Synthesis and Behavior of Poly(vinyl Chloride)-Based Latex Interpenetrating Polymer Networks

L. H. SPERLING, D. A. THOMAS, J. E. LORENZ, and E. J. NAGEL,
*Materials Research Center, Lehigh University, Bethlehem, Pennsylvania
18015*

Synopsis

Poly(vinyl chloride)/poly(butadiene–co–acrylonitrile) interpenetrating polymer networks (IPN's) were synthesized in latex form. Dynamic mechanical spectroscopy as a function of temperature revealed that the glass transitions of the individual networks were broadened and in some cases spanned the entire temperature range between the two individual polymer transitions. This was interpreted to indicate extensive but incomplete mixing between the two networks. Depending on overall composition, the cast or molded films were either plastic or tough elastomers at room temperature. Some aspects of phase continuity and structure, including a graded core-shell model, are discussed.

INTRODUCTION

Poly(vinyl chloride) homopolymer is a stiff, plastic material that usually exhibits a slight degree of crystallinity.[1] With the addition of comonomers, plasticizers, crosslinks,[2,3] filler, or a second polymer component, a wide range of physical and mechanical behavior can be obtained.[4] When poly(vinyl chloride) is blended with an elastomeric second polymer, the modulus, glass–rubber transition behavior, and impact resistance depends upon the amount of elastomer added and upon its compatibility with poly(vinyl chloride).[5]

When two polymers of contrasting properties are mixed, the concomitant two-phased morphology results in nonlinear and sometimes synergistic behavior.[5–15] Ways of mixing the two polymers commonly include melt blending,[6,7] graft copolymerization,[7,8] or the formation of block copolymers.[7–9] While many mechanical blends tend to form coarse phases in the range of 1 to 10 microns, graft and block copolymers develop progressively finer phase domain structures, often in the range of 500 Å to 1 micron. A new method of controlling phase domain size and structure involves formation of an interpenetrating polymer network, IPN.[10–12] A simple way of synthesizing an IPN involves preparation of polymer network I, a swelling in of monomer II plus crosslinker and activator, and polymerization of II in situ. IPN's have been prepared via bulk[10–12] and latex[13,14] polymerization routes.

The synthetic method clearly places the IPN's as a subclass of the graft copolymers. Accidental grafting in the normally defined sense does indeed take place, but the crosslinking of both polymer I and polymer II introduces a new structure-influencing element. When the deliberately introduced crosslinks outnumber the accidental grafts, new morphologies and properties arise. For example, the crosslink density of polymer I controls the phase domain size.[12]

If the two polymers are semicompatible, phase domain sizes of the order of 100 Å may be realized.[10] In this range, interestingly, the phases are smaller than the primary chain molecules. If one of the polymers is above and the other below its glass transition temperature, the extensive but variable mixing of the two species produces the appearance of a very broad glass transition, which spans the range between the two primary transitions.[10,14] Since mechanical vibrations are readily degraded to heat in the vicinity of the glass transition, this property is of interest in noise and vibration control, because semicompatible IPN's then offer the prospect of being able to damp unwanted noise and vibrations over unusually broad temperature ranges.[15]

Matsuo[5] showed that the compatibility of mechanical blends of poly(vinyl chloride) (PVC) with poly(butadiene–co–acrylonitrile) [poly(B-co-AN)] depended on the acrylonitrile content. From a fundamental point of view, the effect of IPN formation offered an opportunity to further investigate the morphology and behavior of an intimately but incompletely mixed polymer pair and compare the results to the corresponding blends. It became of interest to explore the dynamic mechanical behavior of semicompatible IPN's prepared from PVC/poly(B-co-AN), particularly in view of the flame retardancy of chlorine-containing polymer materials.[16] PVC/poly(B-co-AN) IPN's are of interest because of their potential capability to damp unwanted noise and vibration over broad temperature ranges.

The present paper will develop the basic physical and mechanical behavior of several prototype PVC/poly(B-co-AN) IPN compositions synthesized through emulsion polymerization methods. Beyond noise damping capabilities, some of these materials were found to exhibit very high rubber elasticity, while others are very tough leathery or plastic materials.

EXPERIMENTAL

The IPN synthesis 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 emulsion polymerization.

To prepare the seed latex, 100 ml of deionized water was introduced into a 190-ml glass pressure bottle along with 0.25 g potassium persulfate ($K_2S_2O_8$) initiator and 1.5 g sodium lauryl sulfate (SLS) emulsifier. A crosslinking agent, tetraethylene glycol dimethacrylate (TEGDM) was added next in an amount 0.4% by weight of the intended vinyl chloride content. This mixture was shaken to dissolve the solids, and the solution was then sparged for 5 min with nitrogen. The solution was next frozen in a sealed pressure bottle and weighed. Vinyl chloride gas from a pressure cylinder was liquified and introduced into the pressure bottle until the increased mass was slightly more than the desired amount (9–27 g). The vinyl chloride was then allowed to boil off until approximately 0.3 g excess remained in the bottle.

The bottle was capped with a gas-tight seal, weighed, and the exact mass of vinyl chloride in the bottle determined. The capped bottle was rotated at about one revolution per second in a 50°C water bath for no less than 7 hr. After this period, the vinyl chloride was completely reacted.

The latex was filtered to remove any traces of coagulated polymer and used as a seed latex for the second polymerization. New initiator (0.25 g $K_2S_2O_8$)
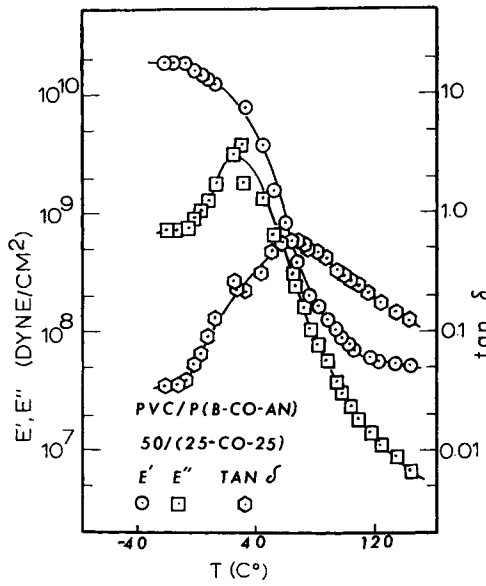
Fig. 1. Dynamic mechanical spectroscopy of PVC/poly(B-co-AN) 50/(25-co-25).
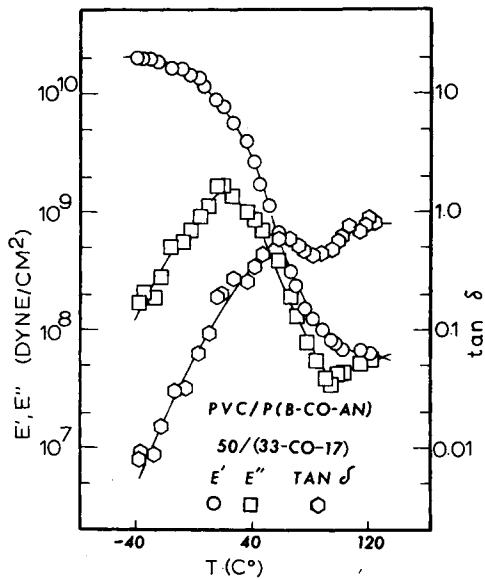

Fig. 2. Dynamic mechanical spectroscopy of PVC/poly(B-co-AN) 50/(33-co-17).
This composition has a broader glass transition than shown in Fig. 1.

plus acrylonitrile and TEGDM (0.4% by weight based on acrylonitrile plus butadiene) were added to the PVC latex and dissolved.

Because addition of the subzero-temperature liquid butadiene caused freezing and consequent coagulation of the preexisting latex, two different methods were used to introduce the required proportion of the butadiene to the seed latex. In the first method, 100 ml of the latex along with the new initiator, crosslinker, and required acrylonitrile were first charged into a pres-
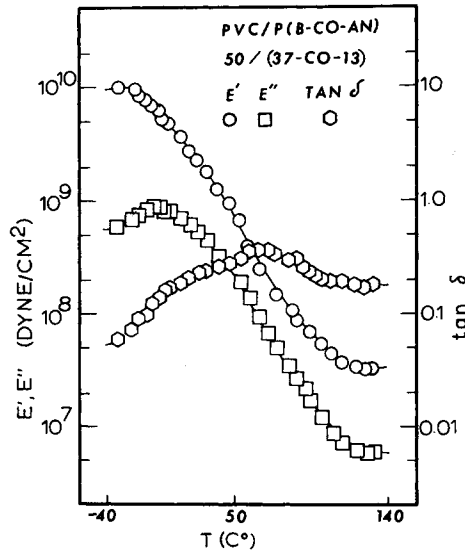
Fig. 3. Dynamic mechanical spectroscopy of PVC/poly(B-co-AN) 50/(37-co-13). Further reduction of AN content causes further broadening.
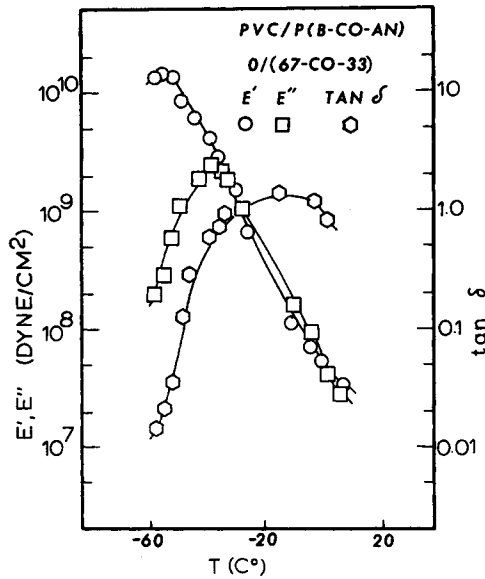

Fig. 4. Dynamic mechanical spectroscopy of the poly(butadiene–co–acrylonitrile) 67-co-33 random copolymer, illustrating its glass transition behavior.

sure bottle identical to that used for the vinyl chloride polymerization. Paraffin wax was melted and poured into the bottle until a layer about 1 cm thick covered the liquid surface. When the wax was cooled, the liquid butadiene was poured onto the wax surface; the correct amount of butadiene was achieved by the same weighing procedure used for the vinyl chloride. The bottle was capped and the contents allowed to reach room temperature before tumbling was begun. The polymerization was carried out at 40°C for a mini-
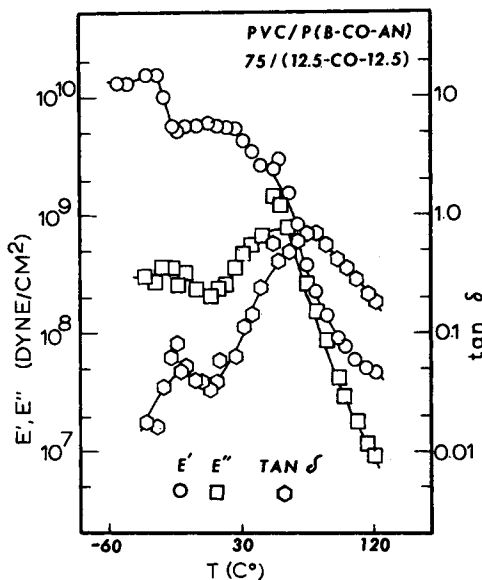
Fig. 5. Dynamic mechanical spectroscopy of PVC/poly(B-co-AN) 75/(12.5-co-12.5), showing the effect of high PVC content.

mum of 12 hr. The wax particles were easily removed when the latex IPN was filtered.

The second method for the introduction of butadiene made use of balloons. After the new initiator, crosslinker, and acrylonitrile had been added, a balloon was hung inside the bottle and stretched over the outside lip of the bottle to secure it. The butadiene was poured into the balloon, which hung above the surface of the latex and the acrylonitrile phase. The same weighing process was again employed before capping. The butadiene was again allowed to warm up before contacting the latex. Unreacted butadiene gas was vented after the polymerization and the finished IPN latex removed.

The several compositions synthesized are shown in Table I. The composition is listed as per cent PVC/per cent poly(B-co-AN). Since some of these

TABLE I
IPN Compositions

Sample	Composition PVC/poly(B-co-AN)	Film former
A	75/(12.5-co-12.5)	no
B	75/(17-co-8)	no
C	75/(19-co-6)	no
D	75/(25-co-0)	no
E	50/(25-co-25)	no
F	50/(33-co-17)	yes
G	50/(37-co-13)	yes
H	50/(50-co-0)	no[a]
I	25/(50-co-25)	yes
J	0/(67-co-33)(no PVC)	yes

[a] This experiment was repeated by Mr. G. Omotoso, who found that a film of substantially zero strength was formed; i.e., the latex particles probably did not properly coalesce. The reason for this behavior is not known.
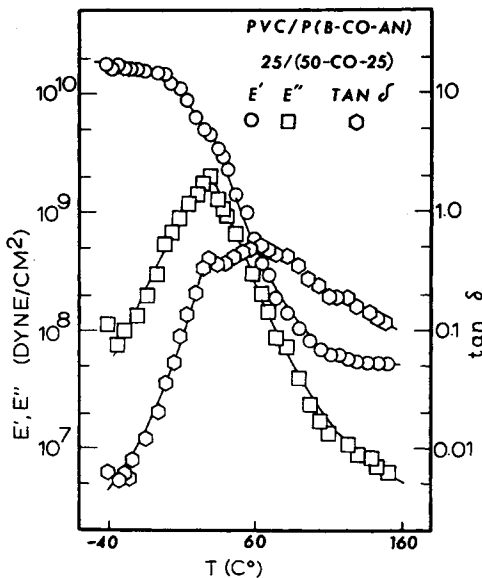
Fig. 6. Dynamic mechanical spectroscopy of PVC/poly(B-co-AN) showing the effect of low PVC content.

materials were film formers and others not, that information is also shown. The film-forming samples were prepared directly by drying the latex. The nonfilm-forming samples were first coagulated and then molded to form suitable sheets.

Dynamic mechanical data at 110 Hz were obtained on a Rheovibron between $-40°C$ and $+160°C$. The storage modulus E', the loss modulus E'', and the loss tangent tan δ were recorded. Stress–strain data were obtained on an Instron with a 50-lb load cell.

RESULTS

In general, the several films and sheets so formed were either tough, leathery materials or highly extensible elastomers. The latter gave the impression of being self-reinforcing products. It was noted that even though the individual latex particles were not crosslinked to one another, very little creep was observed on deforming the elastomeric materials between 100% and 300%. This qualitative observation suggests that the PVC component may have significant phase continuity.

Dynamic mechanical spectra are reported on samples E, F, and G in Figures 1, 2, and 3, respectively. The dynamic mechanical spectra of 2:1 poly(B-co-AN) copolymer, sample J, is reported in Figure 4 for comparison. Samples E, F, and G exhibit very broad glass transition regions, but significant differences do exist among the three. While E has a single, well-defined tan δ peak, sample F displays two peaks. The tan δ values for sample G remain nearly constant over the temperature range of 0°C to +150°C. Although higher acrylonitrile contents promote increased compatibility, sample F appears to have the greatest degree of phase separation. However, these com-
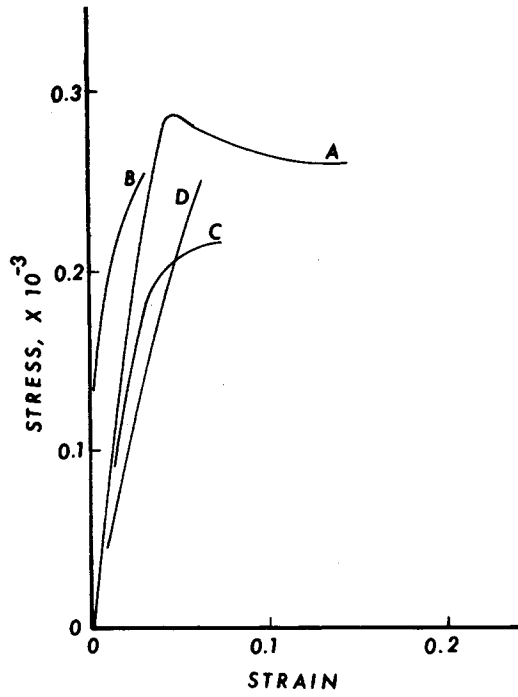
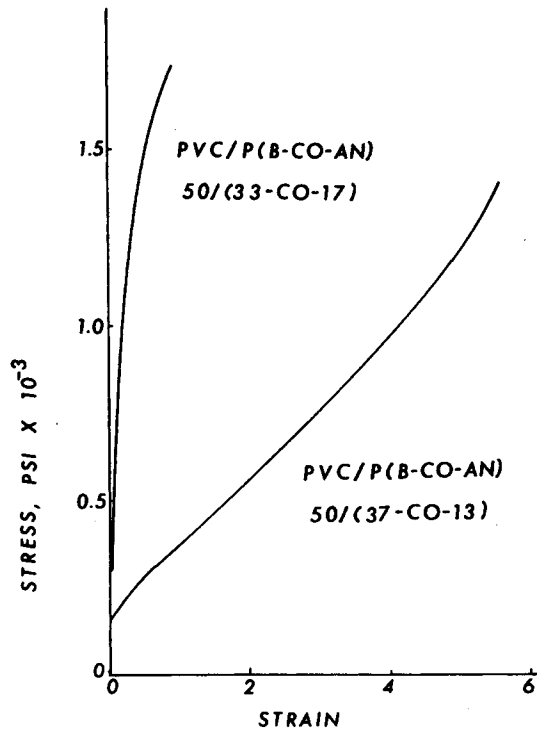Fig. 7. Stress–strain studies on stiff samples.   Sample A showed a yield point.

Fig. 8. Stress–strain studies on elastomeric compositions.   Sample PVC/poly(B-co-AN) 50/
(37-co-13) exhibited a 500% extension before failure.

positions all have considerably more rubber than the normal elastomer-toughened PVC materials.

Inclusion of greater amounts of PVC sharpens the tan δ peak, but does not significantly raise the temperature range of damping, as illustrated by sample A in Figure 5. Lower PVC contents, as shown in Figure 6 for sample I, shift the tan δ peak downward, but not as far as expected from the data previously shown in Figure 4. The literature value for the glass transition of PVC is 87°C, although the melting temperature of 212°C[17] may contribute to the high-temperature damping characteristics.

The appearance of the several IPN damping spectra are consistent with the earlier finding of Matsuo[12] that PVC forms semicompatible mixtures with poly(B-co-AN). The data suggest that some of these materials will make good prototypes for broad-temperature damping, especially in the temperature range of 40°C to 150°C. This range is higher than the range obtainable with methacrylic/acrylic latex IPN's,[8,9] which is limited at the high end by the glass transition of poly(methyl methacrylate) at 107°C (at 0.1 Hz). The acoustical damping properties of these materials will be reported elsewhere.[18,19]

Stress–strain data for several leathery materials are reported in Figure 7. Sample A is seen to exhibit a yield point. The corresponding data for two elastomeric materials is shown in Figure 8. Sample G extends over 500% before failure, developing a tensile strength of over 1300 psi.

DISCUSSION

The dynamic mechanical data indicate broadened and ill-defined glass–rubber transition regions, which strongly suggests that intimate mixing of PVC and poly(B-co-AN) molecules has been achieved. On the basis of the work of Williams[20,21] and Sperling and co-workers,[13,14] there may be a core-shell structure or, more probably, a graded core-shell structure, where the PVC core gradually becomes enriched in poly(B-co-AN) as one travels from the center of the latex particle to the surface. Some of the materials investigated, however, had high moduli at room temperature, suggesting phase continuity for the PVC portion. In those compositions, some PVC undoubtedly extends to surface of the individual latex particles.

It is of interest to compare the film-forming capacity (Table I) to the dynamic mechanical spectroscopy data. In order to form a film at room temperature, the individual latex particles must be capable of extensive deforma-

TABLE II
Rheological Behavior of PVC-Based IPN's

Sample	Film Former	E', dynes/cm^2, at 20°C	Temp. of E'' peak, °C
A	no	6×10^9	+50
E	no	1.2×10^{10}	+22
F	yes	9×10^9	+18
G	yes	2.5×10^9	−8
I	yes	7×10^9	+25

tion, which is to say that some coordinated, long-range molecular motion must be available within the required conditions. Restated, some portion of the glass transition region must be at or below room temperature. Table II summarizes the storage moduli at 20°C, and the temperature at which E'' reaches its peak value, correlating this to film-forming capacity (from Table I), for selected materials. Samples A and E have E'' peaks above room temperature and do not form films. Samples F and G have E'' peaks below room temperatures and do form films. Sample I, which does form a film, must be near the borderline. Film formation also correlates to some extent with the value of the storage modulus at 20°C, softer materials promoting film formation. It must be remembered, however, that these IPN's do not behave as classical homopolymers or random copolymers. Phase separation coupled with extensive mixing produces considerable broadening of the glass–rubber transition and a general toughening action.

In this preliminary study of PVC-based IPN's, it was shown that tough films with broadened apparent glass transitions can be formed. In a forthcoming study, we plan on examining the morphological features of these materials with the aid of electron microscopy.

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