

Morphology and Mechanical Behavior of Poly(vinyl Chloride)/Poly(butadiene-co-Acrylonitrile) Latex Interpenetrating Polymer Networks

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Synopsis

A series of poly(vinyl chloride)/poly(butadiene-co-acrylonitrile) interpenetrating polymer networks (IPNs), all having 50/(25-25) weight compositions, was synthesized in latex form. The latex particles were studied after each step of the two-staged polymerization and after molding or casting. Transmission electron microscopy together with dynamic mechanical spectroscopy suggest a graded composition within the latexes, in which the poly(vinyl chloride) seed latex network I forms a core that is partially penetrated by the poly(butadiene-co-acrylonitrile) network II, yielding increased amounts of poly(butadiene-co-acrylonitrile) in the shell of the latex particles.

INTRODUCTION

A latex interpenetrating polymer network (IPN) consists of a unique type of polymer blend synthesized by emulsion polymerization techniques. A seed latex of crosslinked polymer I is first made; monomer II is then added together with crosslinker and activator (but no new soap) and polymerized on the original seed latex particles.¹⁻⁴ In a latex IPN, each interpenetrating network microcosm is contained within an individual latex particle,¹ as opposed to bulk IPNs where each network extends throughout the macroscopic sample.⁵⁻⁷

Because of the small entropy of mixing long chains,^{8,9} polymers I and II usually exhibit phase separation similar to most polyblends, grafts, and blocks.^{10,11} The presence of the double networks in a bulk IPN, however, controls morphology, giving rise to phase domains ranging from 100 to 1500 Å.^{5,12}

The morphology of latex IPNs may also be expected to show complexities, including possible core-shell and cellular structures. Core-shell morphologies of latex particles were suggested by the work of Grancio and Williams¹³ for homopolymers; and ABS latex graft copolymers, synthesized via a two-stage polymerization system, show both the core-shell structure and a cellular structure within the core.¹⁵ Cellular structures are known in bulk IPNs^{5,14} and in graft copolymers.^{11,16} Important variables in terms of latex IPN morphology include the relative amounts of the two polymers, order of synthesis, crosslink density of each network, solubility of monomer II in polymer I, and the size of the primary latex particle relative to polymer chain dimensions. Thus, below a certain latex particle size the cellular structure may not form,¹ but a fine structure may still be possible.

Poly(vinyl chloride) (PVC) homopolymer constitutes a stiff, plastic material that usually exhibits a slight degree of crystallinity.¹⁷ When PVC is blended

with an elastomeric second polymer, the modulus, glass-rubber transition behavior, and impact resistance depend upon the amount of elastomer added and upon its compatibility with PVC.¹⁸ Matsuo¹⁸ showed that the compatibility of mechanical blends of PVC with poly(butadiene-co-acrylonitrile) [poly(B-co-AN)] increased with acrylonitrile content. Sperling et al.¹⁹ previously studied several prototype PVC/poly(B-co-AN) latex IPN compositions by means of dynamic mechanical spectroscopy (DMS) of cast films and molded sheets made from the latexes. They suggested that poly(B-co-AN) network II showed a gradient shell composition on the exterior of the PVC seed latex polymer I network core.

The present experiments were undertaken for three reasons: (1) The morphology of an IPN latex particle has never been established experimentally, in spite of speculations based on mechanical data. The relationship between the individual particles and the morphology of the bulk material also has not been established for latex IPNs, although this is known for materials such as ABS plastics. (2) Mechanical blends of similar PVC/P(B-co-AN) compositions¹⁸ appear to be compatible or nearly so. The corresponding degree of compatibility in IPNs might be greater or less than in the blends, depending on whether the crosslinks tended more to hold the two types of chains in juxtaposition or to keep the core and shell components separate. (3) Earlier studies on semicompatible latex IPNs^{1-3,19} had indicated that such materials made good noise and vibration dampers. The present study continues to explore the interrelationship between molecular mixing and the width of the loss peaks.

The present paper studies a particular composition of the PVC/poly(B-co-AN) latex system in detail. The emphasis is on transmission electron microscopy of the materials to establish the morphologies in the latexes and their relation to the cast and molded forms. In combination with DMS results, this gives a more complete picture of the effects of synthetic detail on phase size and continuity and the extent of molecular mixing between polymer networks I and II.

EXPERIMENTAL

Synthesis

The latex IPNs were synthesized by a two-stage emulsion polymerization technique. The first stage consisted of making a seed latex of crosslinked PVC polymer I and then introducing the monomer II mixture of butadiene and acrylonitrile and crosslinker followed by a second polymerization. The recipe for the seed latex was: deionized H₂O, 115 ml; sodium lauryl sulfate (SLS) emulsifier, 0.3 g; vinyl chloride monomer, approximately 20 g; potassium persulfate (K₂S₂O₈) initiator, 0.25 g; tetraethylene glycol dimethacrylate (TEGDM) crosslinker, 0.4% by wt of monomer.

The above polymerization ingredients were charged as follows: 102 ml deionized H₂O was introduced into a 190-ml glass pressure bottle and warmed to 50°C. Then 3 g of 10% (by wt) water solution of the SLS emulsifier was added and stirred. The bottle was cooled down to room temperature, and then the initiator was added in solution form as 0.25 g/10 ml H₂O. The crosslinking agent was next added dropwise (about four to five drops). The bottle contents were then sparged for about 10 min with nitrogen gas to drive off oxygen, and the bottle

was sealed immediately. The contents were next frozen and weighed. Vinyl chloride gas from a pressure cylinder was liquefied (inside a 190-ml glass pressure bottle placed in a liquid nitrogen bath) and introduced into the polymerization bottle on top of the already frozen contents. The monomer was allowed to boil off to the desired weight, and the bottle was then capped with a gas-tight rubber seal and weighed again, and the exact mass of vinyl chloride in the bottle was determined and recorded. The capped bottle was then put in a 50°C water bath where it was tumbled at about 1 ppm for no less than 7 hr, yielding a completely reacted product. A thin syringe needle was inserted in the bottle through the rubber seal to test for the presence of any unreacted monomer at the end of polymerization.

The PVC latex was filtered to remove any traces of coagulated polymer and used as a seed latex for the second polymerization. New initiator (added in solution form as 0.25 g/10 ml H₂O) plus TEGDM crosslinker (0.4% by wt based on acrylonitrile plus butadiene) were stirred into the seed latex. The bottle was then sparged with nitrogen gas for about 5 min and the acrylonitrile monomer was weighed directly on top of the seed latex, 50% by wt based on PVC. Butadiene gas from a pressure cylinder was liquefied as above and introduced into the bottle directly on top of the floating acrylonitrile. The butadiene was allowed to boil off to the desired amount. The bottle was then capped and put into a 40°C water bath where it was tumbled for a minimum of 12 hr for a completely reacted product. The final composition was a 50/(25-25) poly(vinyl chloride)/poly(butadiene-co-acrylonitrile).

A portion of the finished latex (10-15 ml) was dried in open Petri dishes at room temperature to form cast films. The rest of the latex was coagulated (a small portion of saturated NaCl solution may be used), washed with water and 2-propanol, and finally molded at a pressure of about 5500 psi and at approximately 190°C to form suitable sheets.

Because addition of the cold liquid butadiene may cause freezing and some coagulation of the seed latex, a balloon technique was suggested for introducing butadiene¹⁹ and employed in some of the preparations. After the new initiator, crosslinker, and acrylonitrile had been added, a balloon was hung inside the bottle above the surface of the seed latex and the floating acrylonitrile. The balloon was secured by stretching it over the outside lip of the bottle and the butadiene was poured into it. The balloon was slashed at two or three points on its neck so that the butadiene would finally escape when tumbling began. The same weighing process was again employed before capping the bottle.

Transmission Electron Microscopy (TEM)

The latex particles of both the seed and the finished two-stage emulsions were viewed in the TEM. The as-synthesized latex was diluted with deionized water until the proper concentration was obtained (about one and two drops per 16 ml water for the seed and the finished latex, respectively). A drop of the diluted latex was placed on a microscope grid and excess fluid was removed. The grid was then inserted in the TEM for direct viewing of the latex particles. Shadowing the latex particles with a heavy metal (Pt) or staining the finished latex with osmium tetroxide (OsO₄) before viewing was also done. For staining, a drop of the diluted finished latex was placed on the microscope grid and the grid was

exposed in OsO_4 vapor for about 3 hr. The OsO_4 selectively attacks the double bonds of the polybutadiene component and hardens the latex particles. (The rubbery polybutadiene component will allow the latex particles to flatten and coalesce.) Micrographs were taken, and the sizes of both the seed and the finished latex were established and compared.

The morphology of the cast films and molded sheets was also examined by TEM. Specimens were "rough trimmed" with a razor blade so that the end regions were tapered into the shape of a truncated pyramid having sides of ~ 0.2 mm. The specimens then were exposed to OsO_4 vapor for several days and subsequently vacuum treated to remove volatile material. Then a Porter-Blum MT-2 ultramicrotome equipped with a diamond knife was used to obtain sections about 600 Å thick at room temperature. The thin sections were put on microscope grids and directly viewed and photographed in the TEM. Some specimens were first ultramicrotomed, and then the thin section was exposed to OsO_4 for about 45 min before viewing in the TEM. Soft cast or molded specimens were embedded in epoxy before sectioning.

Dynamic Mechanical Spectroscopy (DMS)

All DMS studies employed a Rheovibron direct-reading viscoelastometer, Model DDV-11, at a frequency of 110 Hz. The temperature range employed was -120 to $+150^\circ\text{C}$, with a heating rate of about $1^\circ\text{C}/\text{min}$. As required by the instrument, the sample dimensions were of the order of $0.02 \times 0.2 \times 1.4$ cm.

RESULTS

The seed and finished latexes both showed a considerable distribution of particle sizes. The seed latex particles (Fig. 1) ranged from about 150 to 550 Å while the finished latex (Fig. 2) showed bigger particles, ranging from about 450 to 800 Å. The tiny particles seen in the stained finished latexes (Fig. 2) are believed to be traces of butadiene-acrylonitrile copolymer formed during the second

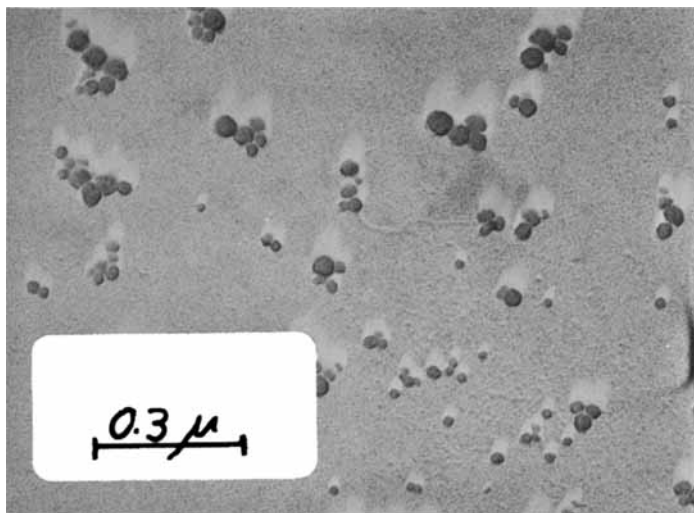


Fig. 1. Electron micrograph of PVC seed latex, shadowed with Pt.

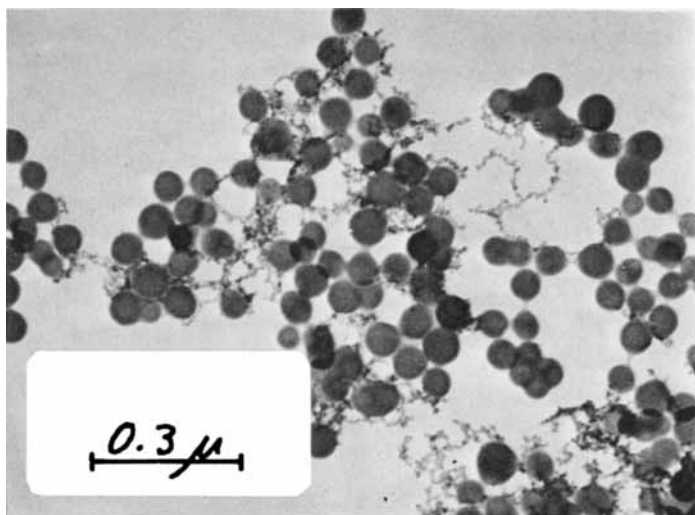


Fig. 2. PVC/P(B-co-AN) finished latex. Electron micrograph of OsO₄-stained particles.

polymerization. The total volume of these particles, however, is negligible and should not seriously affect the morphology or the physical and mechanical properties of the bulk material. Unstained finished latexes showed much more coalescence in the TEM, but their sizes were similar to those shown in Figure 2.

The films that were cast from finished latexes usually cracked during drying and showed low toughness. After heating in an oven at about 90°C for about 30 min they became softer and tougher; apparently the individual latex particles coalesced better at the elevated temperature and formed a more continuous film. When balloons were used to introduce the butadiene monomer during the second polymerization, the resulting films showed varied behavior, ranging from discontinuous and brittle to continuous tough films. The molded sheets generally showed leathery behavior, with the ones synthesized by using balloons again showing varied behavior. The morphology of the latter specimens in TEM, however, indicated no detectable differences.

The morphologies of the cast films and molded sheets stained with OsO₄ were similar (Figs. 3 and 4). They both showed a two-phase structure, with the dark phase being the more continuous. The light phase consists of the PVC seed latex, and the surrounding dark network is believed to contain the stained poly(B-co-AN) component. For comparison, the morphology of an unstained material is shown in Figure 5.

The DMS results of cast films and molded sheets (Figs. 6–9) showed broad glass transition regions with single well-defined $\tan \delta$ and E'' peaks. The appearance of these spectra is consistent with the earlier findings of Matsuo¹⁸ that PVC forms semicompatible or compatible (depending on the amount of acrylonitrile present) blends with poly(B-co-AN).

DISCUSSION

The TEM morphologies suggest a tendency toward core-shell latex structures, as found by Kato¹⁵ upon the step addition of a comonomer during emulsion polymerization. On the other hand, the DMS results suggest extensive molecular

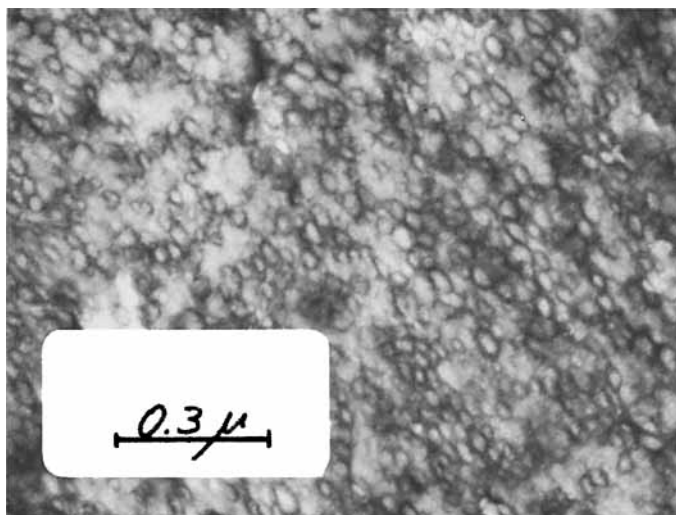


Fig. 3. PVC/P(B-co-AN) cast film. Electron micrograph of film exposed to OsO_4 for about 45 min after it was sectioned. Film was preheated at 90°C for about 30 min before sectioning.

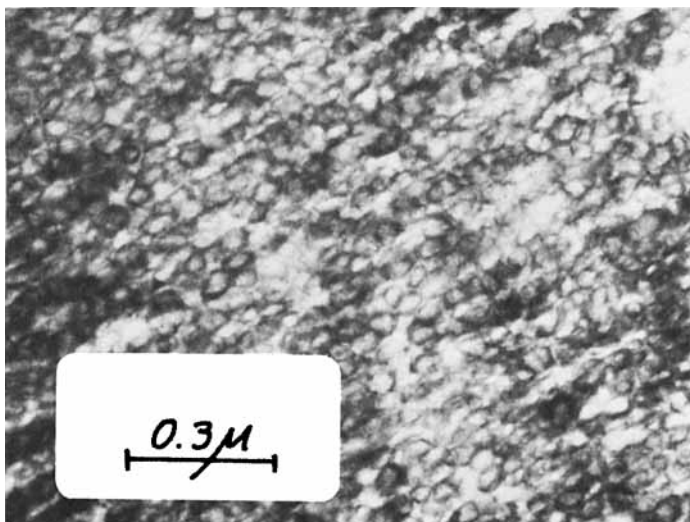


Fig. 4. PVC/P(B-co-AN) molded sheet. Electron micrograph of sample stained with OsO_4 before sectioning.

mixing of the PVC and P(B-co-AN) in the bulk materials. The most reasonable overall interpretation is that the finished latex particles have a gradation of P(B-co-AN) content, increasing from the interior to a maximum at the exterior. Sufficient butadiene is present at the exterior to give strong OsO_4 staining and to permit film formation in cast latexes, although mechanical properties are improved considerably by further coalescence during heating cast films or molding under heat and pressure.

Although the picture developed here remains only semiquantitative, it is more complete than before,¹⁹ and it relates latex and bulk characteristics rather than considering them separately. Support for this picture follows.



Fig. 5. PVC/P(B-co-AN) cast film. Electron micrograph of unstained sample.

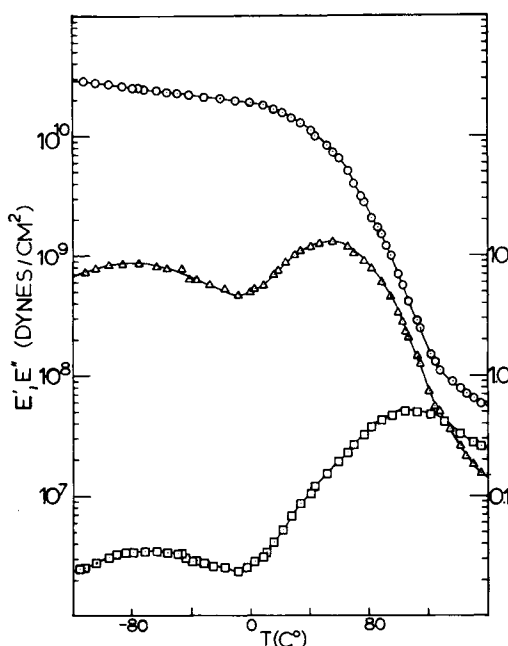


Fig. 6. Dynamic mechanical spectroscopy of molded sheet: (○) E' ; (△) E'' ; (◻) $\tan\delta$.

Transmission Electron Microscopy

Two limiting cases can be considered for TEM image contrast of the finished latexes (Fig. 10). In the first case, Figure 10(a), the latex spheres are taken to be homogeneous in composition and to stain uniformly with OsO_4 . In TEM, the particles would be darkest in the interior, as expected for the image of any sphere viewed in transmission.

In the second case, Figure 10(b), the latex spheres are taken to have a stained shell that is sharply demarcated from an unstained core. The transmission image

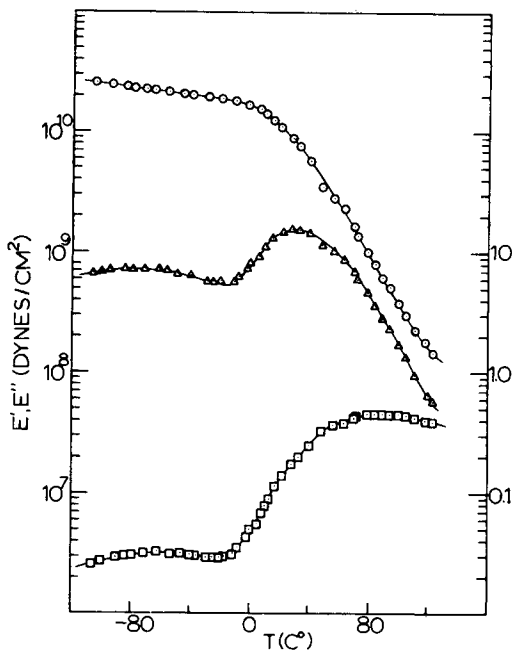


Fig. 7. Dynamic mechanical spectroscopy of cast film formed from the same emulsion as in Fig. 6. The peaks here are shifted to lower temperatures. Film was preheated at 90°C for about 30 min before testing: (○) E' ; (△) E'' ; (◻) $\tan\delta$.

is darkest immediately outside the core, and the core is much brighter than in the homogeneous case.

The actual stained latex (Fig. 2) appears to lie between the two limiting cases. Most particles are slightly but definitely darker near the exterior than in the center, consistent with a higher concentration of polymer II, P(B-co-AN), toward the exterior. An early stage of latex coalescence is apparent from the necks between particles, but these are light in the micrograph because they are only 70 to 150 Å thick.

For the core-shell limiting case, Figure 10(c) shows that ultramicrotomed thin sections can exaggerate the image contrast between core and shell. This effect is apparent in the micrographs of Figures 3 and 4, which show touching dark rings of the same diameter range as the finished latex particles.

Without staining, the contrast reversal found in the thin section of Figure 5 is expected, with the PVC-rich latex cores absorbing the electron beam more strongly than the P(B-co-AN)-rich shells. The latex particles still retain their identity in Figure 5, although not as strikingly as in Figures 3 and 4.

Dynamic Mechanical Spectroscopy

The glass transition temperatures for the cast or molded latexes of Figures 6-9 range from 30° to 55°C, based on the temperature maxima in E'' . These temperatures can be compared with T_g estimated from the usual random copolymer equation²⁰:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} \quad (1)$$

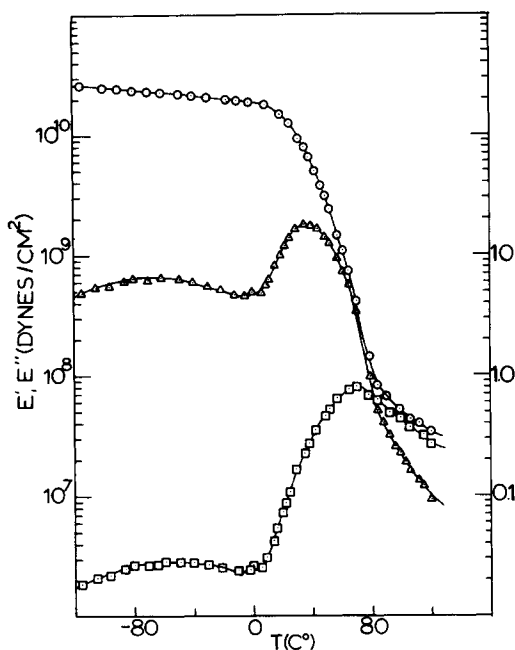


Fig. 8. Dynamic mechanical spectroscopy of molded sheet. Emulsion was synthesized using balloons to add butadiene. The material is softer than that in Fig. 6 because the shell is richer in polybutadiene: (○) E' ; (△) E'' ; (◻) $\tan\delta$.

where w_i is the weight fraction of material with homopolymer T_{g_i} . With T_g values of 87, -90, and 130°C for PVC, PB, and PAN,²⁰ respectively, eq. (1) gives $T_g = 23^\circ\text{C}$. Since T_g is normally reported for a frequency of about 0.1 Hz,^{20,21} the value should be increased by some 18–21°C to allow for the $\sim 10^3$ increase in frequency. The corrected T_g of about 43°C agrees fairly well with the observed T_g values, confirming the notion of a single T_g for the present system.

The glass transitions are also broadened, as already noted. Matsuo et al.,¹⁶ however, found sharper transitions for various mechanical blends of PVC with P(60B-co-40AN), indicating high compatibility. The present materials, therefore, appear to have sufficient molecular mixing to show a single T_g , but with compositional gradations that produce considerable broadening.

As can be noted in Figures 8 and 9, the transitions are somewhat sharper when butadiene is added by means of balloons, as described earlier. There is no ready interpretation of this finding. The butadiene might reach the emulsion particles later than the acrylonitrile and give a butadiene-rich shell, but there is no indication of the presence of polybutadiene with its low T_g of about -90°C.

All of the E'' and $\tan\delta$ curves show a broad, low β -transition peak at about -60 to -80°C. This is similar to the β -peaks for PVC^{17,22} but displaced downward somewhat in temperature. Matsuo et al.²² found a similar displacement in their mechanical blends, consistent with the present results.

General

The combined experimental results agree with a graded composition in the latexes in which the crosslinked PVC seed latex is partially penetrated by butadiene and acrylonitrile monomers, which then polymerize *in situ*. Sharp phase

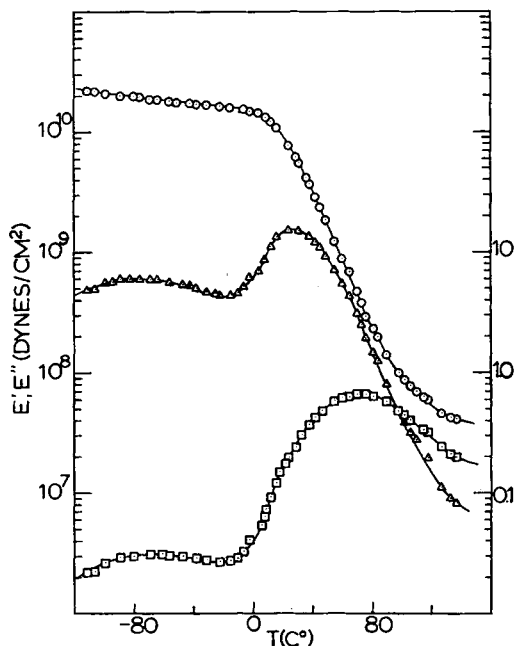


Fig. 9. Dynamic mechanical spectroscopy of cast film formed from the same emulsion as in Fig. 8. A more continuous and softer film than in Fig. 7 is formed because the shell is richer in polybutadiene: (○) E' ; (△) E'' ; (□) $\tan\delta$.

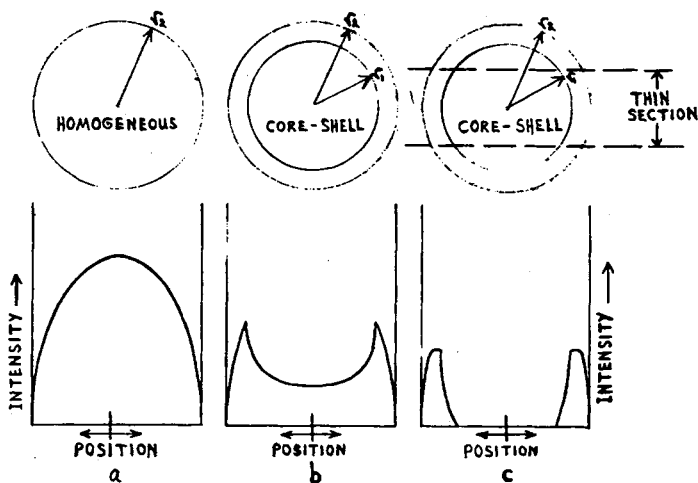


Fig. 10. Idealized image intensities for transmission electron microscopy of latex particles: (a) homogeneous latex, (b) core-shell latex, (c) ultramicrotomed thin section through core-shell latex. Core/shell ratio, calculated assuming 50 wt % PVC/50 wt % P(B-co-AN) and polymer densities of 1.39 and 1.06 g/cm³, respectively, gives $r_2 = 1.31r_1$.

separation is not evident from either TEM or DMS results, but heavier OsO₄ staining indicates that the outer portions of the latex particles are richer in butadiene.

Intimate mixing of the monomers and polymers used here is reasonable, based both on solubility parameters, Table I,¹⁷ and the previously observed compati-

TABLE I
Solubility Parameters of Selected Monomers and Polymers¹⁷

Structure	Solubility parameter	
	Monomer	Polymer
Poly(vinyl chloride)	7.8	10
Polybutadiene	7.1	8
Polyacrylonitrile	10.5	13

bility of the polymers.²² Presumably, the polar acrylonitrile can swell readily into the PVC seed latex particles, along with appreciable amounts of butadiene. Polymer II, when formed, is highly compatible with the PVC, but its amount (and possibly butadiene content as well) increases toward the exterior of the finished latex particles. The presence of the rubbery copolymer makes film formation possible, particularly in view of its concentration at the outside where the particles are in contact during coalescence.

In ABS materials Kato¹⁵ has shown that individual polybutadiene latex particles can develop poly(styrene-co-acrylonitrile) glassy domains in their interiors as well as in surrounding shells so that both discontinuous and continuous glassy polymer forms on molding. In the present system, the high compatibility of the polymers and the presence of crosslinking in both components probably preclude the formation of separate cellular phase domains. However, the morphology and properties of the bulk materials are clearly inherited directly from the size and composition gradients in the finished latex particles.

It is interesting to compare the width of the E'' peaks at half-maximum, as these provide semiquantitative guides to the amount of molecular mixing of the two polymers in question. The data shown in Table II are helpful. Thus the polybutadiene homopolymer does not alter the breadth of the PVC transition. However, the nitrile rubber-PVC blend increases the transition from 27 to 40°C, approximately. Electron microscopy¹⁸ indicates that the PVC/P(B-co-AN) 100/(30-co-20) blend is virtually compatible. Hence, in this special case, like Figures 6 and 7, the broader transitions may indicate less molecular mixing. Unfortunately, the compositions are not identical.

An interesting possibility exists that the double network of the IPN may be preserving some semblance of a core-shell morphology, even if the blend of the same two polymers of this composition ought to be miscible in all proportions. Of course, the core-shell structure arises from the special surface effects prevalent in two-component emulsion polymerizations. The electron microscopy results indicated at least a partial retention of a core-shell morphology, and the dynamic mechanical behavior studies showed incomplete mixing. Hence, while the IPN structure limits phase domain size in bulk polymerizations, it may be causing the retention of separate domains in the latex case.

TABLE II

Polymer	Half-width, °C
PVC homopolymer (22)	27
100/15 PVC/PB blend (22)	27
100/(30-co-20) PVC/P(B-co-AN) (22)	40
Figures 6 and 7	50
Figures 8 and 9	40

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