor along with 70.5 g of a 2% NH<sub>4</sub>OH solution and was deoxygenated by bubbling nitrogen for at least 0.5 h through the diluted, but still stable, latex. If necessary, ammonia was added to maintain the pH of the latex above 8.5. The nitrogen flow rate was then reduced to a low level and the temperature increased to 50°C before the addition, dropwise over 15 min, of the methyl methacrylate monomer, the crosslinker, if present, the stabilizer at 0.5 wt % of rubber and the *tert*-butyl-

hydroperoxide at 0.3 wt % of rubber. After a further period of 15 min, the amine activator (1.75 g of a 10% w/v solution) was added. The reaction was then allowed to proceed for 24 h under continuous stirring to complete the polymerization. Samples were taken at intervals to establish, gravimetrically, the degree of conversion of monomer to polymer. Once formed, the composite latex had good long-term stability if protected with an antibacterial agent, Panacide (BDH Ltd.). To form a sheet for subsequent mechanical tests, the latex was cast at room temperature in open glass trays to give a final sheet thickness of ca. 1.5 mm. Once dry, the sheet was removed from the tray and transferred to a vacuum oven (40°C) to remove any last traces of monomer that may be present. The dried sheet was then leached with deionized water to remove any water-soluble impurities from the rubber. The leaching process was continued for 3 days, during which period the water was changed several times. The sheet was then returned to the vacuum oven until it was thoroughly dry.

### Techniques

Dynamic mechanical data were obtained by using a Polymer Laboratories DMTA apparatus in both the bending and shear modes. The instrument was operated at a frequency of 10 Hz and at a heating rate of 2°C/min.

Tensile testing on dumbbell testpieces was conducted using a microprocessor-based Nene 3000 tensometer controlled from an Amstrad 1512 computer. The tests were performed at ca. 20°C and at a strain rate of 20 mm/min. Transmission electron micrographs were obtained with a Model HU-11B Hitachi electron microscope. OsO<sub>4</sub> was used as a preferential stain for the NR component.

## RESULTS AND DISCUSSION

The use of hydroperoxides as initiators alone without the addition of an activator puts a series of constraints on their ultimate applications. They are not particularly effective because either they require high temperatures for decomposition or the resultant radicals are inefficient. When used in crosslinking reactions, they also have a tendency to produce undesirable side products.

Initiation systems comprising organic hydroperoxides and iron (II) salts have been used extensively in low temperature emulsion polymerizations.<sup>12</sup> It is often advantageous to reduce the level of iron in an activated hydroperoxide initiation system for at least two reasons. It may cause discoloration and it may catalyze oxidative degradation.<sup>12</sup> Investigation into supposedly iron-free activated peroxide systems resulted in the development of polyamine activators. Polyamines are capable of decomposing organic peroxides vigorously and polyalkylenepolyamines have a powerful activating effect in the emulsion polymerization<sup>12</sup> of monomers such as styrene. Two structural requirements are believed<sup>12</sup> necessary if successful activation is to occur. First, the amine must contain within the same molecule amine groups of different substitutions, either primary and secondary or primary and tertiary. Second, the amine groups must be separated by no more than two carbons.

There is some doubt whether most hydroperoxide-pentamine systems are iron-free. It may be that traces of an iron-polyamine complex interacts with

TABLE I  
Composition Details<sup>a</sup>

Sample	NR (wt %)	PMMA (wt %)
100NR-0PMMA	100	0
90NR-10PMMA	90	10
90NR-10PMMA (1.0)	90	10
80NR-20PMMA	80	20
80NR-20PMMA (1.0)	80	20

<sup>a</sup>The presence of (1.0) in the sample code indicates that the PMMA has been crosslinked with 1 mol % of divinyl benzene.

the hydroperoxide to exert a catalytic influence. The hydroperoxide is, in general, water-insoluble whereas the polyamine will remain in the aqueous phase producing a locus of polymerization at the rubber-water interface.<sup>3</sup>

The hydroperoxide-polyamine system used in this study, *tert*-butylhydroperoxide-tetraethylene pentamine, has been discussed.<sup>3,13-17</sup> The conditions of useage are given by Bloomfield and Swift<sup>4</sup> for various monomers. For MMA, room temperature is sufficient to complete the polymerization, but for styrene<sup>3</sup> a temperature of about 50°C is necessary. The MMA reaction is strongly exothermic.

As stated earlier, the principal objective of this study was to produce novel materials including IPNs and semi-IPNs based on NR latex. The materials to be discussed are listed in Table 1. The number in brackets in some of the

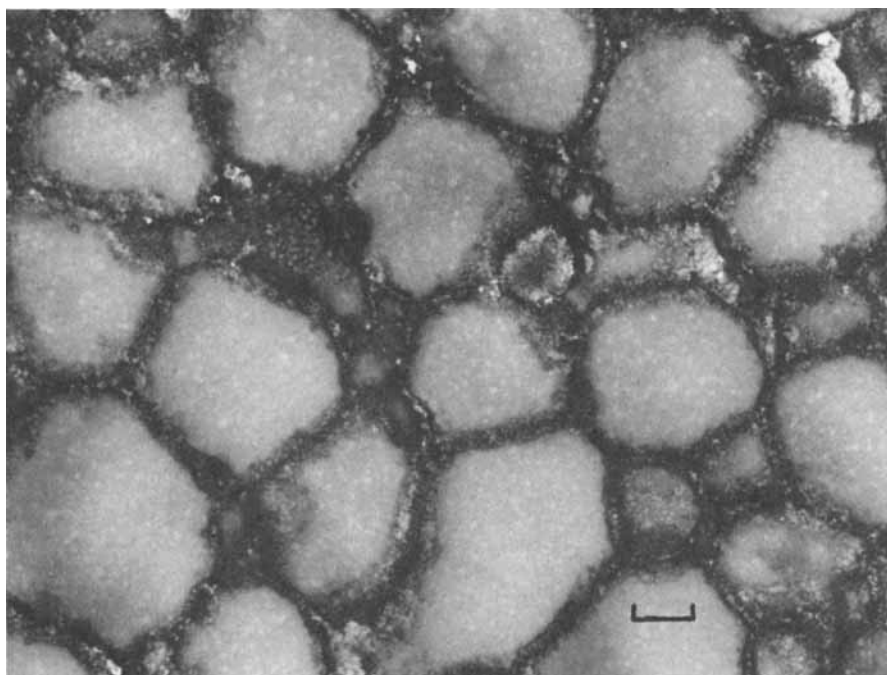


Fig. 1. Transmission electron micrograph of the 80NR-20PMMA (1.0) material. The scale mark represents 294 nm.

TABLE II  
Dynamic Mechanical Data (10 Hz) for the NR Transition Region

Sample	$T_g$ (°C)	Half-peak width (°C)
CNRL736/A <sup>a</sup>	-44	13
100NR-0PMMA	-44	13
90NR-10PMMA	-45	14
90NR-10PMMA (1.0)	-45	18
80NR-20PMMA	-44	15
80NR-20PMMA (1.0)	-39	13

<sup>a</sup>As-received natural rubber.

sample codes indicates that the second component, PMMA, has been crosslinked with 1 mol % of divinyl benzene based on MMA monomer.

The latexes produced were of good long-term stability and conversions of MMA to PMMA were 100% in all cases. An exotherm causing a temperature rise of around 12°C was observed during the first hour of the polymerization. This initiator system produced materials which did not film-form very satisfactorily at PMMA concentrations greater than 10 wt %. This problem was encountered<sup>3</sup> at around 22 wt % for materials in which the second polymer was polystyrene. Film cracking, using similar initiator systems, has been reported by Bloomfield and Swift.<sup>4</sup> The cast films were transparent and similar to NR films in appearance. However, they were somewhat stiffer and less tacky than a NR film.

A limited number of these materials were investigated using transmission electron microscopy (see Fig. 1). This is an electron micrograph of the 80NR-20 PMMA (1.0) material. First, it is clear that a very heterogeneous morphology exists which is similar to that already reported<sup>3</sup> for identically

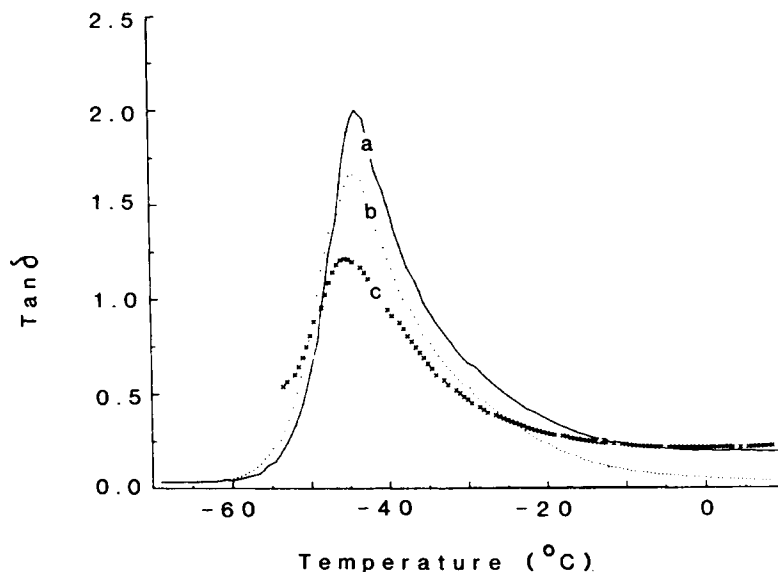


Fig. 2.  $\tan \delta$  vs. temperature plots at 10 Hz of the 100NR-0PMMA (a), 90 NR-10PMMA (b) and the 90-10PMMA (1.0) (c) materials.

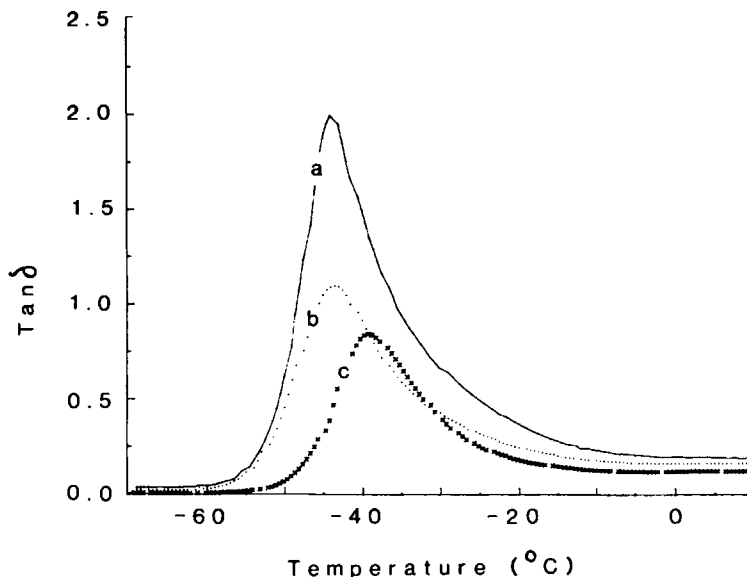


Fig. 3.  $\text{Tan } \delta$  vs. temperature plots at 10 Hz of the 100NR-0PMMA (a), 80NR-20PMMA (b) and the 80NR-20PMMA (1.0) (c) materials.

prepared NR-polystyrene materials. The question that arises is are these domains or particles the original NR latex particles into which the MMA has been polymerized or are at least some of them essentially pure PMMA particles formed from the original monomer droplets present in the aqueous phase? The weight of the evidence suggests the former.

The average diameter of the original NR latex was determined experimentally by light scattering to be 514 nm. By the incorporation of 20% by weight of PMMA the average diameter should be increased to 560 nm approximately, while the determined value, again by light scattering, after 24 h polymerization was 579 nm which is well within experimental error. If a significant number of the very large particles formed from polymerized monomer droplets were present, it is likely that a higher average diameter would result. The average diameter of the domains in the micrograph is around 670 nm, somewhat larger, but at least of the same order as that measured for the final latex.

TABLE III  
Dynamic Mechanical Data (10 Hz) for the PMMA Transition Region

Sample	$T_g$ (°C)
90NR-10PMMA	—
90NR-10PMMA (1.0)	129
80NR-20PMMA	130
80NR-20PMMA (1.0)	132

TABLE IV  
Stress-Strain Data

Sample	Initial modulus (MPa)	Tensile strength (MPa)	Elongation to break (%)
CNRL736/A <sup>a</sup>	0.64	3.27	753
100NR-0PMMA	0.68	2.26	807
90NR-10PMMA	1.58	4.94	720
90NR-10PMMA (1.0)	2.44	8.19	727

<sup>a</sup>As-received natural rubber.

The micrograph also shows that the individual domains appear to consist of both stained NR and unstained PMMA and, also, the fact that the particles on coalescence have distorted, sometimes considerably, is indicative that they are substantially NR in composition. With the NR-polystyrene materials there was stronger evidence<sup>3</sup> for some polymerization of monomer droplets. As MMA is significantly more water-soluble than styrene, transfer of MMA from droplets to the NR latex particles will be faster.

Table II and Figures 2 and 3 show some of the dynamic mechanical results in the NR glass transition ( $T_g$ ) region for these materials. Comparison of the data for the as received NR and the 100 NR-0 PMMA material shows no shift in  $T_g$  and no peak broadening indicating that if this initiator system is crosslinking the NR it is not doing so to any significant extent. The same observation was made earlier.<sup>3</sup> It is clear from Figures 2 and 3 that changing the composition from 0 to 20% PMMA causes no change in the position of the

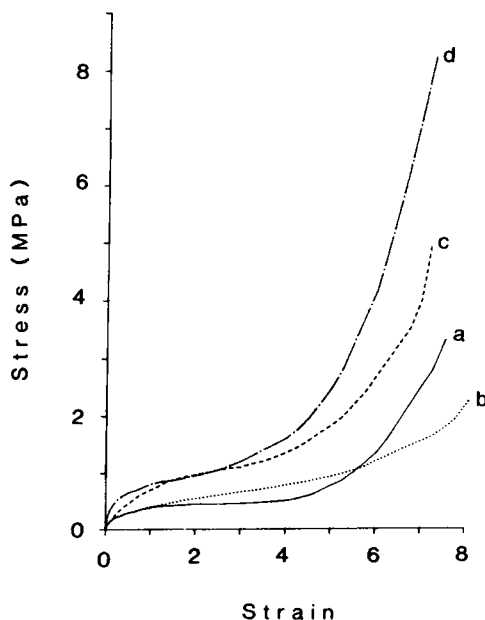


Fig. 4. Stress-strain curves (20°C) of the as-received natural rubber (a) and of the 100NR-0PMMA (b), 90NR-10PMMA (c), and 90NR-10PMMA (1.0) (d) materials.

NR  $T_g$ , but on crosslinking the PMMA in the 80NR–20PMMA (1.0) material a just significant shift in the transition results, though there is no change in half-peak width. Despite the indication of a minor extent of enforced mixing in the 80NR–20PMMA (1.0) sample taking the dynamic mechanical analysis results as a whole indicates that the materials show little or no evidence of mixing. Table III shows the corresponding PMMA  $T_g$  data. Again, there is no evidence of any mixing.

The stress–strain data obtained for a selection of these materials are presented in Table IV and in Figure 4. Comparison of the as-received NR with the material exposed to the initiator system (100NR–0PMMA) shows that at strains above 400% the as-received NR exhibits more strain–induced crystallization, than is the case for the clearly partially crosslinked 100NR–0PMMA sample. The incorporation of PMMA in linear form (90NR–10PMMA) yields a dramatic increase in both initial modulus and tensile strength, without a very marked reduction in extensibility. A further improvement in these properties results when the PMMA is crosslinked. It is also the case that the blends show substantially greater (ca. five times) hysteresis loss than the as-received NR.

J. R. wishes to thank both the SERC and Revertex Ltd. for financial support.

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Received June 30, 1989

Accepted July 18, 1989