Microstructure of Peroxide Prevulcanised Latex Films

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The technique of styrene swelling/polymerisation/electron microscopy has been used to study the structure of films made from peroxide prevulcanised latex (PPVL). The results show that in PPVL which has been made by the usual method, i.e. by using an activator in the aqueous phase, the distribution of crosslinked rubber is very different from that in sulphur-cured or radiation-cured prevulcanisates. In PPVL it can be seen that the small rubber particles are vulcanised in their entirety but the larger particles show a very different structure. Each large particle is only vulcanised in a layer near its surface, and the centre of the particle is unvulcanised or poorly vulcanised. This observation has been confirmed by solvent-swelling measurements on films made from different particle size fractions of PPVL. This phenomenon could explain why PPVL films show a high degree of tension set. By contrast, in a PPVL made using a more rubber-soluble, thermally-activated peroxide (dicumyl peroxide) all the rubber particles were crosslinked throughout.

A method of visualising the vulcanised areas in unsaturated elastomers1 has been used to estimate the crosslink density of vulcanised elastomer blends2–3 and, more recently, to study the structure of various prevulcanised and post-vulcanised natural rubber (NR) latex films4. The procedure involves equilibrium swelling of the dried latex film with styrene followed by polymerisation of the styrene. This causes a phase separation between the rubber and the polystyrene which will be discussed in more detail later. The polymérisation also makes the sample rigid enough for an ultra-thin section to be cut at ambient temperature. The cut section is then stained with osmium tetroxide to show up the rubber network when observed by transmission electron microscopy (TEM). The first micrographs of PPVL films obtained by this method showed an unusual structure4. This paper describes subsequent work done on several PPVL films to provide a better understanding of the crosslink distribution in these materials.

MATERIALS AND METHODS

Most of the PPVLs were prepared by the method described previously5,6. The t-butyl hydroperoxide (tBHP) was added as a 70% aqueous solution (Interox) to 20% potassium laurate solution and half the water required to dilute the latex to 50% solids content. The amount of potassium laurate used was 0.25 parts per hundred rubber (p.p.h.r.). This mixture

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was added with stirring to a commercial HA (High ammonia) latex concentrate at 60°C. The fructose was added as a 20% solution at the start of the reaction followed by the rest of the water. A fructose/tBHP mole ratio of 0.6 was used unless otherwise stated. The mixture was stirred continuously (under a sheet of polythene to reduce evaporation) for 7 h and a few drops of concentrated ammonia solution were added occasionally to compensate for evaporation losses. The PPVL used to make the films in Figures 1 and 2 was made by using 7mmol tBHP/100 g rubber which was all added to the latex at the start of the reaction. The PPVL film in Figure 3 was made using 5mmol tBHP/100 g rubber which was added to the latex in five equal hourly aliquots during the first 4 h of the reaction. Cast, unleached films of both PPVLs were used for the electron microscopy analysis.

The cumene hydroperoxide (CHP) PPVL was made in a similar way but in this case it was necessary to emulsify the 80% CHP solution (Aldrich) with the soap (potassium caprylate at 0.25 p.p.h.r.) and half of the water before adding dropwise to the HA latex at room temperature with stirring. After stirring for 45 min, the temperature was raised to 60°C and stirring was continued for another 45 min. Then the fructose and the rest of the water were added and the mixture was stirred at 60°C for 7 h. A CHP concentration of 10mmol/100 g rubber and a fructose/CHP mole ratio of 1.0 were used.

The highly crosslinked PPVL was made by adding a mixture of the tBHP, potassium laurate and water in five equal aliquots (one every 45 min) to the HA latex in a screw-cap bottle kept in a water-bath at 60°C. All the fructose was added at the start. After each addition of ingredients the bottle was flushed with nitrogen, capped and then swirled to mix. The heat was switched off after 8 h. A tBHP concentration of 20mmol/100 g rubber and a fructose/tBHP mole ratio of 0.6 was used.

Latex was prevulcanised with dicumyl peroxide (DICUP) as follows. The HA latex was diluted to 50% total solids content with water and then a 50% solution of DICUP in toluene was added dropwise with stirring at room temperature in a screw-cap bottle. The bottle was flushed with nitrogen, capped then rotated on rollers for six days at ambient temperature. After flushing with nitrogen again the mixture was prevulcanised by heating in an oven at 70°C for nine days. A DICUP concentration of 12mmol/100 g rubber was used.

Sulphur-prevulcanised latices of medium modulus (MR Revultex) and low modulus (LR Revultex) were supplied by Revertex (Malaysia) Sdn Bhd. RVNRL was provided by the Japan Atomic Energy Institute.

The film of LR Revultex was made by dipping a glass plate into a solution of calcium nitrate in ethanol, drying for 30 sec at 70°C, then dipping into the latex to form a coagulated film. The film was leached as a wet gel for 15 min at room temperature and then dried at 70°C.

Cast films were prepared by pouring latex at 50% total solids content onto a level glass plate and drying at room temperature. Unless otherwise stated, films were leached by soaking in distilled water for two 24-hour periods at room temperature followed by a 30-minute soak in fresh distilled water at 50°C. Films were dried at 70°C.
Samples of dried latex film were prepared for styrene swelling and electron microscopy as follows. A small piece of rubber was swollen to equilibrium in a 1% w/w solution of benzoyl peroxide in styrene containing 10 p.p.m. - 15 p.p.m. of 4-tert-butylcatechol inhibitor as supplied (99%, Aldrich) and 2% w/w of the plasticiser di-n-octyl phthalate. The plasticiser was added to make the polystyrene less brittle and therefore easier to section. Portions of the swollen rubber in excess styrene were heated in gelatine capsules at 68°C for 16 h. Each sample was heated for an additional 4 h at 90°C to complete the polymerisation. Ultra-thin sections (about 100 nm - 150 nm thick) were cut from the swollen, embedded sample at ambient temperature with an RMC MT-7000 ultramicrotome using a 45° freshly cleaved glass knife set at a shallow clearance angle. Where possible, sections were carefully relaxed, while still in the knife trough, by brief exposure to low levels of xylene vapour from a wick which had been dipped in xylene. The wick was removed immediately after any visible relaxation occurred. The sections were collected on nickel grids and stained with osmium tetroxide vapour for 2 h prior to examination in a Phillips EM300 transmission electron microscope operating at 100 kV.

Centrifugal fractionation of latex was carried out by diluting to 30% total solids content (TSC) with 1.8% aqueous ammonia, and transferring to 35 ml centrifuge tubes. These were centrifuged at 4000 r.p.m. for 10 min on a BTL bench centrifuge. The large particle size fraction was prepared as follows; the cream layer was removed with a spatula, redispersed in 1.8% ammonia and the centrifugation was repeated. The cream was removed and coagulated with dilute acetic acid. The coagulum was pressed flat and leached for 2 x 24 h in distilled water at room temperature followed by half an hour in distilled water at 50°C before drying in air at 25°C. The small particle size fraction was prepared as follows: The top 3 cm of latex was discarded after the first centrifugation and removal of the cream. The remaining latex was separated from the visible sediment, diluted with 1.8% ammonia and transferred to ultracentrifuge tubes. The latex was then centrifuged at 10 000 r.p.m. for 10 min in a Beckman L2-65B ultracentrifuge. The resulting latex fraction was decanted, leaving a top layer of coagulated rubber and a bottom layer of sediment behind. This latex fraction was prepared as follows: The top 3 cm of latex was discarded after the first centrifugation and removal of the cream. The remaining latex was transferred to ultracentrifuge tubes. The latex was then centrifuged at 35 000 r.p.m. for 30 min in a Beckman L2-65B ultracentrifuge. The resulting latex fraction was decanted, leaving a top layer of coagulated rubber and a bottom layer of sediment behind. This latex fraction was prepared as follows: The top 3 cm of latex was discarded after the first centrifugation and removal of the cream. The remaining latex was transferred to ultracentrifuge tubes. The latex was then centrifuged at 35 000 r.p.m. for 30 min to ensure that it was free of sediment. The creamed latex was then scooped out of the top of the tubes, coagulated with dilute acetic acid and then pressed, leached and dried in the same way as the top fraction.

The Q values of each film were measured by immersing a small (ca. 0.2 g) piece of dry latex film in excess toluene (BDH Analar grade) for 16 h at 25°C ± 2°C and weighing
Figure 3. Cast unleached PPVL film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
the amount of toluene absorbed. The \( Q \) value is defined as the ratio of the weight of toluene absorbed to the weight of the dry film.

RESULTS AND DISCUSSION

A typical electron micrograph of a polymerised styrene-swollen film of PPVL which had been made by using an activated tBHP system is shown in Figure 1. The dark areas in the micrograph correspond to rubber which has been stained with osmium tetroxide and the light areas are mainly polystyrene. The ovoid shape of the particles is probably a result of the sectioning process wherein the action of the knife edge tends to slightly compress the sample. The equilibrium volume swelling ratio \( Q \) of the film used to obtain this micrograph was 5.8, similar to that of a typical low-modulus sulphur-prevulcanised latex film such as LR Revulx. However, the electron micrographs of these two film after styrene swelling and polymerisation (Figures 1 and 2) show a great difference in structure. Whereas in sulphur-prevulcanisates all the latex particles show a homogeneous network structure but in the PPVL sample only the small latex particles have this appearance. The rubber network in the larger latex particles is concentrated near the particle boundaries.

In sulphur and radiation prevulcanisates all the latex particles show a homogeneous network structure but in the PPVL sample only the small latex particles have this appearance. The rubber network in the larger latex particles is concentrated near the particle boundaries.

The structure seen in the sulphur prevulcanisates is believed to arise from the following processes. During the styrene-swelling stage the rubber and the styrene are fully miscible so styrene swells the vulcanised latex particles until the entropic driving force is balanced by the elastic restoring force of the rubber network. During polymerisation a polystyrene phase is created which is immiscible with the rubber. Thus a phase separation occurs in which rubber chains are forced together between the growing domains of polystyrene, resulting in a mesh structure of rubber threads that is visible under the electron microscope. Threads of rubber are clearly present in between the latex particles as well, but here there is a much greater amount of polystyrene. This is believed to arise partly from styrene-swelling of the thin layer of entangled rubber chains between the latex particles, and partly from migration of polystyrene out of the latex particles during the polymerisation stage.

It is instructive to compare a picture of the same styrene-swollen PPVL film at a lower magnification (Figure 3) with one of an unswollen PPVL film of similar \( Q \) value at the same lower magnification (Figure 4). The latter was sectioned and then treated with uranyl acetate, a compound which stains the protein in the film, thus delineating the particle boundaries. Figure 4 can therefore be used to give an idea of the size range of the rubber particles in the film, though the apparent size of each particle will depend on the level at which the particle was sliced during sectioning. It is clear that the largest particles in Figure 3 are bigger than those in Figure 4. This is in contrast to the situation in sulphur-cured or radiation-cured prevulcanisates where the rubber particles themselves do not show a great increase in size and the bulk of the polystyrene occupies the spaces between the particles.
Figure 4. Cast, unleached PPVL film stained with uranyl acetate. Scale bar is 1 micron.
The distinctive PPVL structure can be explained if the large rubber particles in PPVL have unvulcanised, or poorly vulcanised, centres. Thus the following scenario is proposed for the changes that take place in a PPVL film during the sample preparation process. During the swelling of the latex film by styrene, the central regions of the larger particles become swollen to a greater extent than the more fully vulcanised small particles and outer regions of larger particles. During polymerisation of the styrene the phase separation produces separate domains of rubber and polystyrene. The small uniformly vulcanised latex particles behave in the same way as the particles in a sulphur prevulcanisate, as described above. However each large particle contains a central mass of rubber chains dissolved in a large amount of styrene. As polystyrene forms inside the particle this rubber can be easily displaced to join the network of vulcanised rubber near the particle surface, leaving behind a large solid mass of polystyrene at the centre of the particle.

If the large rubber particles in PPVL really have unvulcanised, or poorly vulcanised cores as the micrographs (Figures 1 and 3) suggest, then a latex film made from large particles should have a higher solvent swelling index, $Q$, than a film made from smaller particles. To test this, a sample of PPVL and a sample of sulphur prevulcanisate latex (MR Revulxin) were fractionated by centrifugation. The $Q$ values of films made from the large and small particle size fractions are given in Table 1.

The results show that whilst the swelling ratio of sulphur-prevulcanised latex films is independent of latex particle size, the large particle size fraction of PPVL has a much higher swelling ratio than the small particle size fraction from the same latex. These results are consistent with the hypothesis that the centres of large rubber particles do not become substantially vulcanised during the normal peroxide prevulcanisation process.

The inhomogeneous nature of the crosslinking in PPVL is not entirely surprising. The tBHP, fructose and trace amounts of iron are all dissolved in the aqueous serum of the latex. Formation of the alkoxy radicals which initiate the crosslinking process therefore occurs in the aqueous phase. These alkoxy radicals react first with the rubber molecules on the surface of the latex particles, removing hydrogen atoms to produce rubber radicals which combine to form crosslinks. The electron micrographs suggest that crosslinking occurs before the alkoxy radicals or rubber radicals can diffuse very far into the rubber particles. In the case of the small particles it seems that the distance that the radicals can diffuse is large enough to result in crosslinking throughout each particle.

In the light of the results presented herein and the above explanation, it is perhaps surprising that the physical properties of PPVL films are as good as they are. However, it has not been possible to make a PPVL film which combines high tensile strength and high modulus. Also PPVL films have been found to possess a relatively high degree of tension set which can probably be accounted for by the domains of unvulcanised or poorly vulcanised rubber. For example, it has been noted that toy balloons made from PPVL have similar properties to balloons made from sulphur prevulcanised latex except that after deflation the PPVL balloons are larger than sulphur-prevulcanised ones of similar strength and thickness. Whilst this may not be a problem...
for balloons, and may even be an advantage in that it would permit faster environmental degradation of burst balloons, high tension set would not be acceptable in other latex products. Some attempts were therefore made to increase the depth of the vulcanised layer in PPVL.

First, the effect of increasing the degree of vulcanisation (as measured by the swelling index) was tested. By using higher concentrations of tBHP and fructose, a highly-crosslinked PPVL with a \( Q \) value of 3.3 was made. Micrographs derived from cast, unleached and water-leached films made from this PPVL (Figures 5 and 6) show that the vulcanised layer has not extended noticeably further into the particles. The finer mesh size within the small particles in this film compared to Figure 1 confirms that a higher crosslink density has been achieved\(^4\). In the highly crosslinked PPVL there is an interesting difference between unleached and leached films. In the unleached film (Figure 5) more polystyrene is visible in the interstices between the rubber particles than in the leached film (Figure 6). In the latter it appears that the small, fully vulcanised particles have merged to form an almost homogeneous mass of crosslinked rubber between the larger, styrene-swollen particles. It is possible that the leaching process, by removing some of the hydrophilic substances from the surfaces of the particles, has increased the amount of rubber-to-rubber contact between the particles. This would reduce the tendency of the polystyrene to migrate from the interior of the particles to the areas between them during polymerisation.

In another attempt to increase the depth of the vulcanised layer, the more rubber-soluble cumene hydroperoxide was used in place of tBHP for the prevulcanisation. The resulting film, which had a \( Q \) value of 6.0, gave a micrograph (Figure 7) showing the same pattern as had been seen for the other PPVL films. This result suggests that it is not the solubility of the peroxide in the rubber which is the significant factor, but the fact that the activation process takes place in the aqueous phase. In order to confirm this, a PPVL was produced using a rubber soluble peroxide, DICUP, with heat rather than an aqueous redox reaction to provide the initiation. Unfortunately, thermal scission of DICUP is slow and inefficient at 70°C. Nevertheless, it was possible to produce a lightly prevulcanised latex which yielded a cast film with a solvent-swelling ratio of 11.0. The electron micrograph of this film after styrene swelling and polymerisation (Figure 8) shows a reasonably homogeneous network within each particle and large areas of polystyrene between the particles. The pattern in this micrograph is similar to those obtained from sulphur and radiation vulcanised latex\(^4\), but different from other micrographs derived from PPVL.

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### TABLE 1. SOLVENT-SWELLING INDICES OF LATEX FILMS

<table>
<thead>
<tr>
<th>Item</th>
<th>PPVL</th>
<th>Sulphur prevulcanisate</th>
</tr>
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<tbody>
<tr>
<td>Whole Latex</td>
<td>5.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Large rubber particle fraction</td>
<td>7.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Small rubber particle fraction</td>
<td>3.2</td>
<td>5.3</td>
</tr>
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Figure 1. Cast, unleached PPVL film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
Figure 2. Dipped and leached LR Revultex film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
Figure 5. Cast, unleached, highly vulcanised PPVL film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
Figure 6. Cast, leached, highly vulcanised PPVL film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
Figure 7. Cast, unleached CHP PPVL film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
Figure 8. Cast, unleached DICUP PPVL film swollen with styrene, polymerised and stained with osmium tetroxide. Scale bar is 1 micron.
CONCLUSIONS

The technique of visualising the microstructure of latex films by styrene-swellmg, polymerisation and osmium tetroxide staining has clearly revealed the inhomogeneous nature of crosslinking in peroxide prevulcanised latex particles. Only the small rubber particles are uniformly vulcanised (and these can have a very high crosslink density) while the large rubber particles are vulcanised only in a layer near their surfaces. This structure is likely to be found in any PPVL which is made by redox-activated processes in which the initiating radicals are generated in the aqueous phase.

Homogeneously crosslinked PPVL can be made by thermal activation of a peroxide which is completely dissolved in the rubber phase. However, in the case of dicumyl peroxide the reaction is too slow and inefficient to be of practical use. What would be required is a rubber-soluble peroxide which can be decomposed thermally at reasonable temperatures (less than 90°C) to produce radicals which are sufficiently active to cause crosslinking of the rubber within a few hours.

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