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### The Preparation of Ipns of Polystyrene-Polyethylene and Poly(Butyl Methacrylate)-Polyethylene and Their Dynamic Mechanical Behavior

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## **THE PREPARATION OF IPNs OF POLYSTYRENE- POLYETHYLENE AND POLY(BUTYL METHACRYLATE)- POLYETHYLENE AND THEIR DYNAMIC MECHANICAL BEHAVIOR**

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### **ABSTRACT**

IPNs based on polyethylene and vinyl polymers were prepared according to a new procedure. We studied the dynamic mechanical behavior of two series of IPNs: polystyrene (PS)–polyethylene (PE)

and poly(butyl methacrylate) (PBMA)-PE at the frequency  $\omega = 1$  Hz and in the temperature region from  $-50$  to  $200^\circ\text{C}$ . Temperature dependences of the components of the dynamic modulus of elasticity  $G'$  and  $G''$  of the networks PS and PBMA have shapes typical of amorphous networks; the corresponding dependences of pure PE show, however, features typical of a semicrystalline polymer. IPNs of the system PS/PE show two-phase behavior. At  $T < 110^\circ\text{C}$ , PE functions as a plasticizer. In the system PBMA/PE, better miscibility of components is seen, and PE exerts a reinforcing effect on the mechanical behavior over the whole temperature region. In both systems, network density increases with increasing PE content in IPNs. Better homogeneity and a slight increase in the network density of IPNs with PBMA/PE in comparison to PS/PE networks are probably caused by a greater number of grafted PBMA chains in the PE network compared to the PS network.

## INTRODUCTION

Much attention has recently been paid to the study of the physicochemical properties of interpenetrating networks (IPNs) [1-5]. While the classical way of polymer mixing usually leads to multiphase morphology because of immiscibility, formation of IPNs via crosslinking reactions can yield more homogeneous systems. In some cases it is the only method that allows preparation of a blend from completely immiscible polymers. The structure of IPNs differs from systems prepared by physical mixing mainly in the fact that both polymers form continuous phases in the whole volume of IPNs; this may be reflected favorably in the physical, especially mechanical, properties.

A special problem for IPNs is the miscibility of the individual components and the existence of an interphase [4]. IPNs show different degrees of phase separation, and this depends primarily on the compatibility of the components. There are systems with phase regions which vary in size from several micrometers (incompatible systems [6]) to several tens of nanometers (intermediate [7]) up to homogeneous systems (without domain structure). These structures specifically affect mechanical behavior. There are two main transition areas for incompatible systems, whereas only one transition is observed for homogeneous systems. With "intermediate" structures there is usually one rather broad transition. IPNs

show improvement of other properties, such as tensile strength [4–7], impact strength, adhesion, and, in some cases, greater sound and shock absorption [8]. Improved tensile mechanical properties were also found for a polyethylene–polystyrene melt-blended system [9] to which a small amount of block copolymer poly(hydrogenated butadiene-*b*-styrene) was added.

Trochimczuk et al. [10–12] prepared IPNs based on polyethylene and polystyrene below the dissolution temperature [10, 11] or in a mixer [12].

We deal here with the preparation of IPNs of immiscible polymers of polystyrene with polyethylene and of poly(butyl methacrylate) with polyethylene. An original procedure was used for the preparation of these two types of IPNs; the crosslinking polymerization of vinyl monomer was initiated in solution (solution of polyethylene in vinyl monomer), in contrast to previous methods [10, 12]. The dynamic-mechanical behavior of these IPNs was studied in the main transition region.

## EXPERIMENTAL

### Sample Preparation

Polyethylene (PE, Bralen RA 2-19 type with a flow index of 1.7–2.3 g/10 min) was dissolved in the corresponding monomer with the crosslinking agent [styrene (S) with a 0.5 mass% of the crosslinking agent divinylbenzene (DVB) or butyl methacrylate (BMA) with 0.5 mass% glycol dimethacrylate (GDMA), always with respect to all blend]. Di-*tert*-butyl peroxide (DTBP) (3 mass%) was then added to the blend. Polymerization of IPNs proceeded in glass forms at 120°C for 5 h, then the temperature was raised to 160°C and polymerization took place for another 1 h. Two series of IPNs were prepared: PE/PS and PE/PBMA. For comparison, pure starting networks of PS and PBMA were prepared from the corresponding monomers with the same concentrations of crosslinking agents as for IPNs. A sample of pure PE was prepared from PE impregnated with DTBP and GDMA (in CHCl<sub>3</sub> solution) after thorough drying by pressing at 160°C and at a pressure of 70 MPa for 1 h. We assume that the polymerization of vinyl monomers and their crosslinking occurred first; this may be accompanied by the incorporation of PE chains into a vinyl network. In the last stages of the reactions, a PE network was formed as a result of the presence of peroxide.

## MEASUREMENTS

Temperature measurement of the complex shear modulus  $G^* (= G' + iG'')$ , where  $G'$  and  $G''$  are storage and loss modulus, respectively) was done on a Rheometrics System Four apparatus. Measurements were done over the temperature interval  $-50 < T < 200^\circ\text{C}$  at a constant frequency of  $\omega = 1$  Hz on samples of  $50 \times 10 \times 1$  mm.

Extraction of the samples was done in boiling xylene for 14 h. The mass gel fraction  $w_g$  was assessed from the sample mass before and after extraction.

## RESULTS AND DISCUSSION

### Extraction Behavior of IPNs

The course of the crosslinking reaction at  $T = 120^\circ\text{C}$  in IPNs can be judged by the dependence of the mass gel fraction  $w_g$  on the reaction time (Fig. 1). The reaction of the system PS/PE was finished in 30 min, while the equilibrium values of  $w_g$  in the PS/PE system were achieved after  $t > 150$  min. This difference is probably caused by the higher glass transition temperature  $T_g$  for PS ( $T_g \approx 90^\circ\text{C}$ ) than for PBMA ( $T_g \approx 40^\circ\text{C}$ ). Figure 1 also shows that there is a more perfect IPN in the system PS/PE ( $w_g \approx 0.95$ ) than in the PBMA/PE system ( $w_g \approx 0.9$ ).

### Dynamic Mechanical Behavior

Temperature dependences of the components of shear modulus  $G'(T)$  and  $G''(T)$  of the PS and PBMA networks have a shape typical of amorphous networks (Figs. 2 and 3). As expected, the temperature position of the main transition region of the PS network ( $\approx 90^\circ\text{C}$ ) is shifted by  $50^\circ\text{C}$  to higher temperatures as compared to the PS network ( $\approx 40^\circ\text{C}$ ). On the other hand, the temperature dependences  $G'(T)$  and  $G''(T)$  of the sample of PE alone show features characteristic of a semi-crystalline polymer (slow decrease in  $G'$  and  $G''$  throughout the temperature region between  $-20$  and  $110^\circ\text{C}$ ). At  $T \approx 115^\circ\text{C}$ , the crystalline phase of PE melts, which is seen as a remarkable decrease in the modulus of both components. The network formed in PE is very thin, and the equilibrium modulus could not be measured (the value of the mass gel fraction,  $w_g \approx 0.9$ , favors the network).

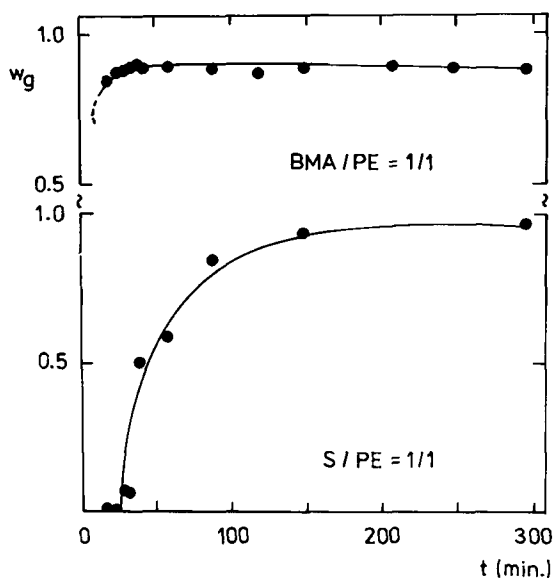


FIG. 1. Dependence of the weight fraction of the gel  $w_g$  on the reaction time at 120°C (after 14 h extraction in boiling xylene).

The existence of two maxima on the temperature dependence of the loss modulus  $G''$  is evidence of the two-phase structure of IPNs of PS/PE (Fig. 2). The two-phase structure is also confirmed by observation of domains in the IPNs of PS/PE by electron microscopy [13]. While the low-temperature maximum ( $\approx 80^\circ\text{C}$ ) is connected with the main transition in the PS phase, the maximum at  $T \approx 115^\circ\text{C}$  corresponds to the melting temperature of the crystalline phase of PE. At  $T < 110^\circ\text{C}$ , PE has a plasticizing effect, and the  $G'$  moduli of IPNs are between the limiting values of the moduli for pure components (both  $G'$  and  $G''$  moduli decrease with an increasing PE content in IPNs).

On the other hand,  $G'$  increases at  $T > 120^\circ\text{C}$  with increasing PE content (Fig. 2). The considerable increase in  $G'$  ( $> 3\times$ ) at temperatures around  $150^\circ\text{C}$  (rubbery area) may be interpreted as a higher density of the vinyl network of PS formed compared to the higher content of the bifunctional monomer (divinylbenzene) with respect to styrene in the reaction mixture. This leads to the highest values of  $G'$  in IPNs with the lowest content of PS of the network.

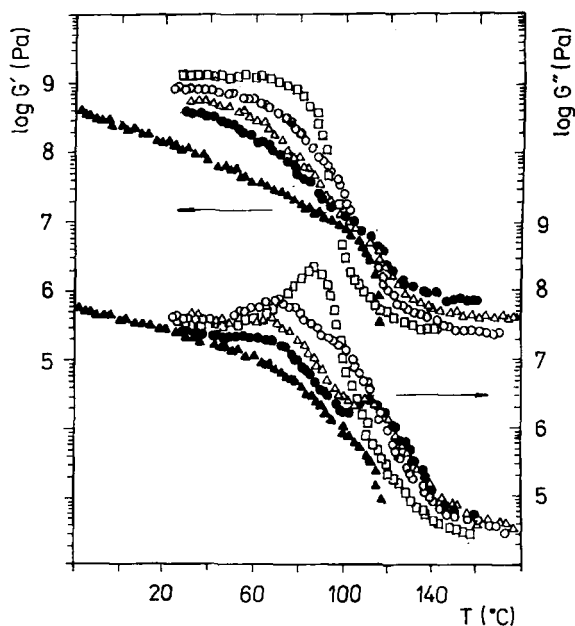


FIG. 2. Dependence of  $G'$  (Pa) and  $G''$  (Pa) on temperature  $T$  ( $^{\circ}\text{C}$ ) for the PS-PE system: ( $\square$ ) PS; ( $\circ$ )  $X_{\text{PE}} = 0.25$ ; ( $\triangle$ )  $X_{\text{PE}} = 0.5$ ; ( $\bullet$ )  $X_{\text{PE}} = 0.60$ ; ( $\blacktriangle$ ) PE.

In the case of IPNs of the system PBMA/PE, PE has a reinforcing effect throughout the temperature region. The character of temperature variations of the components of  $G'$  and  $G''$  moduli confirms the better miscibility of both components of this system in comparison with the PS/PE system. The increase in the  $G'$  ( $\approx 1.5\times$ ) modulus is also smaller at  $T > 130^{\circ}\text{C}$  in this system than in the PS/PE system. A smaller increase in  $G'$  confirms the smaller increase in network density. This is caused by a little lower network efficiency of the bifunctional monomer (glycol dimethacrylate), which also partially cyclopolymerizes with BMA. The homogeneity of the PBMA/PE network in comparison with the PS/PE networks is higher, probably due to the higher degree of incorporation of the vinyl network into the PE network. This may be accounted for by the much greater reactivity of propagating PBMA radicals in transfer reactions to alkanes than of the PS propagating radicals [14].

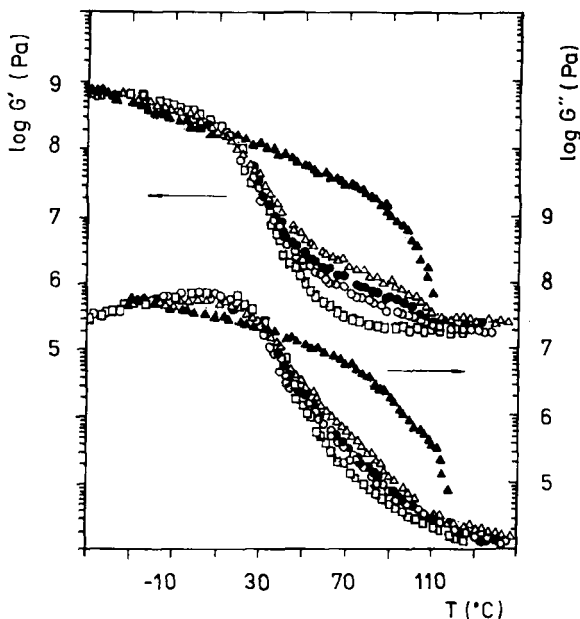


FIG. 3. Dependence of  $G'$  (Pa) and  $G''$  (Pa) on temperature  $T$  ( $^{\circ}\text{C}$ ) for the PBMA-PE system: ( $\blacktriangle$ ) PE; ( $\triangle$ )  $X_{\text{PE}} = 0.63$ ; ( $\bullet$ )  $X_{\text{PE}} = 0.50$ ; ( $\circ$ )  $X_{\text{PE}} = 0.25$ ; ( $\square$ ) PBMA.

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