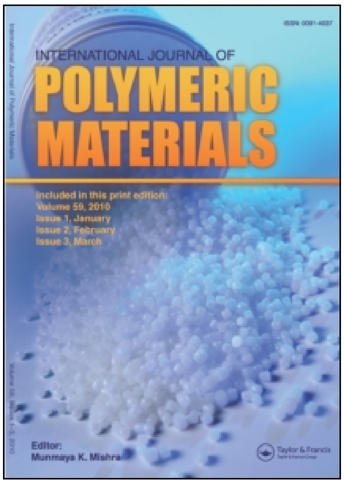

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Latex Interpenetrating Polymer Networks†

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Latex interpenetrating polymer networks are a unique type of polymer blend, synthesized by swelling crosslinked seed latex particles of polymer I with monomer II, plus crosslinking agents, and polymerizing monomer II *in situ*. In a manner similar to polymer blends generally, polymer I and II are incompatible to greater or lesser extents, and phase separate. In IPN materials, however, the phase separation is hindered by the presence of the double networks, giving rise to especially finely divided phase domains.

The synthesis of polybutadiene/polystyrene and poly(ethyl methacrylate)/poly(n-butyl acrylate) latex IPN's is considered, and the dynamic mechanical properties of the resulting films or molded materials is measured as a function of temperature. Two transitions were found for incompatible materials, while one broad transition arises with semicompatible polymer pairs. While regions of true interpenetration are indicated, the effect on the mechanical properties of inverting the order of polymerization suggests the presence of a shell-core phase separation. The origin of the shell-core separation effect is considered qualitatively, the underlying cause being ascribed to the statistics of mixing of polymer I with solvent (monomer II) and non-solvent, surrounding water.

INTRODUCTION

The synthesis of polymer network II within a pre-existing polymer network I results in a unique class of polymer blends. The products of such synthesis, termed interpenetrating polymer networks (IPN's), exhibit most of the properties of polymer blends, but in addition the double network structure provides a novel way of controlling phase domain size and extent of molecular mixing.[1–7] The original sequential IPN's were prepared by swelling a macro-

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scopic polymer network I with monomer II plus crosslinking and activating agents, and polymerizing *in situ*.[1-4,6,7] Another method of preparing these networks involves the simultaneous synthesis of both networks.[5] The preparation of simultaneous interpenetrating networks (SIN's) requires that both reactions be non-interfering and proceed under the same overall conditions. A third way of preparing IPN's involves emulsion polymerization techniques, wherein each interpenetrating network microcosm is contained within an individual latex particle.[8] The present paper will describe the synthesis of latex IPN's and their glass transition behavior. The effect of synthetic detail, such as inverting the order of synthesis, on the temperature dependence of the storage and loss moduli (E' and E'' respectively) will be examined in some detail.

EXPERIMENTAL

Synthesis

Two different series of latex IPN's were prepared. Series I being comprised of incompatible polymer pairs, and Series II comprised of semi-compatible polymer pairs. In Table I and below, the first named polymer served as the seed latex, and the second named polymer was synthesized within the seed latex in a second, later polymerization. When the order of polymerization is reversed, the term "inverse" is employed.

The syntheses were based on standard emulsion polymerization techniques,[9,10,11] as follows: To 300 ml of deionized, deaerated, stirred water at 60°C were added 50 ml of a 10% (W/V) solution of sodium lauryl sulfate,

TABLE I

Latex IPN syntheses

Series	Composition	Characteristics
I	PS/PB	Incompatible polymer pair, toughened elastomer
	PB/PS	Incompatible polymer pair, model high impact plastic
II	PnBA/PEMA and inverse synthesis	Semicompatible, high damping material

PS = polystyrene
PB = polybutadiene
PnBA = poly(n-butyl acrylate)
PEMA = poly(ethyl methacrylate)

followed by 5 ml of a 5% (W/V) of potassium persulfate. The calculated quantity of monomer was added at a rate of about 2 ml per minute. When the first monomer was fully added, a minimum of ten minutes was allowed to elapse. Then a new portion of initiator was added, but no new soap, followed by the second monomer under similar reaction conditions. For polybutadiene the reaction was conducted in a 150 ml pressure tube overnight at 55°C.

Two important departures from standard procedures should be noted[9,10,11]: (1) All monomers contained 0.4% (W/V) of crosslinking agent. Tetraethylene glycol dimethacrylate or diethyleneglycol dimethacrylate was used for the acrylic and methacrylic components, and divinyl benzene was employed with PB and PS polymerizations. (2) The reaction was carried out in two distinct stages. No new soap was added for the second stage polymerization to discourage the formation of new particles. Total polymer concentration of the completed latexes was about 20% (W/V).

The finished latexes were either coagulated with salt plus acid to recover the polymer, washed and dried,[9,11] followed by molding at 150°C for one hour at 50 PSI, or cast as a film and dried for at least one week, to obtain samples suitable for dynamic mechanical spectroscopy studies.

Dynamic Mechanical Spectroscopy

All dynamic mechanical measurements employed a Rheovibron direct reading viscoelastometer, model DDV-II (Vibron, manufactured by the Toyo Measuring Instrument Co., Ltd., Tokyo, Japan.) The temperature range employed was from −130°C to +150°C, with a heating rate of about 1°C per minute. To better correlate with sound damping experiments presently being conducted in our laboratory, a frequency of 110 Hz was employed. As per requirements of the instrument, the sample dimensions were of the order of 10^{-2} cm × 10^{-1} cm × 2 cm.

RESULTS

Series I

Both molded and cast specimens of a 25/75 PS/PB latex IPN were prepared for Vibron studies. The storage modulus, E', and loss modulus, E'', are shown as a function of temperature for the molded material in Figure 1. The cast film exhibited virtually identical mechanical spectra, indicating that the morphology was probably not seriously disturbed by the molding conditions employed. The PB transition at −60°C predominates, followed by a surprisingly well-defined rubbery plateau region at higher temperatures. In all the materials examined in this paper, no effort was made to crosslink the latex

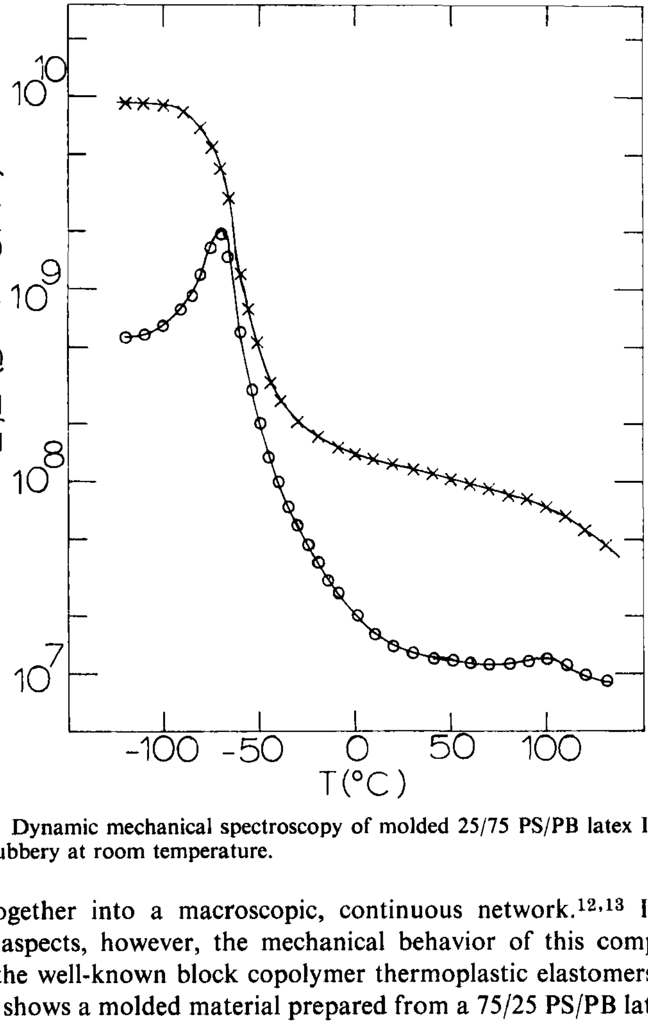

FIGURE 1 Dynamic mechanical spectroscopy of molded 25/75 PS/PB latex IPN. This material is rubbery at room temperature.

particles together into a macroscopic, continuous network.[12,13] In some important aspects, however, the mechanical behavior of this composition resembles the well-known block copolymer thermoplastic elastomers.[14,15]

Figure 2 shows a molded material prepared from a 75/25 PS/PB latex film. Although PS is the preponderant component, the loss peak of the PB transition is still the larger, suggesting phase continuity for the latter. However, the PB transition peak is shifted upwards to —40°C, indicating significant molecular mixing with PS. The *E'* values show a leathery behavior near room temperature.[16,17,18] Inverting the order of preparation has profound consequences on the physical behavior, suggesting a different morphology.[7] The data on 36/64 PB/PS molded material shown in Figure 3 exhibits a sharp PS transition and a stiff, plastic behavior (high *E'*) at room temperature, reminiscent of high impact polystyrenes, which contain a dispersed PB phase.[19,20]

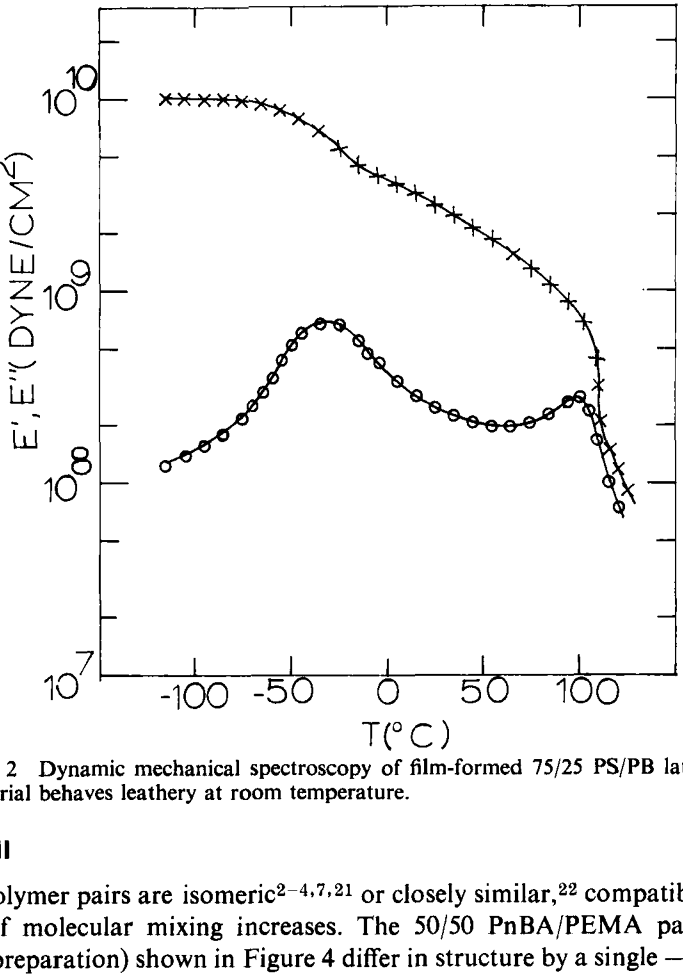

FIGURE 2 Dynamic mechanical spectroscopy of film-formed 75/25 PS/PB latex IPN. This material behaves leathery at room temperature.

Series II

When polymer pairs are isomeric[2-4,7,21] or closely similar,[22] compatibility or extent of molecular mixing increases. The 50/50 PnBA/PEMA pair (and inverse preparation) shown in Figure 4 differ in structure by a single —CH_2— group, plus some molecular rearrangement. Instead of two well-defined glass transitions, a single, very broad transition is apparent. The glass transition temperatures[17] for PnBA and PEMA, respectively, are −56°C and +65°C. The two materials shown in Figure 4, although identical in composition from a classical point of view, have significantly different transition temperature ranges. Most important are the broad damping spectra obtained, which will be discussed further below.

DISCUSSION

The above experiments demonstrate that inverting the order of synthesis alters the transition behavior of the latex IPN. In particular, the second

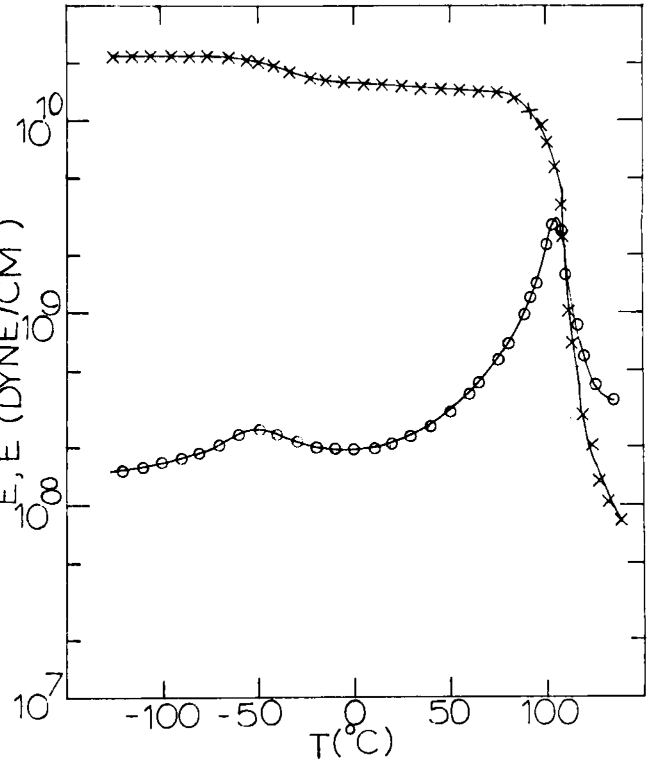

FIGURE 3 Dynamic mechanical spectroscopy of molded 36/64 PB/PS latex IPN. This material resembles impact resistant PS in stiffness and damping characteristics.

polymer network formed tends to exhibit a stronger glass transition (larger drop in E′, larger maximum in E″) than expected from the overall composition, and the seed latex network yields a correspondingly weaker transition. The relative contributions to the transition behaviour can be explained by examining the continuity of the two phases so formed. In 1967 Kato[23] showed that a second polymerization on a seed latex in the preparation of graft-type ABS polyblends resulted in two distinctive morphological features. Our schematic model of the possible structures are shown in Figure 5. The cellular structure may be postulated to arise from monomer II which penetrates into the interior of the polymer I seed latex, and phase separates upon polymerization. Secondly, there appears to be a coating of polymer II on the surface of the seed latex particle. Grancio and Williams[18,24] showed that in homopolymer emulsion polymerizations, the monomer polymerization kinetics behave as if a pure monomer phase exists up to about a 60% conversion. Electron microscopy studies showed that this remaining

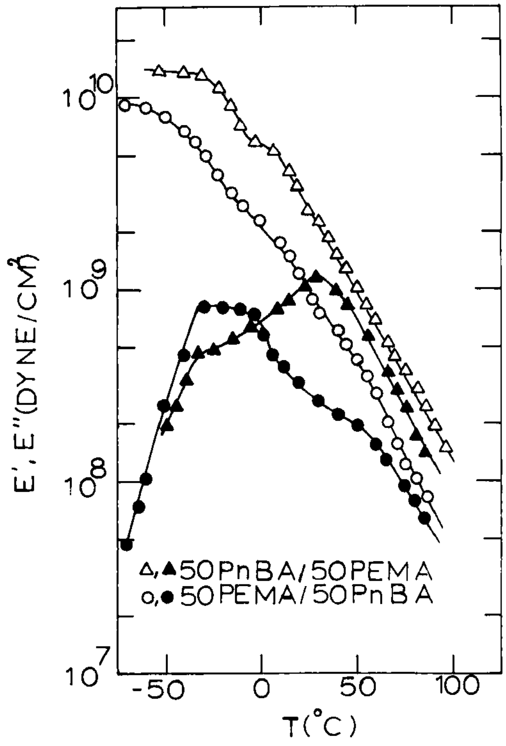

FIGURE 4 Storage and loss moduli on semi-compatible latex IPN's. Note breadth of *E''* peaks.

monomer was concentrated in the outer regions of the latex particles, giving rise to a shell-core effect.

In latex IPN's, the monomer portion that swells into the seed latex network before polymerizing (plus crosslinker) probably gives rise to an inner region of true interpenetration, which we visualize tapers off to a shell structure in the outer regions of the individual latex particle. In addition, we envision the appearance of a fine structure,[4,7] especially in semi-compatible or very small latex particles. The fine structure, which is due to a second-stage phase separation, late in the polymerization of monomer II, consists of segregated regions of polymer II having dimensions of the order of 100Å. The fine structure morphology is discussed in greater detail elsewhere.[4,7]

On molding or film formation, the shell structure will tend to form the continuous, or more continuous phase, explaining the pre-eminence of the polymer II transition. The material within the core contributes nearly normally to the loss term, but only modestly to the storage modulus term. It should be

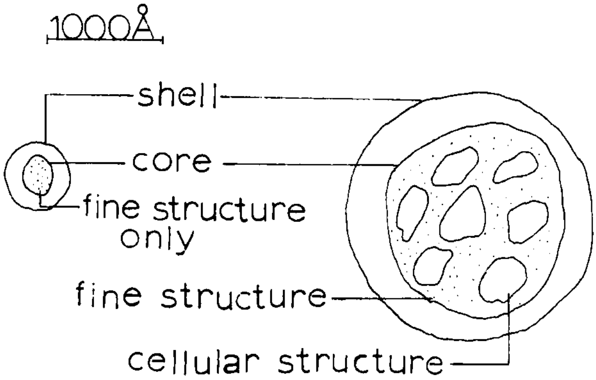

FIGURE 5 Model of predicted latex IPN morphology, showing cellular structures, fine structures, and a shell-core morphology.

noted that with the sequential IPN's studied by us[1–4,6,7] the reverse morphology and mechanical behavior was found. The macroscopic sequential IPN's lack a shell-core effect, and the cellular structure predominates. As a consequence network polymer I forms the continuous or more continuous phase.

Synergistic Damping Effects in Semi-Compatible Polymer Pairs

IPN's prepared from semi-compatible polymer pairs,[3,4,7] such as poly(ethyl acrylate)/poly(methyl methacrylate), or in the present case PEMA/PnBA, exhibit extraordinarily broad damping ability. Similar effects have been noted for semi-compatible blends and grafts.[25] Qualitatively, the damping may be ascribed to the rubbing together of partly mixed stiff and soft molecules.[3] A measure of damping is given by tan δ, which may be defined as

$$\tan \delta = E''/E' \tag{1}$$

A plot of tan δ *vs* temperature is shown in Figure 6 for semi-compatible, and also incompatible latex IPN polymer pairs. The PEMA/PnBA and PnBA/PEMA pairs have broad temperature regions where values of tan δ remain relatively constant. Both the total area under the curves, and the average area per degree are of interest, see Table II. Also tabulated are corresponding PEA/PMMA data from Ref. 7. The semi-compatible IPN PnBA/PEMA and inverse composition stand out as exhibiting the largest average area per degree C through the transition range.

Origin of the Shell-Core Structure

Let us now examine possible fundamental causes of the shell-core structure. Since in a partly reacted latex particle the remaining monomer is concentrated

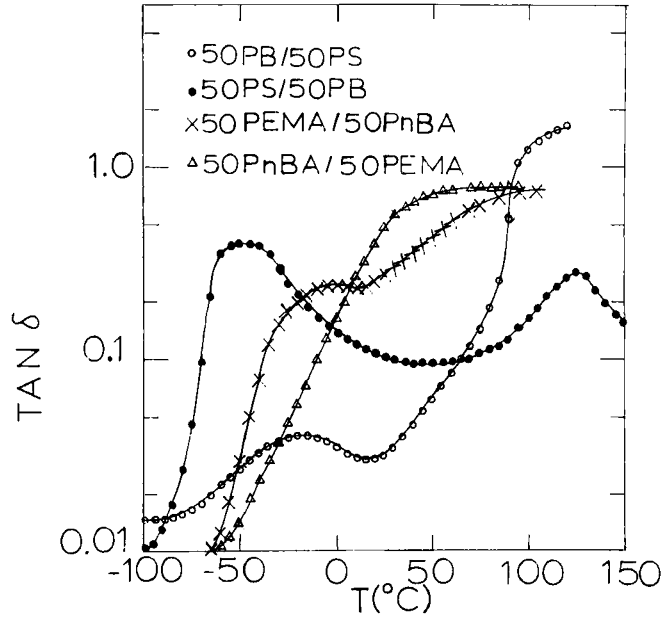

FIGURE 6 Values of tan δ *vs* temperature for incompatible and semi-compatible latex IPN pairs. Chemical makeup as shown.

in the nascent shell and the previously formed polymer resides in the core, regardless of whether or not monomer II is the same as or different from polymer I, the origin of the shell-core structure should be of interest to many emulsion polymerization systems. The crux of the solution can be seen from

TABLE II

Damping Characteristics of IPN's

Samples	Range, °C	Area† under the curve units °C	Area/deg average
50/50 PB/PS	−100 to 120	43.6	0.19
50/50 PS/PB	−100 to 150	45.9	0.18
50/50 PEMA/PnBA	−50 to 75	50.61	0.45
50/50 PnBA/PEMA	−50 to 75	55.4	0.45
†74.4/25.6 PEAB/PS	−50 to 150	70.6	0.35
†72.2/27.8 PEAB/PMMA	−50 to 150	69.4	0.35
†24.6/75.4 PS/PEAB	−5o to 150	40.9	0.20
†27.0/73.0 PMMA/PEAB	−50 to 150	47.1	0.23

†Data from Ref. 7.

‡Area under the curve obtained by plotting linear tan δ *vs* temperatures through the stated temperature range.

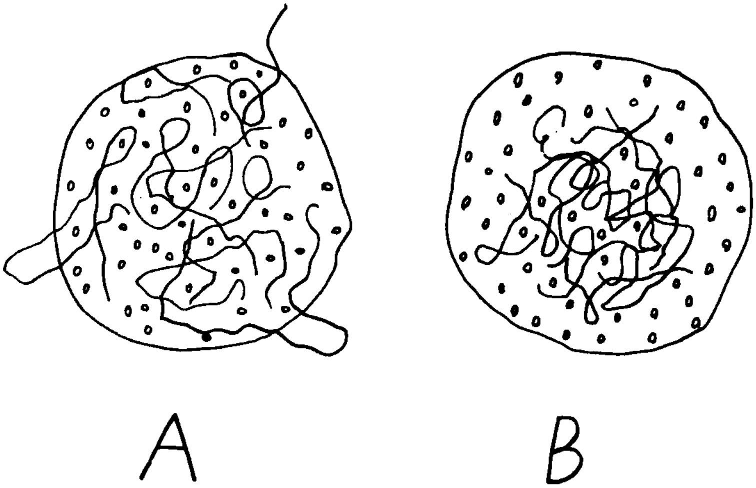

FIGURE 7 Two models of a partly polymerized latex particle. Model A permits some polymer/water contacts, which are "forbidden" in model B.

two aspects: (1) Referring to Figure 7, polymer loops or ends protruding into the aqueous phase as shown in 7A are strongly discouraged or essentially forbidden because of the highly unfavorable heat of mixing that arises upon mixing organic polymer chains and water. (2) Considering the water as part of the "solvent" along with monomer II, let us consider the Flory-type mixing statistics. Inherent in Flory's[26] development (designed from polymer-solvent systems) is the effect of excluded volume, both intra and intermolecular exclusions being considered. According to the said mixing scheme, whenever a polymer molecule is placed in an unrealistic or impossible position, the entire molecule must be lifted out, and placed anew into the medium, each new placement being on a statistical or random basis. The aqueous phase being essentially forbidden, the polymer chains already formed (polymer I) will tend to be concentrated in the central portion of each latex particle so as to avoid polymer-water contacts. Monomer II occupies the remaining sites, mostly near the surface but some within the interior as shown in Figure 7B, and on polymerization forms a more or less permanent shell.

Conclusion

The dynamic mechanical spectroscopy studies reported herein confirm Kato's and also Grancio and Williams' finding of a shell-core structure in emulsion polymerization latices. Using the notions of polymer/solvent mixing statistics developed much earlier by Flory, a qualitative explanation is possible in terms of the positive heat of mixing developed by polymer/water contacts.

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