Studies with Gradient Polymers of Polystyrene and Poly(methyl acrylate)

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ABSTRACT: A series of [*net*-polystyrene]-*ipn*-[*net*-poly(methyl acrylate)] systems with gradients of poly(methyl acrylate) in a polystyrene matrix are prepared and tested mechanically. The results showed no distinct differences from that of corresponding interpenetrating polymer network (IPN) samples with similar compositions, in contrast to the substantially improved fracture strains obtained for [*net*-poly(methyl methacrylate)]-*ipn*-[-*net* poly(methyl acrylate)] gradient systems and their nongradient IPN's in our previous work. Hence, it is concluded that the toughening effect of gradient structure observed is not universally applicable for all gradient systems but it is unique for the acrylic system studied. Moduli-temperature responses and dynamic mechanical spectra of gradients and IPN's prepared in the current study are also presented. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1721–1725, 1999

Key words: gradient polymers; polystyrene-gradient poly(methyl acrylate); interpenetrating polymer network

INTRODUCTION

Gradient polymers constitute a special case of IPN (interpenetrating polymer network) or semi-IPN's.[1] They are both multicomponent multiphase systems with a combination of two(or more) polymers (at least one of which is)in network form having effective molecular interpenetration between them.[2] In a gradient polymer system, the concentration of one of the components (gradient), being chemical and/or physically different from other components, is allowed to change as a function of its position in the sample, producing a certain predetermined gradient profile. The gradient profile can be of any shape—i.e., linear, sigmoidal, parabolic or flat—the latter of which certainly corresponds to the classical (nongradient) IPN structure. In principle, gradient polymers can have gradients in their structures and/or compositions.

Gradient polymeric systems are usually prepared by diffusing a guest monomer into the host polymer (matrix) for certain periods of time to establish the predetermined gradient profile, which is then fixed by polymerization of diffused monomer in situ. In the previous study,[3] we have shown that introduction of polyacrylonitrile gradients into a polystyrene (PS) matrix can help increase the hydrocarbon resistance of the latter substantially. In the same study, the poly(methyl methacrylate)–grad.poly(methyl acrylate) system {which can be presented as "[*net*-PS]-*ipn*-[*net*-PMA] gradient"} after use of the nomenclature recommended by Sperling et al.[2]) is shown to have enhanced toughening characteristics and appreciably high fracture strains, if compared with corresponding nongradient IPN or random copolymers with similar compositions. Results of a similar acrylic system, [*net*-PMMA]-*ipn*-[*net*-poly(2.chloroethylacrylate)][4] gradients have also strongly supported these findings.

With the hope of adding more insight into some of these important results, a series of different types of gradients are prepared and examined in a recent systematic study. In this context, a number of samples with physical (rubbery/or hard gradients in rubbery/or hard matrices) and chemically similar/or different matrices/or gradients are prepared and examined.

The part presented in this article covers some basic findings obtained from a physically similar (rubbery gradients in hard matrix)–chemically different (PS matrix with PMA gradients in it) gradient system, as compared with the previous study. The results of others will be the subject of other communications to follow.

EXPERIMENTAL

Gradient and corresponding nongradient IPN samples are prepared in crosslinked PS matrices by using PMA as the second component at various levels. PS matrices are prepared in specially designed glass walled cells by UV-initiated polymerization. For this, the monomer is mixed with 1.5% photosensitizer (benzoin isobutyl ether, a Stauffer Chem. Co. product) and with 1.2% crosslinking agent (ethylene dimethacrylate, a Polysciences Chem. Co. product). Gradients are prepared by diffusion of MA into crosslinked PS matrices for certain durations at constant temperature, followed by immediate UV-initiated polymerization. The time and temperatures are optimized for need by a series of separate diffusion experiments performed prior to samples preparation stage. Nongradient IPN samples with corresponding concentrations are prepared by delaying the polymerization (i.e., after having the same amount of diffusion into the matrix, the sample is removed and let to stand outside of the system by itself in a closed container for rather long periods of time) and by initiating polymerization after reaching the expected flat profile of diffusant (no gradient case).

All gradient and nongradient IPN samples prepared are stored in a vacuum oven at 35°C until constancy in weight to assure removal of any residual monomer or additives.

The profiles of gradients obtained are not rechecked in this work, mainly because of inconveniences of testing for PS in PMA. Since diffusion coefficient of styrene in PMA and its solubility parameter values are very similar to that of methylmethacrylate, at the same temperature and durations of time and for the same thickness of matrix film, one can expect to have similar para-
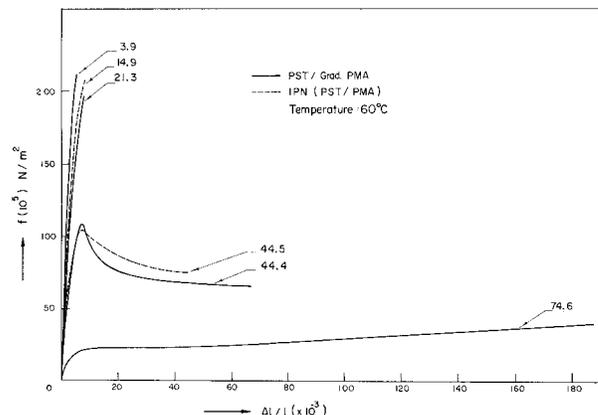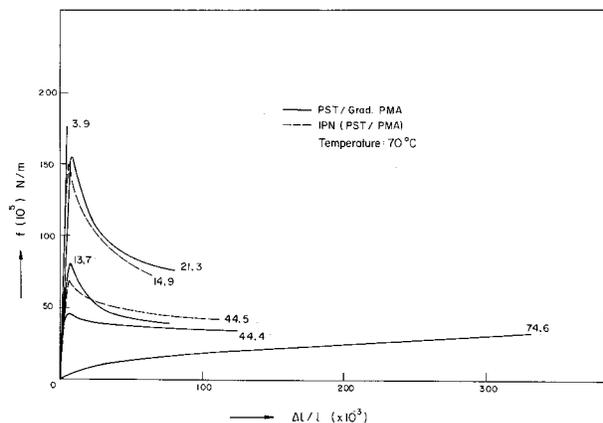

Figure 1   Stress-strain behavior of various PS-Grad. PMA and IPN (PST/PMA) samples at 60°C. (Rate of strain is 0.05 cm/min).

bolic gradient profiles for PS in PMA as in the case of PMMA/PMA gradient system.

Both static and dynamic mechanical tests are applied to the samples prepared. Unidirectional stress-strain experiments are done by a TM-SM Instron Universal Testing system at three different temperatures (60, 70, and 80°C) with at least three samples for each test, and in addition, a Gehman Torsional tester (American Instr. Co.) is used during some viscoelasticity studies. Dynamic mechanical tests are done at four different frequencies selected,(3.5, 11, 35, and 110 cps), from −20 to 110°C.

RESULTS AND DISCUSSION

Stress-strain results at three different temperatures with the general constant strain rate of 0.05 cm/min are presented in Figures 1–3 for gradient and nongradient IPN samples prepared. As can be seen from the first figure, both tensile fracture strain and ultimate tensile strength values for 3.9 and 21.3 phPS gradient samples (numbers correspond to the weight percent PMA per hundredth PS) are very close to each other and that the nongradient IPN with 14.9 MAphPS is in between that of the latter two. The initial moduli of these three samples are approximately the same. However, a further increase of MA contents in the samples are seen to change the mechanical behavior and characteristics of both nongradient and gradient IPN's appreciably, becoming softer and tougher by increase of the soft component concentration, as expected.[3] This most probably is due to the plasticization effect of MA, and the reason

Figure 2 Stress-strain behavior of various net-PS-Grad.PMA and IPN (PST/PMA) samples at 70°C. Rate of strain is 0.05 cm/min.

why the same effect did not show up until rather high concentrations of the latter (21.3 phPS) is an open question for the time being. However, although there is a nice fit between the solubility parameter values of PMA and PS[5] ($\Delta\delta$ is between 1.5 and 0.4), one still can point out the fact that since both matrix and gradient components are crosslinked, there may be a certain delay in the plasticization efficiency. For both types of samples with more than 40 PMAphPS, there is a yielding developed (plastic flow) at which the upper yield point for strain—where yielding initiates—is very close to fracture strains of samples with much lower MA concentrations with no yielding.

The slight improvement observed in toughening of hard matrix by inclusion of increased amounts of MA is somewhat expected as mentioned above; however, the degree of improvements obtained for nongradient and gradient IPN samples with similar compositions of MA are found not too different from each other, in contrast to the previous findings.[3,4] In fact, nongradient IPN with 44.5 PMAphPS exhibits a stress-strain curve similar to that of the corresponding 44.4 phPS gradient sample (Fig. 1). The main differences observed between the two are small, and are in the fracture strains and levels of the curves. Similar results are also observable at higher temperatures (Figs. 2 and 3); and as temperature increases new yield points begin to appear for samples with smaller PMA contents and the effect of the latter becomes more apparent. The differences between nongradient and gradient IPN samples are probably more appreciable for the upper yield and tensile strength values rather than for the fracture strains. For all of the

samples tested, appreciable improvements in various mechanical properties, especially in toughnesses, are observed if compared with that of pure PS matrix. The basic differences between earlier studies[3,4] and those obtained in this study clearly show that the enhanced toughnesses observed for (PMMA-grad.PMA) systems as compared to their nongradient IPN's with same compositions is not a universal finding applicable for all gradient systems, but it is unique for the PMMA–PMA system used.

There are a number of parameters that have to be considered if a comparison is being made between different gradient and nongradient IPN systems. Probably two of these parameters would be the physical state of the components involved (i.e., as hard or soft) and the differences in chemical natures (as a measure of extend of compatibilities). The physical states of both components (matrix being glassy/hard and the second component as soft) are the same for both PS/PMA (this work) and PMMA/PMA (previous study). In addition, $\Delta\delta$ difference for the matrix and for the second component is similar as well (being between 0.4–1.5 and 0.9–1.0 for PMMA/PMA and PS/PMA, respectively).[5] Obviously these two parameters are not sufficient to make a sound comparison and additional factors have to be considered.

Dynamic mechanical spectra of one of the gradient samples (with 25.4 PMAphPS) and matrix are presented in Figures 4 and 5 at four different frequencies employed. The spectra shows the existence of small PMA loss peaks for this sample and the comparable PS peaks. The magnitude of PMA loss peaks is found to increase monotonically and become comparable as its share increase
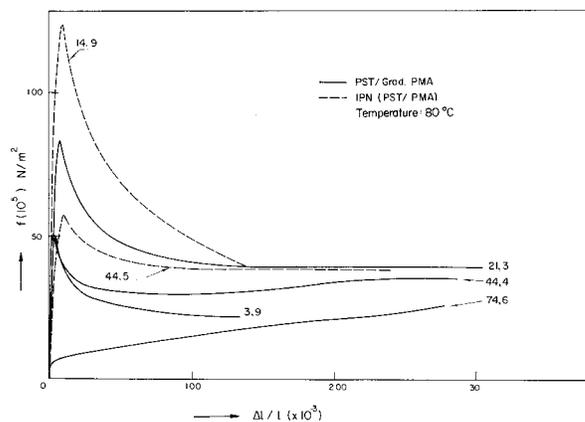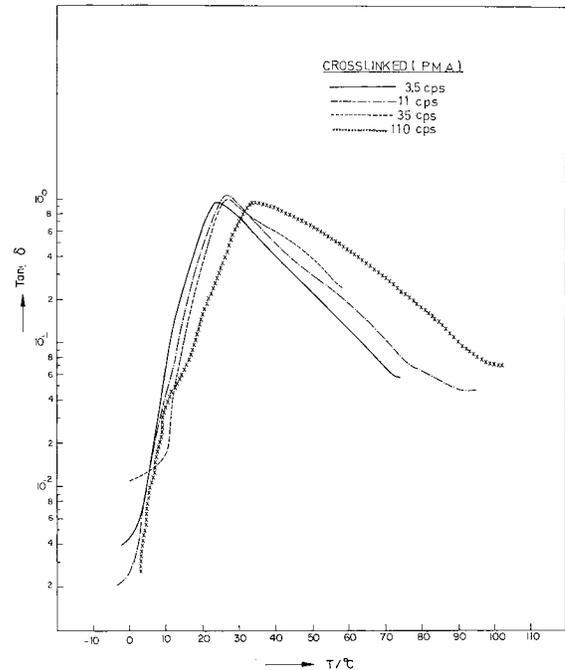

Figure 3 Stress-strain behavior of various [*net*-PS]-*ipn*-[*net*-PMA] gradient and nongradient IPN samples at 80°C. (Rate of strain is 0.05 cm/min).
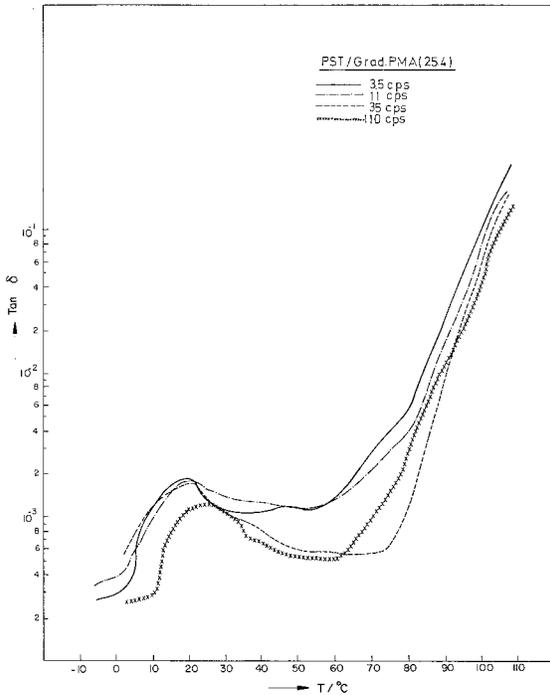
Figure 4 Dynamic mechanical spectra of [*net*-PS]-*ipn*-[*net*-PMA] gradient samples with (25.4)PMAphPS.

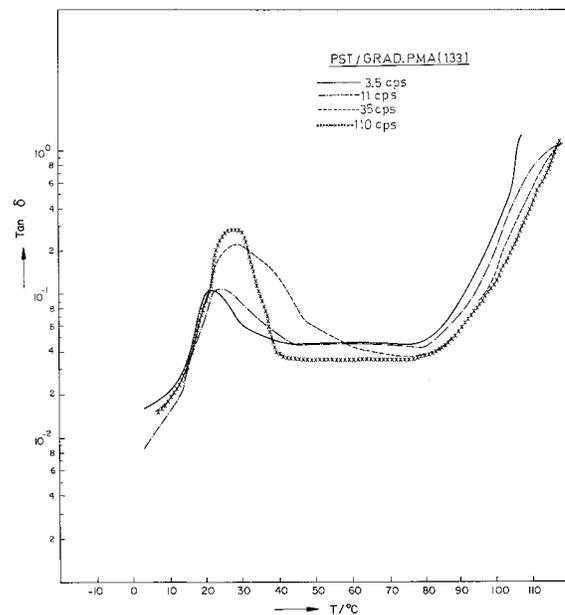**Figure 5** Dynamic mechanical spectra of matrix (crosslinked PMA).

in the system, as expected. Figures 6 and 7 are for two of the gradient samples prepared specifically with as high as possible PMA contents(193 and 293.7 PMAphPS, respectively) to check the effect of excess PMA on properties. As seen, the magnitude of PMA loss peaks are getting really comparable with that of PS in these samples. Due to experimental difficulties involved, clear sharp PS peaks cannot be obtained; although the system had a network structure.

From the dependency of PMA loss peaks on frequency, it would be possible to calculate the energies of activation for the transition, and since it should be closely related to the environment that PMA chains do have, it may be of interest to have at least some valuable qualitative data on microphase separation. Arrhenius-type plots prepared for three gradient and one pure PMA samples are presented in Figure 8, which have yielded at (238 kJ) for the matrix (PMA) as well as for the 293.7PMA phPS samples. Corresponding values for the rest are much higher: (368 and 840 kJ for gradients with lower PMA, for 133 and 25.4 PMA phPS; respectively) showing that even in the case of low PMA contents, the separated PMA-rich phase contains some PS; and, as PMA content increases the phase separated gets richer for PMA (which continues up to the limit of 293 PMAphPS content; where it is almost similar to pure PMA).
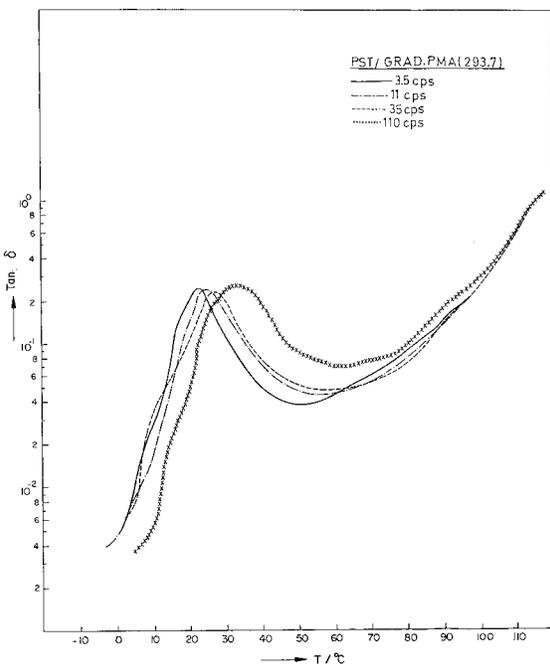
The results of Gehman torsion test is presented in Figure 9 for some selected gradient samples and for pure PS as well as for pure PMA samples, in (the 10-s modulus vs. temperature) format. At this point one should keep in mind that (1) the


Figure 6 Dynamic mechanical spectra of [*net*-PS]-*ipn*-[*net*-PMA] gradient samples with (133)PMAphPS.

Figure 7 Dynamic mechanical spectra of [*net*-PS]-*ipn*-[*net*-PMA] gradient samples with (297)PMAphPS.

torsion results are not expected to correspond to that of tension exactly, where average response of the whole sample for the tension case and mainly the response of surface layers—where the PMA concentration is highest—for the torsion are expected to contribute most; and (2) all of the samples tested were crosslinked by use of the same crosslinker with the same prescription.

As seen from the last figure, slightly crosslinked PS and PMA prepared have transitions around 85 and 15°C; respectively. With the 21.3 PMAphPS gradient sample, it is possible to
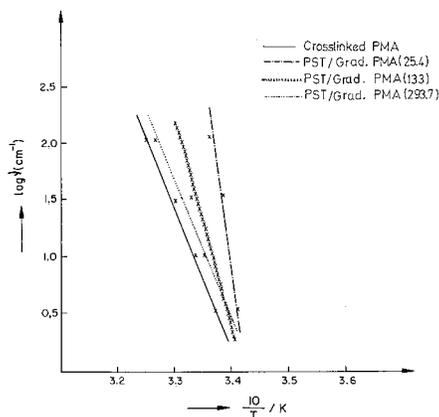
Figure 8 Arrhenius plots for various gradients prepared and PMA matrix used.
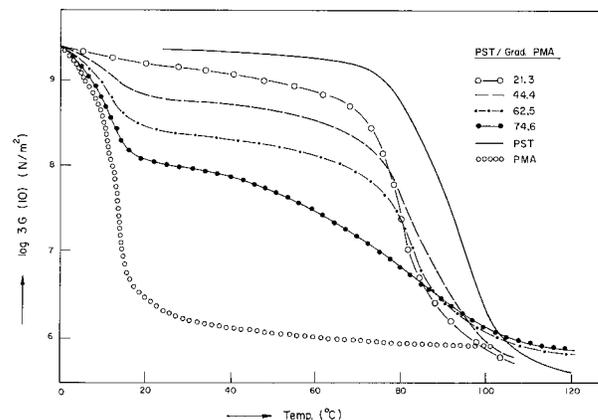
Figure 9 Gehman test results for 10-s modulus versus temperature.

observe changes both in position and shape of the curve, as compared with that of PS. When MA content in the gradient is increased to 44.4 phPS, another transition around 15°C begin to appear. At this point, most probably a second PMA-rich phase is forming in the system. This point is further checked and approved by dynamic tests in our studies. For the same sample, the change in the shape of the curve around PS transition is seen to continue, which is much broader than the previous sample. As PMA content in gradients is increased further, the PMA transition becomes more distinguishable and PS transition gets broader—both of which are the most apparent in the case of gradient 74.6 PMAphPS tested, with gradual decreases in steepness index values. However, the improvement in the degree of toughnesses expected from Gehman test results are not reflected at all in tensile tests, as presented above.

Studies are underway to shed some more light on these systems, the results of which will appear soon.

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