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## Synthesis of Composite Materials Formed by the Interstitial Polymerization of Acrylonitrile in Polyurethane Elastomers and Their Optical Properties

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**Abstract** A method has been described of preparing interstitially polymerized composite materials incorporating polyethylene glycol (P. E. G.) based urethane rubbers in place of polypropylene glycol/oxypropylated glycerol (P. P. G.) ones. The successful manufacture of P. E. G. based composite materials, all using acrylonitrile as the vinyl monomer required a two shot stage process. The results obtained that, although, pure P.E. G. and the P. E. G. based rubbers are crystallisable, the sharp change in optical properties expected due to crystal melting in the composites was not observed due to the urethane phase's failure to crystallise when combined with the vinyl polymer. The impact strength of a 70:30 P. A.N./polyurethane composite was found to treble when the urethane rubber was based on P. E. G. without any loss in modulus. For the poly methy-methacrylate/polyurethane composites described, the best combination of mechanical properties was obtained with samples having 80% poly methylmethacrylate 20% polyurethane by weight. Their optical properties were studied and reported.

**Keywords** Synthesis, composite materials, interstitial polymerization, acrylonitrile, optical properties

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### Introduction

Previous [1-5] work carried out had established that the physical properties of poly methylmethacrylate/poly propylene oxide polyurethane composites, the shear modulus and the Charpy notched impact strength, in particular, were determined principally by the composition. Increasing the percentage of rubber produced an increase in impact strength, with however, an associated loss in shear modulus.

The morphology of the interstitial systems has been studied and it was shown that the composites consisted of polymethylmethacrylate spheres embedded in a continuous polyurethane matrix [2,4,6,7]. It was observed that, at a given composition, the mean diameter of the spheres varied from a few tens of nanometres up to nearly 3 microns. This variation in morphology was correlated with mechanical properties. Generally it was found that the modulus was little affected by domain size up to large (300 nm and greater) domain sizes, but fell off above this size [9, 12, 16, 23]. The Charpy notched impact strength was found to pass through a plateau region, falling off, rapidly at small domain sizes and slowly at large domain sizes [10, 12, 24]. It was, however, established during these studies that the physical properties of samples of the same composition prepared in the usual manner had similar properties regardless of small variations in domain sizes.

For these earlier samples [11, 14, 22], it was noted that for a given composition, the actual preparative routine had important influence on the properties of the resulting composite. These variations in properties were related to

differences in domain sizes and during the study of these phenomena methods of producing samples of a given composition with controlled domain sizes were developed [8, 11, 14, 16].

During the initial studies of interstitially polymerized composite materials, it was observed that in poly acrylonitrile/polypropylene oxide urethane systems, the mean domain size, as estimated from electronmicrographs was remarkably constant [12, 13]. The inclusions of poly acrylonitrile appeared to vary in size with composition but unlike poly methylmethacrylate samples other variables were reported to have no effect [14-16]. This was thought to be due to differences in the solubilities of the vinyl polymers in their respective monomers and was a factor taken into account during this study [17-20].

The phenomenon of thermally reversible opacity was noted previously and detailed surveys were made in previous studies [4, 7, 12, 15, 21-25]. It was concluded that for use to be made of this effect it would be necessary to design systems in which light transmittance changed in a much narrower temperature range (i.e. transparent to turbid in 5-10°C) than that naturally displayed by poly methylmethacrylate/polypropylene oxide polyurethane composites. The key to this rapid change in turbidity would be a rapid change in refractive index of one of the components, ideally as displayed by crystal melting [17, 19, 26]. With this end in mind, a crystallisable polyurethane network was designed using polyethylene glycol, in place of polypropylene glycol and oxypropylated glycerol, in conjunction with 1,4-butane diol(BD) trimethyl propane (THP 2-E thy 1-2-hydroxy metzydol propane diol) and methan-4,4-diphenyl disocyanate (MDI). Composites were synthesized using this elastomer with poly acrylonitrile which was determined to be the most suitable polymer.

## Experimental Methods

### Purification of Starting Materials

#### Purification of methylmethacrylate

The monomer, Hopkin and Willams Laboratory Reagent, after drying over calcium hydride was distilled off the hydride under reduced pressure through a fractionating column. The pressure was adjusted to approximately 10 cm of mercury at which pressure the methylmethacrylate distilled over at about 50 °C (b.p. 51 °C/115 mm Hg). The monomer was used immediately after distillation and was checked for dissolved polymeric material by removing a few mLs to which were added a few mLs of methanol. Turbidity indicated the presence of polymer and this necessitated a further distillation.

#### Purification of acrylonitrile

As supplied (Hopkin and Williams General Purpose Reagent) the acrylonitrile not only contained stabilizer and water but also various hydrolysis products

The presence of ammonia in acrylonitrile which had been distilled was detected by: 1) Adding copper sulphate solution to acrylonitrile in a test tube and shook. A control experiment with pure acrylonitrile was performed.

The acrylonitrile was purified along the same general lines as described [12]. Firstly it was washed with dilute sulphuric acid followed by dilute sodium carbonate solution and then dried using calcium chloride. The acrylonitrile was then decanted into a flask fitted with a reflux condenser and fractionating column and containing calcium hydride. The monomer was refluxed for hours, a calcium chloride guard tube being fitted, and then was distilled at one atmosphere off the calcium hydride, again using a guard tube, the fraction distilling at 77-79 °C being collected (b.p. 78 c/76 mm Hg ).

The monomer was used immediately after distillation, first testing for ammonia as mentioned earlier. It was not necessary to test for polymeric material since even acrylonitrile oligomers are insoluble in the monomer.

#### Purification of propylene glycol, oxypropylated glycerol and polytetramethylene glycol

The method used to dry these polymeric diols and triol was as described previously.

The materials used were commercial materials. The polypropylene glycol and oxypropylated glycerol had molecular weights of 2000 and 3003 and were supplied by ICI Ltd. under the trade names of 'Daltocel B56' and 'Daltocel T56', respectively. The polytetramethylene glycol was obtained from the Quaker Oat Company under the trade name



'Polymeg' and had a molecular of 1040. The above polyols were dried by heating to 110 - 120°C under vacuum, using a dry nitrogen bleed to provide agitation, for approximately two hours, afterwards storing under dry nitrogen.

#### **Purification of polyethylene glycol**

The polyethylene glycols used in this study were commercial materials generously donated by Shell Petroleum Company under the trade names 'Polyethylene Glycol 6000 and Polyethylene Glycol 1500' and having molecular weights of 6000 and 1500 respectively. As supplied the samples contained water and also traces of basic catalysts used in ethylene oxide polymerizations, the latter making it difficult to control the urethane gelation.

The polyethylene glycol (P.E.G.) was placed in a round-bottomed flask fitted with a magnetic stirrer and the glycol was melted using a hotplate and oil bath. When the P.E. G. was completely melted approximately 2% w/w of concentrated hydrochloric acid, was added to neutralise the basic impurities. The mixture was stirred for five minutes and subsequently put on the vacuum line where the excess hydrochloric acid was removed. The flask was maintained at 65 – 70°C and stirred constantly until the pressure fell to 0.05 0.01 mm of mercury and bubbles only formed at long irregular intervals in the liquid glycol. This drying took on average approximately four hours. The glycol was usually used as soon as it was dry but if storage was necessary the flask was flushed with dry nitrogen before sealing. Storage was avoided if possible however since this led to remelting of the glycol, this being the easiest state to deal with.

#### **Purification of methan4,4diisocyanate (M.D.I)**

The M. D.I. was distilled under vacuum (b.p. 150 °C/0.1 mm Hg) using an air cooled condenser to give a white crystalline solid melting point 37°C. The M.D. I. was used in the liquid state, taken straight from distillation, since this facilitated weighing. In addition, for consistent results, storage of M.D.I. under any conditions was avoided.

#### **Purification of butane 1.4 diol**

Molecular sieve, grade 4a, was used as a drying agent for the butane diol. After storage for 2 days over molecular sieve with regular shaking the butane diol was distilled under reduced pressure, a water pump, using an air condenser. The first fraction at 121- 122 °C was discarded and the bulk was collected at 235°C,  $n_D = 1.4465$  (b.p. 235°C,  $n_D = 1.4467$ ). After use, the butane diol was stored over molecular sieve and the storage flask was flushed out with dry nitrogen.

#### **Purification of 2 ethyl-2 hydroxymethyl propane diol (Trimethylolpropane T.M.P)**

Trimethylolpropane was used as a crosslinking agent for the urethane gel in preference to glycerol since owing to its greater hydrogen content it is much easier to dry, small trihydroxy compounds being notoriously difficult to obtain moisture free.

The T.M.P. used, B. D.H. Laboratory Reagent, was dried by placing in a round bottomed flask with a magnetic stirrer and melting the white crystalline solid. The flask was then placed on the vacuum line and maintained at 60 °C with stirring for several hours at pressures of 0.05 mm mercury or less.

The T.M.P. was added to the reaction mixture in the liquid state since this facilitated dissolution. After addition, the flask, used for drying, was pumped down and filled with dry nitrogen for storage. Before use, the T.M.P. was melted (m.p. 58 °C) and pumped down until it was totally degassed.

The free radical initiator azobisisobutyronitrile (A.Z.D.N.) (Genitron) was used as supplied, as were Dibutyl tin dilaurate (D.B.T.L) and 1,4-Diazabicyclo[2,2,2] octane (D.A.B.C.O), the urethane catalysts.

The A.Z.D.N, however, was stored in the refrigerator. D.A.B, C.O. being a diamine, tended to absorb water and therefore it was stored in a dessicator over silica gel. It was more convenient to store the D.B.T. L. on top of a drying oven, i.e. slightly above room temperature to avoid solidification since it was simpler to add to the other reagents whilst in the liquid phase, i.e. dropwise from a Pasteur pipette, and it dissolved more easily in the reaction mixture, localized volumes of high concentration thus being avoided.



### Preparation of Composite

94.38 g of P.E.G. 1500 (0.062 moles) was poured into a 100 mL pressure equalized addition funnel and kept under a steady flow of dry nitrogen. Into a two-necked 250 mL round bottomed flask was placed 32.40 g of M.D. I. The addition funnel was placed in the side arm and a glass ink stirrer with seal was fitted to the central neck after the air in the flask had been flushed out by the nitrogen flow from the funnel. The reaction was then carried out under a slight pressure of dry nitrogen. The flask was placed in an oil bath maintained at 65–70 °C and the contents of the addition funnel were maintained in a molten state using an industrial hot air blower. When the M. D. I. was at 60 °C, after 15 minutes, the P.E.G. was added drop wise to the vigorously stirred mixture in the flask over hours and the flask was maintained at 65 °C with stirring for another  $\frac{1}{2}$  hour. The prepolymer prepared above was then dissolved in 309 g of acrylonitrile. To this solution were added 2.83 g of butan-1,4- diol (0.031 moles) and 2.80 g of 2,ethyl 2,hydroxyme thy propane diol (0.022 moles). The mixture was warmed using a warm air b lower and shaken to ensure dissolution of the latter before cooling to room temperature. 0.31 g of A.Z. D.N. was added to the solution, this dissolved rapidly on shaking, and finally 0.2536 g of D.A.B.D. The mixture was left until thickening had approximately 20 mins, degassed and poured into moulds After 1 hr the mixture had gelled and three hrs. Later the moulds were placed in a water bath, 50 °C, for four days.

The above example serves to illustrate the general preparative routine followed.

The molar ratios used were:

|       |       |     |        |
|-------|-------|-----|--------|
| P.E.G | M.D.I | B.D | T.M.P. |
| 1     | 2.06  | 0.5 | 0.34   |

### Preparation of Pure P.E.G.-Polyurethane Rubbers

The initial preparation of the prepolymer was as described for the preparation of the, P.A.N./P.E.G. composites except that after the final stirring of half an hour it was necessary to add the B.D and T.M.P. directly to the prepolymer as rapidly as possible, to avoid moisture contamination. The flask was then flushed with dry nitrogen and stirring was resumed for a further ten minutes at 65 °C to ensure a completely homogeneous mixture.

In the case of bulk samples the mixture was then simply left overnight after de gassing in the flask under dry nitrogen at 65-70%. By the following day gelation had occurred and the sample was obtained by breaking the flask.

For sheet samples, after stirring for ten minutes, the samples were degassed and then poured onto polyethylene terephthalate film (I.C.I. "Melinex") which had previously been dried by placing in a vacuum oven at 100 °C and 0.5 mm pressure for several hours. The "Melinex" was supported by a sheet of glass. A copper wire gasket was used and the mixture was then covered with another sheet of dried melinex care being taken to avoid air bubbles. Finally a sheet of glass was used to support the upper melinex film. The mould was held together using spring clips and was placed overnight in an oven fitted with a fan and set at. The melinex could be peeled off the samples leaving a smooth film of P.E.G rubber film with parallel faces.

### Refractive Index Determinations

An Abbé refractometer was used in conjunction with a sodium discharge lamp (wavelength 589 nm). A modified lower stage was fitted when examining glassy specimens, the normal lower stage being used for rubber samples and films. Temperature control was effected using a Shandon thermos tat unit which maintained the temperature of a 5 L reservoir to 0.01 °C and pumped the water through jackets surrounding the sample. For glassy materials the sample average dimensions were 0.2 cm thick, 0.9 cm wide by 2 cm long. The edges and one face were ground smooth, the remaining face being ground and then polished using a cloth disc and grades 1 and 2 A of Perspex polish supplied by ICI Ltd., Plastics Division. Measurements were made firstly on homopolymers and composites at 20 °C to examine composition effects. Equilibrium being maintained in the reservoir by passing cold water, circa 15 °C, through a copper coil immersed In the reservoir to provide an ambient temperature. 1 bromo naphthalene was used as an immersion fluid and for these samples there was no detectable swelling on standing as reported for polymethylmethacry late samples. Where measuring the refractive x at various temperatures 10/15 mins was allowed for the system to attain thermal equilibrium, results quoted being averages of five readings.



Rubber samples in the form of thin films, the preparation of which has been described previously, were peeled off the melinex and the fresh surfaces adhered to the top prism. The standard lower prism was used for these measurements, the sample being squeezed between the two faces. The remainder of the procedure was similar to that used for composite samples.

The measurements of turbidities of composite materials at various temperatures were determined from absorbance measurements made on a Perkin Elmer 402 U.V. visible spectrophotometer.

Absorbances were recorded over the visible range from 350 nm to 850 nm wavelength, although turbidities were only calculated at 590 nm since in this way by following the smooth curve any inaccuracies at 590 nm were avoided. 590 nm was selected as the wavelength to calculate turbidities at since this is approximately the same as the sodium D line (A 589 nm) at which the refractive indices of the materials were measured. The temperature of the sample was controlled by placing it in a small oven fitted with windows. This was simply a brass tube of rectangular cross section, wound laterally with copper wire as a heating element. This assembly was contained in an asbestos box fitted with windows and a small lid. The sample was suspended from the lid by a metal clip. A couple of small sealed tubes, designed to hold thermocouples, were also inserted through the windings. The oven was mounted on an adapted standard U.V. cell holder and the complete unit was then placed in the spectrophotometer in the normal manner. Two pieces of glass, as used in the oven construction, were placed in the cell holder in the reference beam, to compensate for intensity lost at the oven windows.

Oven temperature was controlled by a Eurotherm unit linked to an A.C. power supply unit. This delivered up to 25 V to the windings on the oven. Although the Eurotherm unit displayed the temperature as measured by its thermocouple, the scale was not accurate. A second thermocouple used in conjunction with a Comark electronic thermometer was required for accurate temperature measurements.

## Results and Discussion

The urethane reactions were shown, using infra-red spectrometry, to have gone to completion as far as the Isocyanate was concerned, the band at  $2270\text{ cm}^{-1}$  characteristic of unreacted N-C-O being absent in a mull of the sample and in solution. The traces obtained from the gel permeation chromatograph are shown in Figures 1 and 2.

### Introductory Note on Polymer Composites

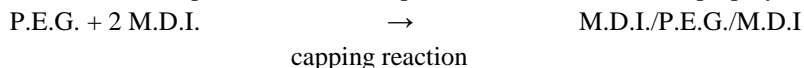
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The traces obtained from the gel permeation chromatograph are shown in Figures 1 and 2. Since the instrument was calibrated using carefully fractionated samples of P.E.G. of various molecular weights, it might not be expected that the products from the capping reactions would fit the calibration curve. In fact, the results fit the predicted molecular weights very well and it corresponds to a molecular weight of 564 greater than that of the pure polyethylene glycol.

The most obvious feature from the traces is the narrowness of the molecular weight distribution considering this is a commercial unfractionated material. This is because it is prepared by an anionic polymerization technique. In Figure 1(a) the peak is centred at an elution volume of 22.6 mL, corresponding to a true molecular weight of 6600 for the pure polymer.

A low molecular weight tail, down to mol. wt. 850, can be observed extending up to an elution volume of approximately 27 mL with relatively little higher molecular weight material. This can be compared with Figure 1(b) which is the trace for the capped polymer.

The most important differences are the presence of a new peak at 29.8 mL elution volume corresponding to a molecular weight of 270, and the overall height of the peak is reduced slightly but the area, as expected, remains the same owing to the presence of higher molecular weight material, dimers and possibly trimers, broadening the low elution volume side of the peak. Dimerisation produces free M.D.I. in the prepolymer as follows:



P.E.G. + 4.M.D.L.  $\rightarrow$  M.D.I./P.E.G./M.D.I/P.E.G/M.D.I.+M.D.I  
and production of other oligomers produces more excess M.D.I. In the gelation reaction in composite manufacture this would be free to react with the various hydroxy components added for chain extension and crosslinking. However, in this case the excess M. D. I. has reacted with the methanol:

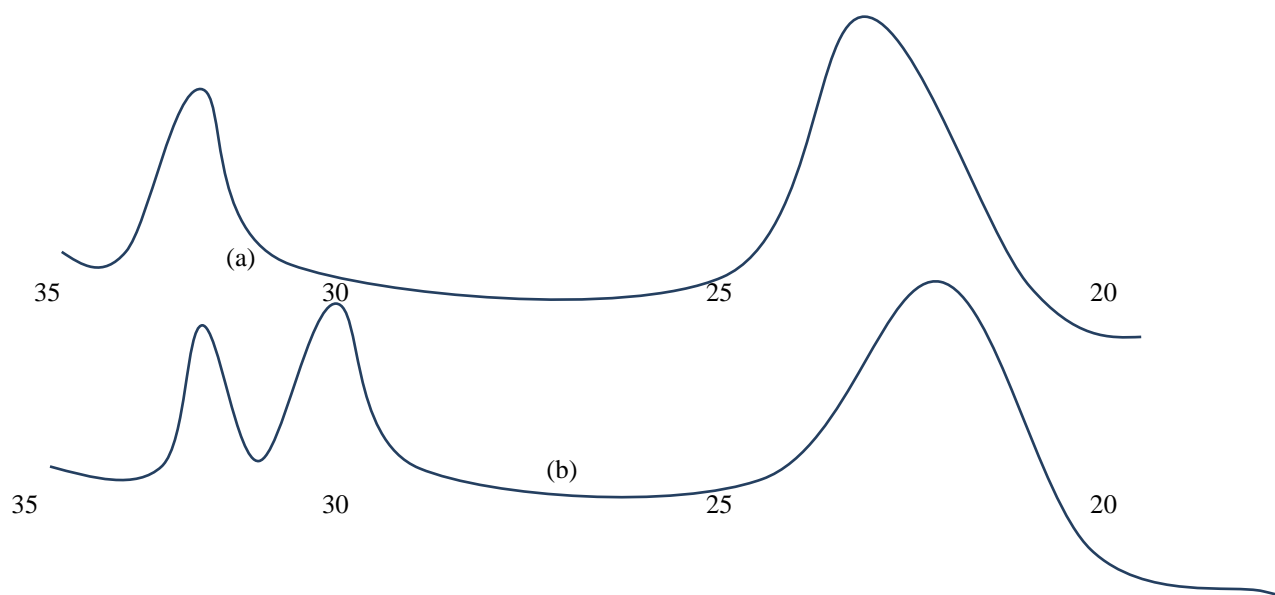


Figure 1: G.P.C. Traces of P.E.G. 6000: (a) Pure P.E.G 6000; (b) M.D.I. capped P.E.G. 6000

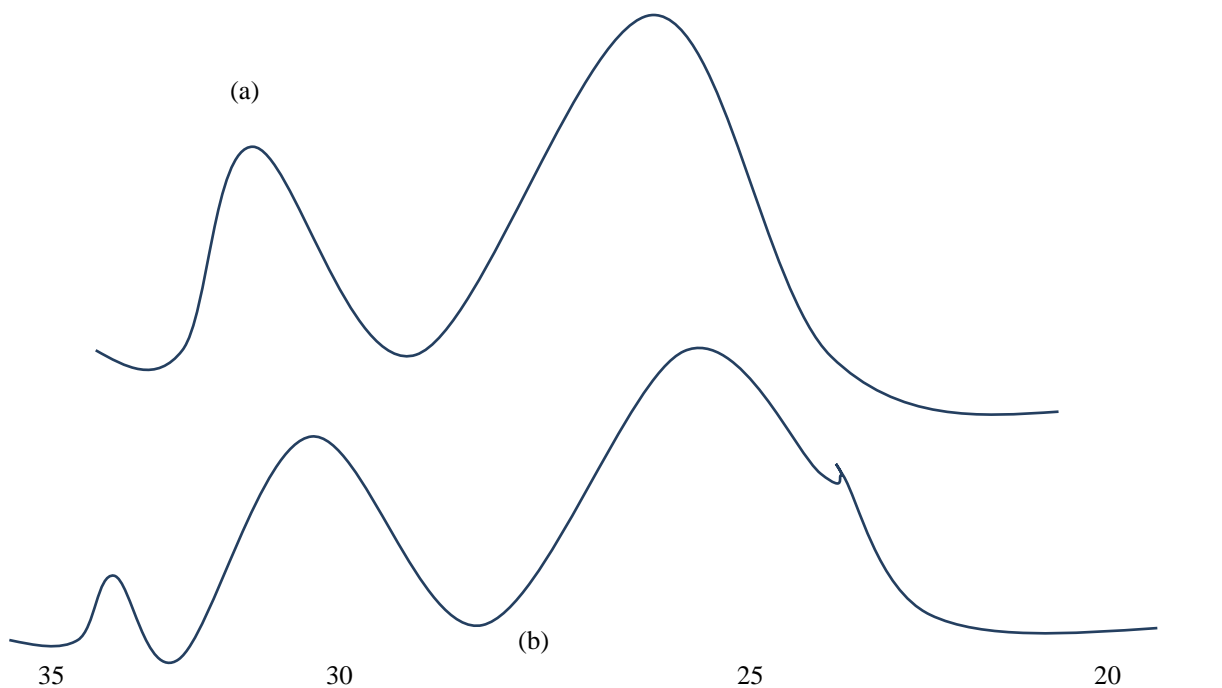


Figure 2: G.P.C. Traces of P.E.G. 1500: (a) Pure P.E.G. 1500; (b) M.D.I. capped P.E.G. 1500

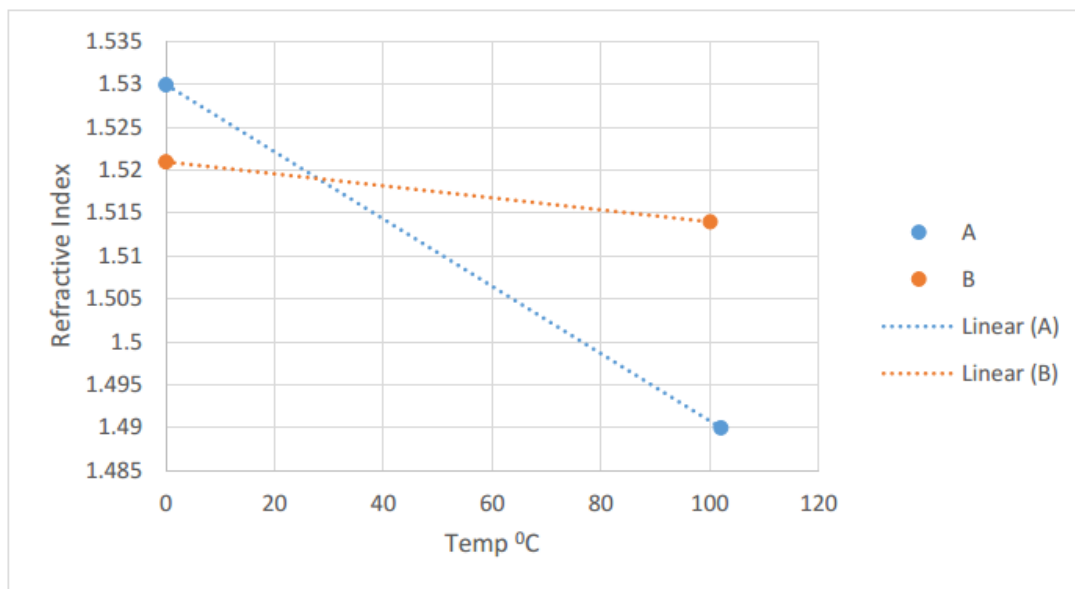
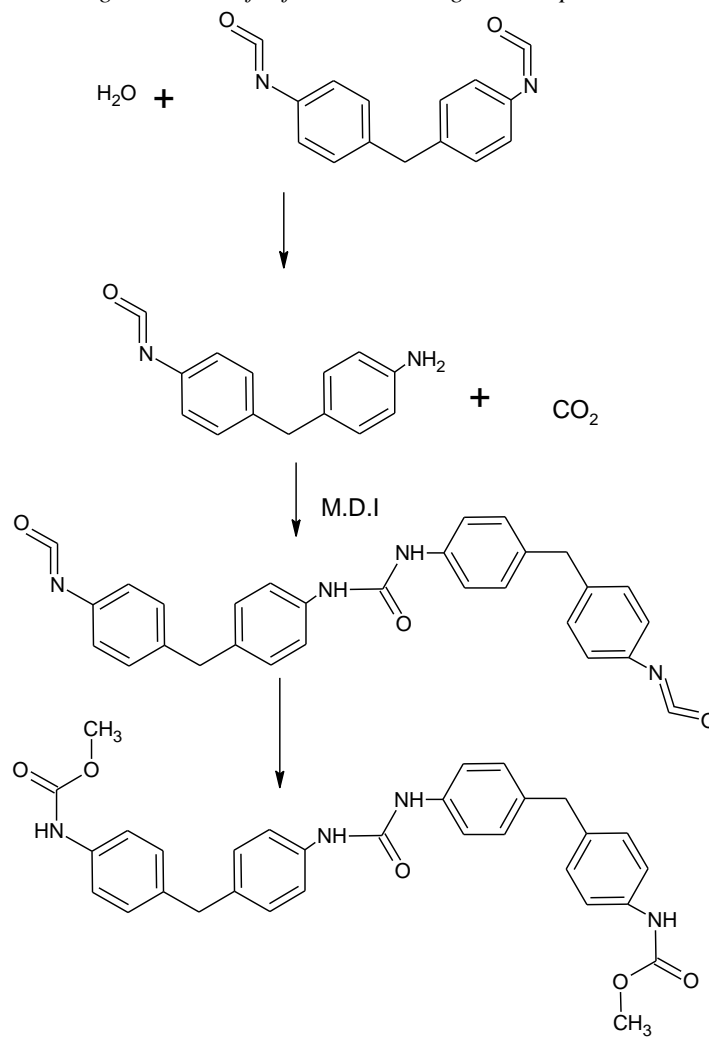


Figure 3: Plot of refractive index against temperature



The resulting compound has a molecular weight of 314 and thus explains the appearance of the peak at 29.8 mL elution volume. The major peak occurs at virtually the same elution volume, 22.6 mL, and the low molecular weight sides of the peaks in Figures 1(a) and 1(b) are completely superposable in shape. This apparent lack of positive evidence for capping in the polymer owing to the two peaks, pure polyol and prepolymer, being at the same elution volume approximately can be explained by the insensitivity of the instrument to molecular weight changes of 500 at this molecular weight. One can also argue that since chain extension is definitely displayed in this sample the isocyanate and hydroxyl groups are reacting. For chain extension to be favoured, rapid reaction is required which would be expected for primary alcoholic groups at the temperature used. The superposability of the low molecular weight sides of the two peaks completely rules out the presence, in any significant numbers of cyclic products as expected.

Evidence for the capping of the polyethylene glycol in the lower molecular weight case, Figures 2 (a) and 2 (b), is much more clear cut. The pure polyethylene glycol trace Figure 2(a) shows a main peak centered at 25.5 mL elution volume, corresponding to a molecular weight of 1600.

The prepolymer gives a much more informative trace than in the high molecular weight case. The major peak occurs at an elution volume of 25 mL, corresponding to a molecular weight of 2000. However, in this case, there is more positive evidence of chain extension. A second peak is centered on 23.6 mL elution volume, i.e. molecular weight 3500, corresponding to the dimer. The high molecular weight tail shows that the trimers and tetramers too are present in significant quantities.

As expected from this large amount of chain extension, the peak corresponding to excess M.D. I. is much greater than in the case of the P.E.G. 6000. There is, in addition, a small peak at 27.8 mL elution volume, corresponding to a molecular weight of 610, and the origin of this is not clear. The only reasonable explanation to date is that during refluxing on the steam bath water entered the reacting mixture and reacted with the M. D.

This product could react further with water to give trimers or even higher oligomers or react with the methanol to form.

The product has a weight of 548 and can therefore explain this peak. The low molecular weight side of the main peak is again superposable in both traces, the pure glycol plot being shifted to lower elution volumes again showing that formation of cyclic products in significant quantities does not occur

Thus these data show that ring formation, as predicted by simple statistical arguments, does not occur to an appreciable extent but that there is some chain extension in the system, producing free M.D.I. which would effectively act as an excess in the ensuing gelation reaction.

Furthermore, it was noted that the amount of chain extension occurring in the low molecular weight case was significantly higher than in the high molecular weight case. This would be expected since the major factors influencing chain extension are: the effective concentrations of the two components, the rate at which they react and the rate of mixing. Since both polyols considered have primary hydroxyl groups it was assumed that they reacted equally quickly. The two conditions which favour chain extension, assuming all other parameters equal, e.g. temperature, rate of stirring, rate of addition etc., are therefore, the high concentration of P.E.G. around dispersing drops immediately after addition, the relatively high concentration of reacted M.D.I. molecules, with respect to free M.D.I. Present in the mixture when P.E.G. addition was nearly complete. The first effect could be controlled to a large extent by employing a high rate of stirring and limiting the temperature so that the drop had time to disperse before reaction occurred. Looking at this effect, however the concentration of hydroxyl groups in a drop of P.E.G. 1500 is quadruple that in an identical drop of P.E.G. 6000 and since the rate of chain extension must be proportional to the square of the concentration of P.E.G., under favourable conditions, the rate of chain extension.

In this initial reaction must be sixteen times more rapid for P.E.G. 1500 than P.E.G. 6000; however this effect would, in fact, to some extent be reduced owing to the higher viscosity of the P.E.G. 6000 leading to a longer time spent in local areas of higher concentration. Under the conditions used, when the last few drops of P.E.G. were added to the reaction mixture chain extension was much more probable than the capping reaction since the concentration of free M.D.I. was low. The arguments applied to dispersion effects will be much more applicable under these conditions since, a drop of P.E.G., as it disperses, will tend to use up all available free M.D. I. units,





assuming equal reactivity between Isocyanate groups on free M.D.I. units and reacted units. Thus, this second effort can be lessened by efficient stirring, however similar concentration arguments would predict much greater chain extension for the lower molecular weight P.E.G. The amount of chain extension can be reduced by using a diisocyanate such as toluene diisocyanate where the reactivity of the isocyanate group on the capped polymers is an order of magnitude at least below that on the free di isocyanate. However, it was found to be undesirable to use toluene diisocyanate in these interstitially polymerized systems since the capped polymeric isocyanate groups were insufficiently reactive to gel under the conditions used in composite preparation.

The parameters governing the turbidity of interstitially polymerized composites have been investigated previously. The optical properties of the system were described semi-quantitatively in terms of the refractive index difference between the two phases, the mean domain size and the volume fractions of the two phases.

Turbidity in composite materials arises from the refractive index difference between the two phases and thus, before treating the turbidity of these materials in a theoretical manner, it was necessary to examine the refractive indices of the pure components and of the composites at room temperature.

Rubber samples in the form of thin films, the preparation of which has been described previously, were peeled off the melinex and the fresh surfaces adhered to the top prism. The standard lower prism was used for these measurements, the sample being squeezed between the two faces. The remainder of the procedure was similar to that used for composite samples.

Figure 3 shows the plots of refractive index against temperature for polyacrylonitrile homopolymer and polyurethane. The polyurethane used for these measurements was similar to that used in most of the composite samples made. It consisted of P.E.G. 1500, capped with M.D.I. and chain extended and cross linked with B.D. and T.M.P. respectively to give anMc of 4180. The refractive index of polyacrylonitrile found  $n_D^{20} = 1.5185$  and temperature coefficient  $-0.975 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  agree well with some previously reported results but Shavit *et al* report lower values for  $n_D^{20}$ . These values are possibly different due to the different natures of the residual catalysts present in their samples. The polyurethane was found to have a refractive index  $n_D^{20}$  of 1.5178 and a temperature coefficient of  $-3.387 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ .

From Figure 3 it can be seen that the refractive indices of the two phases are matched at  $17.3^\circ\text{C}$ . At this temperature one expects no scattering of light from the sample due to the domain structure and the transmittance would be similar to a glassy homopolymer. By subtracting the gradients of the two lines a differential coefficient was obtained for the refractive index difference between the phases in a composite material at different temperatures. This quantity was labeled " $\alpha$ ". The refractive index difference between the phases ( $\Delta n$ ) could thus be expressed in the form

$$\Delta n = \alpha \Delta T$$

Where  $\Delta T$  is the difference between the temperature we are considering and  $17.3^\circ\text{C}$ , the temperature at which the refractive indices were matched. For the system examined  $\alpha = 2.412 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . This quantity can be used to calculate the change in composite turbidity with temperature.

In Figure 4 are plotted the refractive indices of composites containing various percentages of rubber by volume against volume fraction. The graph is linear, showing that mixing the two phases does not affect the refractive indices of the two phases due to interactions and also providing confirmation of the accuracies of refractive indices of the two homopolymers.

Thus it was confirmed that for any composition, at least up to 50% polyurethane, the refractive index of the composite could be calculated from the refractive indices of the rubber and polyacrylonitrile and volume fraction of one component using the equation quoted earlier

$$n = \phi n_1 + (1 - \phi) n_2$$



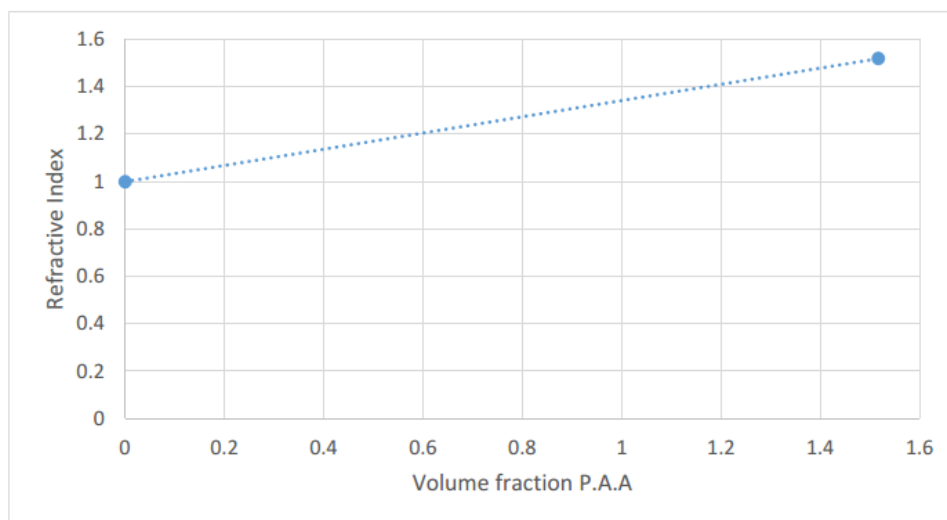


Figure 4: Plot of composite refractive index against volume fraction P.A.N.

The result of the above two points is that the samples should display high transparency and the results obtained for various compositions are quoted below.

**Table 2:** Sample composition, temperature and turbidity

| Sample Composition Weight & P.A.N | Temperature | Turbidity $\text{cm}^{-1}$ |
|-----------------------------------|-------------|----------------------------|
| 90                                | 26.2        | 0.274                      |
| 80                                | 26.0        | 0.416                      |
| 70                                | 26.0        | 0.490                      |
| 60                                | 26.0        | 0.840                      |
| 50                                | 26.5        | 1.0016                     |

This means that a sheet of the 70:30 material 0.2 cm is thick will transmit approximately 83% of incident radiation allowing an 8.8% loss in intensity due to reflection at the two surfaces and 8.2% by internal scattering.

**Table 3:** Varied compositions and their turbidities

| Sample Composition | Turbidity / $\phi (1 - \phi)$ |
|--------------------|-------------------------------|
| 90:10              | 3.04                          |
| 80:20              | 2.60                          |
| 70:30              | 2.34                          |
| 60:40              | 3.50                          |
| 50:50              | 4.00                          |

It can be seen in Table 3 that the effect of has been partially corrected. The  $\tau/\phi (1-\phi)$  being approximately equal to 3.2. One would still expect some variation since composition also effects  $B(y)$  to a limited extent. The main point to be made from these results is the transparencies of these samples compared to conventional rubber toughened thermoplastics especially when viewed from the mechanical point of view, the combination of modulus and, impact strength of the 70: 30 sample in particular making these composite materials worth examining further.

**Table 4:** Composition and their Charpy notched impact and shear modulus

| Composition P.A.N./P.U. | Charpy notched impact Strength ( $\text{kJ m}^{-2}$ ) | Shear modulus ( $\text{G N m}^{-2}$ ) |
|-------------------------|---|---------------------------------------|
| 100/0                   | -   | 1.950                                 |
| 90/10                   | 0.96  | 1.350                                 |
| 80/20                   | 7.40  | 0.950                                 |
| 75/25                   | 12.36   | 0.759                                 |
| 70/30                   | 63.90   | 0.560                                 |
| 60/40                   | 52.60   | 0.300                                 |
| 50/50                   | 50.40   | 0.156                                 |



Effect of the mean theoretical molecular weight between Crosslinks (Mc)

The results obtained varying this parameter are listed in Table 5.

**Table 5:** Effect of the mean theoretical molecular weight between Crosslinks (Mc)

| Mc    | Charpy notched impact Strength (kJ m <sup>-2</sup> ) | Shear Modulus (GN m <sup>-2</sup> ) |
|-------|--|-------------------------------------|
| 2090  | 48.3   | 0.583                               |
| 4180  | 63.9   | 0.560                               |
| 4590  | 61.7   | 0.588                               |
| 6591  | 28.6   | 0.725                               |
| 13180 | 15.5   | 0.783                               |

70:30 P.A.N./ P.U. - rubber NCO: OH = 0.95 1.0

Both impact strength and modulus are dependent upon the Mc of the polyurethane elastomer. The impact strength goes through a maximum and the modulus through a minimum in the Mc =  $-4-5 \times 10^3$  region. High moduli and low impact strengths have previously been reported<sup>82</sup> for interstitially polymerized systems with Mc's of less than 4000, however, samples with higher Mc values were not examined.

This trend in results reflects the behaviour of crosslinked rubbers. That this would be so would have been expected since the urethane elastomer is the continuous matrix and fracture is a high strain situation. It has been well established [12, 24] that, as the degree of crosslinking of a rubber is increased, the tensile breaking stress rises to a maximum and then decreases. The maximum becomes less obvious as the strain rate is decreased, obviously not the impact case. Maxima are often observed in systems where a variable has two effects on the system. In this case increasing the degree of crosslinking increases the orientation hardening and breaking stress.

#### Effects of vinyl initiator concentration (A.Z.D.N)

Table 6 shows the effect on shear modulus and impact strength the vinyl initiator concentration (AZDN = abobisisobutyronitrile)

**Table 6:** A.N./ P.U. - P.E.G. rubber, 70/30 w/w%, Mc = 4180

| (AZDN)% | Charpy notched impact Strength (kJ m <sup>-2</sup> ) | Shear Modulus (GN m <sup>-2</sup> ) |
|---------|--|-------------------------------------|
| 0.05    | 60.5   | 0.57                                |
| 0.10    | 63.9   | 0.56                                |
| 0.20    | 61.4   | 0.56                                |
| 0.50    | 57.1   | 0.55                                |
| 1.00    | 64.7   | 0.53                                |

The impact strength remains approximately constant, this would be expected since toughness is in the main due to the urethane phase not affected by vinyl initiator concentration.

**Table 7:** Effect of the time difference between the gel point of the P.U –elastomer A.B.D. polymerization of P.A.N. at 45 °C

| t (hours) | Charpy notched impact Strength (kJ m <sup>-2</sup> ) | Shear Modulus (GN m <sup>-2</sup> ) |
|-----------|--|-------------------------------------|
| - 0.67    | 20.4 + 5.8   | 0.548                               |
| 0.00      | 26.7 + 4.6   | 0.555                               |
| 2.0       | 59.7 + 11.6  | 0.560                               |
| 4.0       | 56.3 + 3.8   | 0.550                               |
| 7.0       | 58.6 + 7.2   | 0.545                               |
| 27.5      | 60.9 + 6.7   | 0.557                               |
| 48.0      | 67.9 + 5.8   | 0.551                               |
| 168.0     | 59.5 + 8.3   | 0.553                               |

P.A.N./P.U.-rubber , 70 : 30 w/w%, Mc = 4180

The modulus, however, is decreased slightly by increasing the initiator concentration, this reduction, however, only just becoming significant at the highest concentration used. P.A.N. might see to be less sensitive to changing



initiator concentration than P.M.M.A when the above results are compared with those of Vyroda who studied P.M.M.A. interstitial systems. However, direct comparison is difficult since the results for P.M.M.A. are reported for an 80: 20 w/%, material and these results are 70: 30. The reduction in percentage of vinyl phase present obviously reduces the effect variation in one property of the homopolymer can have on the system as a whole.

Table 8 shows that in changing "t" shear modulus changes negligibly whilst the impact strength rises rapidly to its optimum value two hours after gelation. (N.B. The negative value of "t" indicated that the sample was placed in the elevated temperature bath this length of time before a similar sample maintained at room temperature gelled). Gelation of the urethane phase took place in all samples before the beginning of the vinyl polymerization.

These results differ from those previously for P.M.M.A. (P.U. interstitial systems). Vyvoda did not observe any significant change in impact strength with "t". At higher temperatures, however, circa 70 °C, low values of shear modulus were reported at "t" values. This was possible in the P.M.M. A./P.U. negative systems because of the longer gel times required by that particular urethane. Polypropylene glycol with oxypropylated glycol was used and this, containing secondary alcohol groups, reacts with isocyanates much more slowly than polyethylene glycol with primary hydroxyl groups.

In the P.E.G- systems, at all reasonable temperatures, the urethane gelation was complete before the vinyl polymerization induction period had elapsed. It is interesting to note, however, that in the P.A.N./P.E.G. systems there is an effect on the impact strength. In the previous report With the P.M.M.A. and polypropylene oxide based diols and triols the obvious effect of incomplete network formation at the commencement of vinyl polymerization i.e. low modulus, is apparent and transferring this argument to the present system it would appear that there is some change at the micro level which occurs either after complete gelation or just at complete gelation. Complete gelation is distinguished here from the point at which the system ceases to be pourable i.e. the "gel point" which often occurs at 70-80% reaction in these systems· the nature of this change at the moment is open to conjecture, but there might be some reorganization of the chains to a less random situation which would be enhanced to some extent by crosslinking.

**Table 9:** Effects of water on the interstitial composites

| % Water | Charpy notched impact Strength (k J m <sup>-2</sup> ) | Shear Modulus (G N m <sup>-2</sup> ) |
|---------|---|--------------------------------------|
| 0       | 13.7  | .56                                  |
| 3.4     | 23.7  | .50                                  |
| 6.2     | 35.4  | -                                    |
| 8.4     | 39.6  | -                                    |
| 9.3     | -   | .30                                  |
| 19.3    | -   | .42                                  |

P.A.N./P.U. – P.E.G. rubber, 70 : 30 w/w%, Mc = 4180

Polyethylene glycol is soluble in water and the pure polyurethane, a crosslinked elastomer with an Mc of 4180, was found to take up 1.5 g of water per 1g of material. Since in the composite material the urethane is the continuous phase, it was expected that the composites would absorb significant quantities of water and that this would affect the properties. Table IX illustrates the effects on the mechanical properties of immersing samples in water for different times. It is firstly very evident that a large percentage of water is taken up by the urethane since 20% swelling is obtained of a composite of which only 30% is elastomer (i.e. swellable by water). Before discussing the results obtained for impact strength and shear modulus it must be pointed out that the results for impact strength are relatively low. It was decided to use a low impact strength material since this illustrated the point more clearly. The sample used was a negative-gel-time sample but a normal sample was tested in parallel.

## Conclusion

The effect of water on the impact strength in the usual sample was a steady reduction but the values were of relatively little Significance since the samples were plasticized to such a degree that little crack propagation occurred before the sample deformed sufficiently to pass between the supports. These results will not be quoted except to say that up to approximately 5% water no difference in impact strength was noted but the samples became



progressively more difficult to break completely in the N.I.S. test. From the table it can be seen that the water has a dramatic effect on both the impact strength and the modulus. The impact strength is practically trebled on going from 0 – 9% water whilst the modulus is halved. It is of interest to note that when the samples were allowed to take up 20% water that the modulus is seen to rise again.

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