

The chemical resistance of the different films was measured with accelerated conventional tests. It was found that the properties of varnishes prepared with or without hexa were similar. They appear to be superior to those of the corresponding commercial films.

A wide range of suggested driers concentrations was found in related literature. Table 3 shows the effect of several driers proportions on the hardness of films. Not only was the film hardness severely diminished when decreasing the Co amount, but also the drying time was greatly increased. Further, lead was found to be inconvenient for an adequate gloss retention. Thus, for our particular case it is recommended to use 1% Co, giving a 'print free' drying time of two hours.

In conclusion, an excellent varnish may be obtained by heating 40 parts of a novolac ($\bar{M}_n = 560$), 40 parts of tung oil, 20 parts of polymerized linseed oil (200 poise at 20°C) and 3 parts of hexamethylenetetramine, for 10 minutes at 220°C, thinning with white spirit in a 1:1 weight ratio and adding 1% Co with respect to total oil.

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Polymeric systems for acoustic damping: 2. Preparation and properties of a poly(vinyl isobutyl ether)—poly(methyl acrylate) interpenetrating polymer networks

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Introduction

Interpenetrating polymer networks (IPN) constitute a class of materials in which two usually distinct networks are intimately combined. There are a variety of synthesis methods¹⁻⁵, but broadly speaking a three-dimensional network of the first component is established in the presence of the monomer plus crosslinking agent of the second component which is then polymerized also to give a three-dimensional network. A number of recent reviews⁶⁻⁸ of various aspects of these materials are available.

The majority of IPN's exhibit phase separation, but the size, shape and extent of connectivity of the phases can be varied considerably by altering the mutual compatibility of the constituent polymers⁹, the crosslink density—particularly of the first formed network¹⁰, the synthesis method^{5,11} and the composition^{4,11}.

An IPN formed by swelling crosslinked polyvinyl isobutyl ether sheet in methyl acrylate containing a crosslinking agent, and then polymerizing this monomer, has been investigated using, principally, dynamic mechanical spectroscopy. In an earlier paper¹² reference was made to the suitability of such materials for acoustic damping. It is believed that this material has interesting properties from this point of view.

Experimental

Polyvinyl isobutyl ether (Lutonal ICK) was kindly donated by B.A.S.F., while the methyl acrylate and divinyl benzene were supplied by Cambrian Chemicals. Table 1 has characterization data for the uncrosslinked polyvinyl isobutyl ether. Crosslinked sheets of polyvinyl isobutyl ether were prepared by milling the polymer on an unheated Farrell two-roll mill and then adding 2.5 g of the crosslinking agent, tertiary butyl peroctoate, per 100 g of polymer. After this addition milling was continued for a further 10 min. Sheets were then cured in a hot press at 120°C for 30 min.

Sheet samples were swollen in methyl acrylate containing 1% by wt of divinyl benzene as crosslinking agent and 0.2% by wt of initiator (AIBN) to give a final composition of

Table 1 Characterization data for the uncrosslinked polyvinyl isobutyl ether

$\bar{M}_n \times 10^{-3}$ ^a	282
\bar{M}_w/\bar{M}_n ^b	1.86

^a Membrane osmometry. Toluene at 37°C

^b Gel permeation chromatography. Chloroform as solvent

67% by wt of crosslinked polymethyl acrylate. The swollen gel was placed in a metal mould sealed with a Teflon coated rubber gasket and the methyl acrylate polymerized at 85°C for 8 h. The IPN sheets were placed in a vacuum oven at room temperature for 10 days prior to use to remove any traces of unreacted methyl acrylate and divinyl benzene. Crosslinked polymethyl acrylate sheet was prepared, as in the second stage of the IPN synthesis, using 1% by wt of divinyl benzene.

The stress-strain tests were conducted on standard dumb-bell specimens using a Howden tensometer at a strain rate of 2.5 cm min⁻¹, while the dynamic mechanical measurements were performed using a Rheovibron Dynamic Viscoelastometer (Model DDV-II-B) at a number of frequencies (3.5, 11, 35 and 110 Hz) and at a rate of temperature change of 1°–2°C min⁻¹.

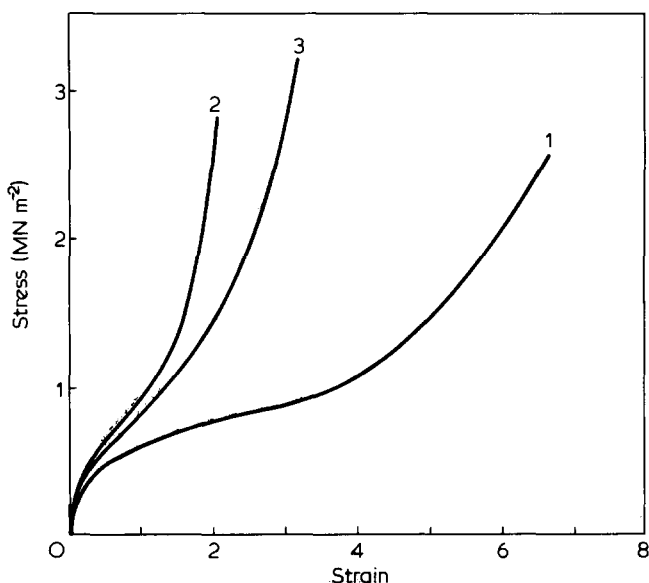


Figure 1 Stress-strain curves for crosslinked polyvinyl isobutyl ether (1), crosslinked polymethyl acrylate (2) and the IPN (3) at 20°C

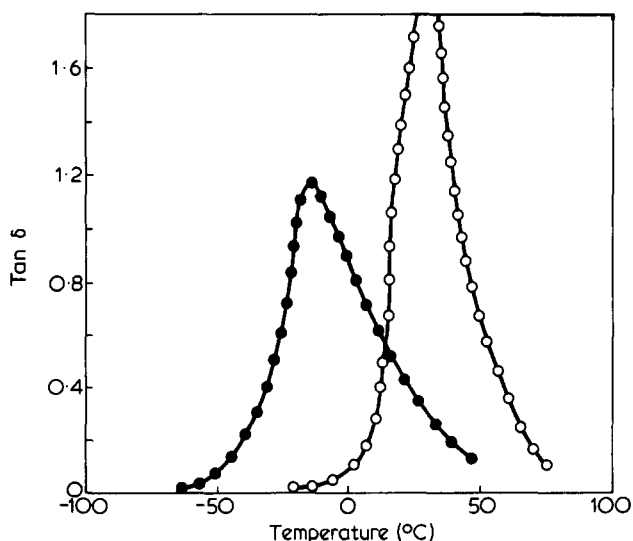


Figure 2 Tan δ versus temperature plots of crosslinked polyvinyl isobutyl ether (●) and crosslinked polymethyl acrylate (○). Frequency, 3.5 Hz

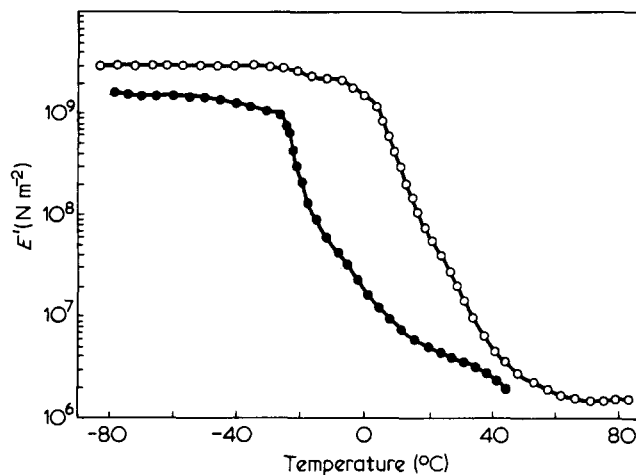


Figure 3 Dynamic storage modulus (E') versus temperature plots of polyvinyl isobutyl ether (●) and polymethyl acrylate (○) cross-linked networks. Frequency, 3.5 Hz

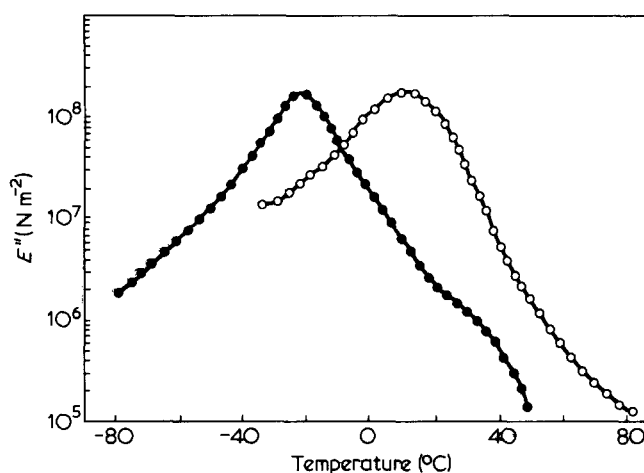


Figure 4 Dynamic loss modulus (E'') versus temperature plots of polyvinyl isobutyl ether (●) and polymethyl acrylate (○) cross-linked networks. Frequency, 3.5 Hz

Table 2 Dynamic mechanical data (3.5 Hz)

	T_g (°C)	$\tan \delta_{max}$
Crosslinked polymethyl acrylate	30	~2.0
Crosslinked polyvinyl isobutyl ether	-15	1.2
IPN	26	1.8

Results and Discussion

The stress-strain behaviour (Figure 1) of the 67% by wt polymethyl acrylate IPN is intermediate in terms of moduli to the corresponding homopolymer networks; but the stress at break is greater than for either the polymethyl acrylate network or for the crosslinked polyvinyl isobutyl ether. The toughness of the IPN is about twice that of the crosslinked polymethyl acrylate.

Figure 2 shows the $\tan \delta$ versus temperature plots for the polymethyl acrylate and the polyvinyl isobutyl ether homopolymer networks at 3.5 Hz, while Figures 3 and 4 present the dynamic storage modulus (E') and dynamic loss modulus (E'') versus temperature trends, respectively.

For polymethyl acrylate mechanical¹³⁻¹⁶ and dielectric¹⁷⁻²² investigations have shown the existence of two relaxations originating from main chain (glass transition) and side group motions, respectively. The apparent activation energy of

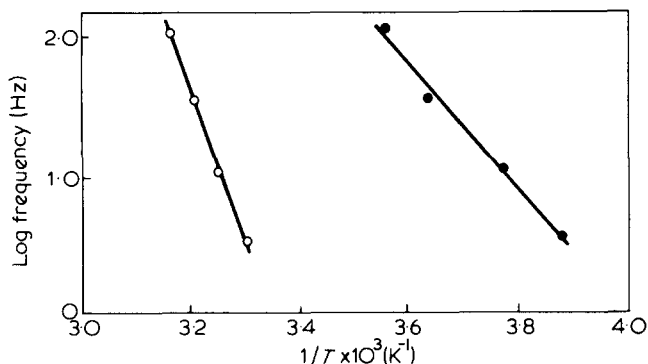


Figure 5 Log frequency versus $1/T$ plots for $\tan \delta_{max}$ data for polyvinyl isobutyl ether (●) and polymethyl acrylate (○)

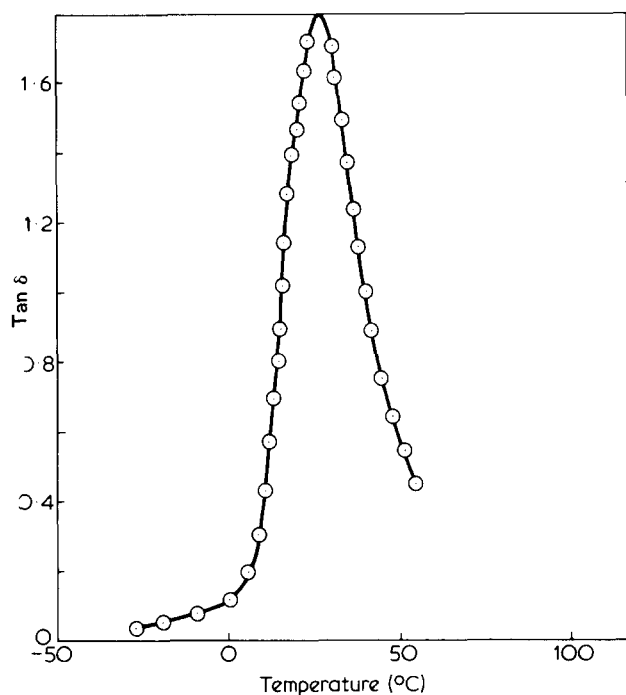


Figure 6 $\tan \delta$ versus temperature plot of the IPN. Frequency, 3.5 Hz

the main (glass) transition has been reported as 239 kJ mol^{-1} derived from dielectric data²¹ which agrees moderately well with the value of 214 kJ mol^{-1} from the $\tan \delta$ data in this work (see Figure 5). Table 2 presents a summary of the $\tan \delta$ - temperature data for both the homopolymers and the IPN.

The literature concerned with the polymethyl acrylate minor transition has been reviewed by McCrum, Read and Williams²³. They reported that a minor transition has been observed in $\tan \delta$ - temperature plots at -120°C at a frequency of 1 Hz. In this study this temperature was not reached, but it can be seen from the E' curve in Figure 3 that a minor transition is evident at around -25°C . This transition is discernible in such plots at correspondingly higher temperatures for experiments conducted on this mildly crosslinked sample at 35 and 110 Hz. The E'' versus temperature curve (Figure 4) also flattens out at around this temperature.

Figures 2, 3 and 4 show the $\tan \delta$, E' and E'' versus temperature plots for the crosslinked polyvinyl isobutyl ether.

The glass transition occurs at -15°C (Table 2) and the maximum value of $\tan \delta$ ($\tan \delta_{max}$) is 1.2. The apparent activation energy (Figure 5) was found to be about 87 kJ mol^{-1} . Schmieder and Wolf²⁴ and Thurn and Wolf²⁵ have reported a number of secondary transitions for various polyvinyl ethers. For the sample used in this work, there is an indication in both the E' and E'' plots of a minor transition at about -45°C . Above the T_g the polyvinyl isobutyl ether softens at about 35°C which is in agreement with earlier work²⁴.

The $\tan \delta$ versus temperature plot for the IPN (Figure 6) shows a glass transition temperature of 26°C which is very close to that of the polymethyl acrylate (30°C), but it does have a slight tail on the low temperature side. However, from the E' and E'' versus temperature plots it is clear that this IPN is a two-phase system. This is shown by the maximum at 10°C and the shoulder at -17°C in the E'' versus temperature plot and by the dynamic storage modulus slope changes at about -18°C and 9°C . These temperatures are, within a few degrees, the same as those of the homopolymers. Thus, it seems that the system is well phase-separated in the sense that the two phases are largely pure homopolymer.

For all the frequencies investigated, the breadth of the damping peak (E'') and its relative constancy in magnitude over the -20° to 20°C range, plus the fact that E' does not change dramatically over this region, makes this a potentially interesting material for acoustic damping applications.

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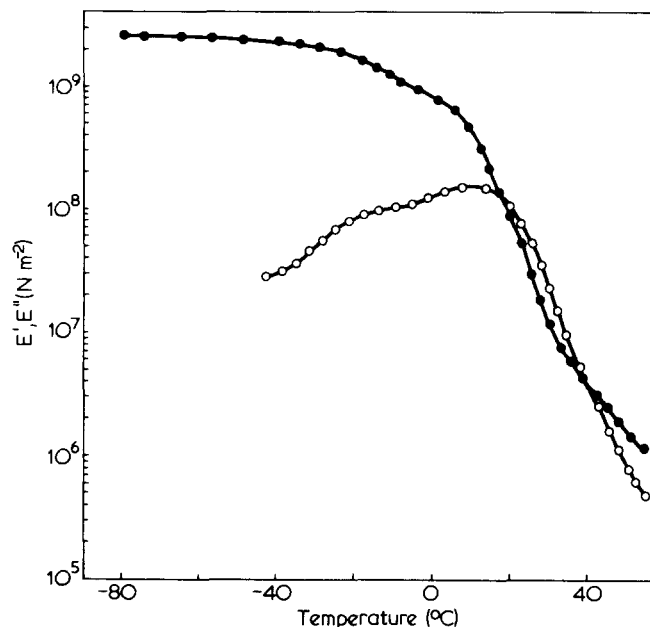


Figure 7 Dynamic storage modulus (E') - (●) and dynamic loss modulus (E'') - (○) versus temperature plots for the IPN. Frequency, 3.5 Hz

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Modulus and strength of filled and crystalline polymers*

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Introduction

When inclusions have a higher elastic modulus than the matrix, the chief effect of the filler is to increase the moduli of the composite. Theories of varying degrees of refinement have been reviewed^{1,2} to account quantitatively for spherical filler particles and uniaxially oriented infinitely long fibres. For aligned chopped fibre composites, Halpin and Tsai² introduced a simple set of approximate equations which were later employed by Halpin and Kardos³ to study the elastic moduli of partially crystalline polymers. Recently, Porter and his colleagues^{4,5} have found that the Halpin-Tsai equation does not provide a correct estimation of the crystal shape in semicrystalline polyethylene.

Based on a recent model developed by the author^{6,7}, the relation of the modulus of semicrystalline polymers and the shape of crystallites will be discussed here. Because stress concentration factors are very critical parameters in the study of fracture and strength of heterogeneous materials, a relation is proposed for their determination which includes the effects of particle shape and volume concentration of fillers.

Modulus

The modulus of a crystalline polymer has been considered by Takayanagi⁸. His series-parallel model gives the effective

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tensile modulus

$$E_{11} = \left[\frac{\psi}{\theta E_m + (1-\theta)E_f} + \frac{1-\psi}{E_f} \right] \quad (1)$$

where the subscripts *f* and *m* identify the crystalline and amorphous phases. The amorphous region is of volume $\psi\theta$ and the crystalline region $(1-\psi\theta)$. The basic problem with the model is how to decide the values of ψ and θ .

In an alternative approach, Halpin and Kardos³ employ the Halpin-Tsai equation² to determine the modulus of semicrystalline polymers from the crystal shape characterized by the aspect ratio l/d . For a uniaxially oriented morphology the tensile modulus is given by

$$E_{11}/E_m = (1 + \epsilon\eta\phi)/(1 - \eta\phi) \quad (2)$$

where $\eta = (E_f/E_m - 1)/(E_f/E_m + \epsilon)$, $\epsilon = 2(l/d)$ and ϕ is the volume fraction of crystals.

From electron diffraction measurements of ultradrawn polyethylene, Crystal and Southern⁹ observed extended chain crystals approximately 200–250 Å in diameter and 5000 Å long. The properties of high-density polyethylene are⁵