

Molecular composites of poly(*p*-phenylene benzobisthiazole) with thermoplastics: coagulation studies

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The solubility limits of solutions of poly(*p*-phenylene benzobisthiazole) (PBZT), poly(ether-ether-ketone), and two nylons (du Pont, Zytel[®]42 and Zytel[®]330) in methane sulphonic acid (MSA) were determined by turbidimetric titration with water. The solubilities rank as follows: Zytel[®]42 > Zytel[®]330 > PEEK > PBZT. The coagulation of solutions of these polymers was examined in two limiting cases: very slow (exposure to water vapour) and very fast (immersion in a water bath) coagulation rates. The slow coagulation of ternary solutions shows that PBZT may either precipitate first from the composite solutions or coprecipitate with the thermoplastic depending on their relative solubility. The immersion coagulation process can be described by a simple diffusion model and the diffusion coefficient of water in the polymer solution is determined to be on the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Our results suggest that PBZT will coagulate first from ternary solutions of PBZT, nylon, and MSA during wet-spinning, resulting in a continuous microfibrillar network structure of PBZT followed by the precipitation of nylon.

1. Introduction

The transformation of a polymer solution into a gel or solid by means of a non-solvent is generally referred to as coagulation. Coagulation is a complex process, where phase equilibria, the kinetics of phase separation, and changes of morphological structure of the polymer are all potentially important. The coagulation process appears to be a critical step in the development of the fibre morphology and properties in the PBZT system. In fact, the morphology and tensile properties of wet PBZT fibre are quite similar to the air-dried fibre [1]. In order to explain the behaviour of the PBZT/thermoplastic molecular composites, one must understand how the morphology develops during the coagulation process.

Usually, molecular composites (MC) are prepared by dissolving rigid rod and flexible-coil polymers in a mutual solvent to form an isotropic mixture. The ternary solution is then spun into a composite fibre or film by immersion (rapid) coagulation with a non-solvent; this process has been suggested as a method for the preparation of MC [2–4]. This approach is distinguished from the common practice of filling polymers with chopped glass or carbon fibres by the fact that the reinforcing phase is actually formed during the spinning process.

There are two crucial prerequisites for molecular composites to be obtained. The first is that rod and coil polymers are well-mixed in the solvent. Secondly,

the ternary solution must be coagulated rapidly with a non-solvent such that the finely dispersed rod/coil mixture is frozen in spite of the thermodynamic driving force for phase separation. Cotts and Berry [5] showed that PBZT molecules have a strong tendency to form metastable aggregates, even in dilute MSA solution, due to a strong intermolecular interaction. The term rapid coagulation in the context of molecular composites is vague. It has been hypothesized that the immersion coagulation was rapid enough to lock in the fine dispersion of the rigid rod macromolecules in a flexible coil matrix [6]. However, there is no substantial evidence that any true molecular composite has ever been prepared. It has been recognized that the rate of coagulation during fibre formation in solution spinning affects fibre characteristics [7]. Nevertheless, no attention has been paid to the consequences of spinning and coagulation of solutions containing two polymers with different rates of coagulation. Booth [8], Paul [9], and many others [10–15] have shown that the coagulation of polymer solutions during a wet-spinning process is often diffusion-controlled, for a variety of polymer and solvent-coagulant pairs. It is unlikely that kinetics would overcome thermodynamics (i.e., rod-coil phase separation might occur), especially when coagulation is limited by diffusion. The thermodynamic (solubility) and kinetic (rate of coagulation) aspects of coagulating a ternary solution of rodlike and flexible polymers in a

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solvent are studied in this paper. The effects of rate of coagulation on the resultant composite morphology is also discussed.

2. Experimental procedure

2.1. Materials

Poly(*p*-phenylene benzobisthiazole), PBZT, was synthesized by Wolfe *et al.* [16] by the polycondensation of terephthalic acid with 2,5-diamino-1,4-benzenedithiol dihydrochloride in polyphosphoric acid (PPA). The two PBZT samples used in this study had intrinsic viscosities of 18 and 27 dl g⁻¹ in methanesulphonic acid, MSA, corresponding to molecular weights of 30 000 and 38 000 and aspect ratios of approximately 300 and 380, respectively. The nylons used were du Pont semi-crystalline Zytel®42 which is Nylon 6,6 ($T_m = 255^\circ\text{C}$) and amorphous Zytel®330 ($T_g = 130^\circ\text{C}$). The poly(ether-ether-ketone), PEEK, was provided by Imperial Chemical Industries ($T_m = 340^\circ\text{C}$). The solvent, MSA, was obtained 98% pure from Aldrich Chemical Company. Before preparing the composite solutions, the polymers were dried for one day in a vacuum oven at 70 °C at a pressure of 66.65 Pa. The polymer solutions were prepared by mixing predetermined weights of the polymers with MSA. The mixing apparatus consisted of a variable speed stirring rod in a glass flask. The system was kept under a dry nitrogen atmosphere for the duration of the mixing process, which ranged from three days to a week.

2.2. Slow coagulation in a humid environment

The coagulant was first introduced from the vapour phase. Isotropic solutions containing 2 wt % of 0/100, 25/75, 50/50, 75/25 and 100/0 PBZT/Nylon 6,6; 0/100 and 50/50 PBZT/Zytel®330; 0/100 and 30/70 PBZT/PEEK in MSA were prepared under a nitrogen atmosphere and placed in separate petri dishes. They were then transferred to a sealed glass chamber that contained a flask of water. The increasing relative humidity of the chamber due to water evaporation, measured by a digital hygrometer, coagulated the composite solutions which formed two-phase (gel/clear solution) or three-phase (gel/clear solution/white precipitate) systems. To remove the absorbed clear solution in the gels, the gels were sandwiched between porous Gore-Tex® sheets and an outer absorbent layer and held between steel platens in a hydraulic press at approximately 20 MPa for 10 minutes. The resulting films were washed with distilled water for a week to remove the residual acid and then once again sandwiched between Gore-Tex® and absorbent and dried at 130 °C in a vacuum oven at a pressure of 66.65 Pa.

A Perkin-Elmer DSC-4 differential scanning calorimeter (DSC) was used to investigate the thermal behaviour of the films. Samples of 5 to 10 mg were used at a scan rate of 20 °C min⁻¹. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere on a Perkin-Elmer TGS-2 system, at temper-

atures from 50 to 700 °C at a heating rate of 10 °C min⁻¹, also with 5 to 10 mg of sample. The elemental analysis [17] of the films for carbon, hydrogen and nitrogen are performed by modified Pregl-Dumas technique and sulphur by Schoniger combustion decomposition followed by the classical barium titration for sulphate to examine the weight ratios of PBZT to thermoplastic in the gels.

2.3. Solubility

The solubilities of polymers in the mixtures of solvent and coagulant were determined by the so-called coagulation value – a traditional phase equilibrium measurement [18]. This number is defined as the volume of coagulant required for precipitating polymer from a unit volume of a dilute polymer solution at a given concentration and temperature. In order to obtain the phase equilibrium information near the concentration of interest for fibre spinning, 2 wt % polymer solutions (PBZT, Nylon 6,6, Zytel®330 and PEEK) in MSA were used in this study. The mixtures were continuously stirred using a magnetic stirrer or a mechanical stirring rod and water was slowly added until the solution became turbid (for nylons and PEEK solutions) or changed colour (for PBZT solution).

2.4. Rapid coagulation by immersion

The coagulation in an actual spinning process is difficult to observe, so model experiments must be used. We have used the method devised by Epstein and Rosenthal [12] to observe the coagulation of a static polymer solution with water under an optical microscope. Pure polymer solutions (1 and 2 wt % PBZT; 2 wt % Nylon 6,6 and Zytel®330) and isotropic composite solutions (2 and 4 wt % 50/50 w/w; 4.2 wt % 10/90 w/w PBZT/Zytel®330) were studied. A thin layer of polymer solution was placed on a microscope slide and sandwiched with a cover glass on top. The slide was then positioned in a petri dish on an optical microscope and distilled water as a coagulant was introduced into the petri dish. When coagulation of PBZT/MSA or PBZT/nylon/MSA solution occurs, the solution changes colour from green to orange-red forming a distinctive, sharp interface. The coagulation of nylon/MSA solution simply turns clear solution to an opaque gel, also forming an interface. This allows the diffusion process to be followed by an optical microscope under 100 × magnification. The interface progresses toward the centre of the slide during the coagulation process.

A series of model coagulation experiments were carried out to estimate the time required to coagulate a fibre spun from a 330 μm spinning die. Four drops of 2 wt % PBZT solution in MSA were placed separately between microscope slides and four circular cover glasses of different radii, 9.0, 6.0, 4.5 and 2.8 mm. These samples were immersed in the water bath to measure the change in radius of the coagulation front and the time required for the coagulation to reach the centre of the solution between the glass slides.

3. Results and discussion

3.1. Slow coagulation by humidity

The relative humidity of the sealed chamber reached 100% in two days. As the humidity increased within the first few hours, the surface of the originally dark green PBZT and PBZT composite solutions turned yellowish-green and finally to orange-red gels. During the green to orange transition, a transparent liquid was exuded from the gel. A few days later, the orange-red gel was observed to be surrounded by the clear liquid as the polymer solution in each petri dish continued to absorb water. All of the polymer solutions absorbed nearly 150 wt % water from the vapour phase 12 days later because of the hydrophilic nature of the acid in the solutions. In this extreme case, the coagulation proceeds slowly by diffusion of water vapour into the polymer solution [19].

For the Nylon 6,6/MSA solution, the mixture remained clear without precipitation. However, the PBZT/MSA and all of the PBZT/Nylon 6,6 composite solutions separated into an orange-red gel and a clear liquid solution. When 10 ml of the clear solution was added to 50 ml of water in a beaker, a white precipitate was observed and collected for analysis. As indicated by the DSC in Fig. 1, the white precipitate exhibited a melting transition of Nylon 6,6 while the films prepared from orange-red gels showed no thermal transitions up to 300 °C. The TGA scans for the weight loss of PBZT, Nylon 6,6 and gels are shown in Fig. 2. This shows that the gels slowly coagulated by humidity were essentially indistinguishable from pure PBZT (curve (e)), and the white precipitate was the same with Nylon 6,6 (curve (a)). In addition, the corresponding weight losses of Nylon 6,6 were observed for molecular composites of PBZT/Nylon 6,6 of different compositions prepared from the traditional spinning process [3]. The elemental analysis indicated that the film slowly coagulated from a 2 wt % solution of 50/50 PBZT/Nylon 6,6 in MSA had a PBZT/Nylon 6,6 weight ratio of 129/1; this ratio would have been unity had a molecular composite been prepared from this composition. Thus, the clear liquid contained essentially only MSA, water and Nylon 6,6 while the gels were nearly pure PBZT.

White precipitates were observed on the bottom of clear solutions in both Zytel®330/MSA/water and PEEK/MSA/water solutions. When 10 ml of these clear solutions were added to 50 ml water no further precipitates were observed. It appeared that both Zytel®330 and PEEK had completely precipitated when 150 wt % water was absorbed by the original solutions in MSA. For the PBZT/Zytel®330 composite solution coagulated by humidity, the orange-red gel formed first, followed by a layer of white precipitate on the bottom of the petri dish. The TGA scans of pure PBZT, pure Zytel®330, the orange-red gel and the white precipitate are shown in Fig. 3. This shows that the white precipitate was indistinguishable from pure Zytel®330 (curve (c)). The orange-red gel consisted of approximately 80 wt % PBZT and 20 wt % Zytel®330. Some Zytel®330 appeared to precipitate in the PBZT gel and could not be removed by the pressing process.

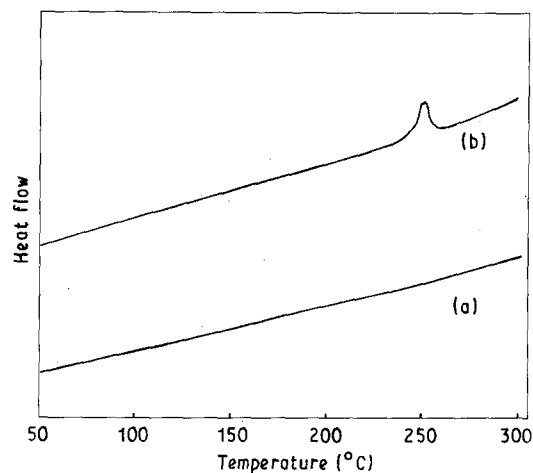


Figure 1 DSC scans of (a) the white precipitate and (b) the orange-red gel, coagulated by humidity, prepared from a 2 wt % 50/50 PBZT/Nylon 6,6 solution in MSA.

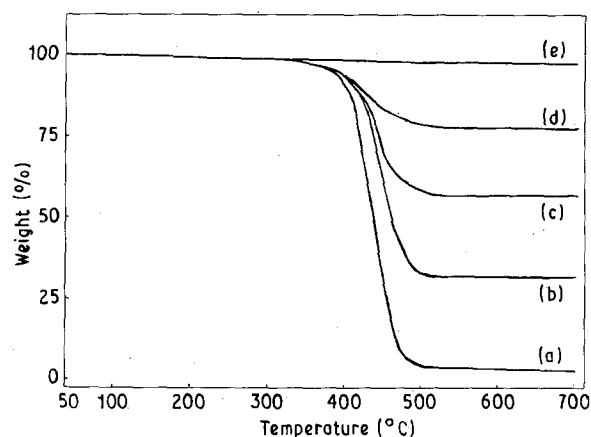


Figure 2 TGA scan of as-spun PBZT/Nylon 6,6 films and fibres prepared from the traditional spinning process by rapid (immersion) coagulation (a) 0/100, (b) 25/75, (c) 50/50, (d) 75/25, and (e) 100/0 PBZT/Nylon 6,6. TGA scans for the gels slowly coagulated by humidity are indistinguishable from curve (e), which is pure PBZT.

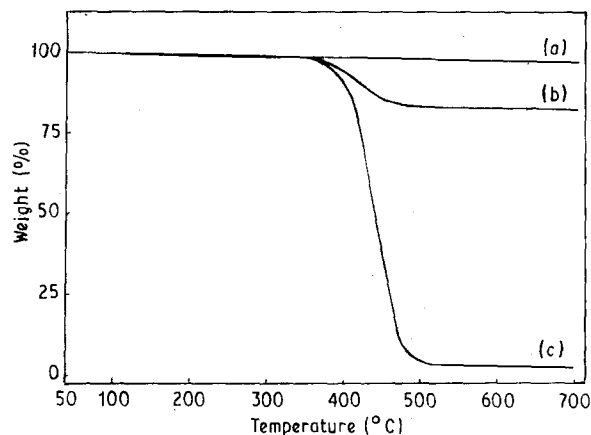


Figure 3 TGA scans of (a) PBZT, (b) the gel coagulated from a 2 wt % 50/50 PBZT/Zytel®330 solution by humidity and (c) Zytel®330.

For the PBZT/PEEK composite solution, after 12 days of slow coagulation, only an orange gel was formed with no other precipitates detected. The TGA scans of the orange gel, PEEK and PBZT are shown in Fig. 4. Nearly 45 wt % of PEEK residue remained

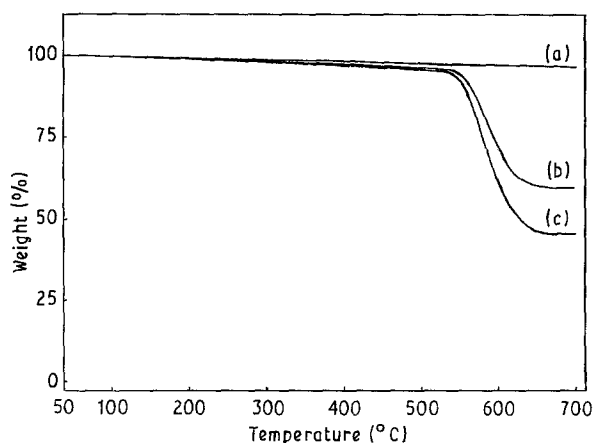


Figure 4 TGA scans of (a) PBZT, (b) the gel coagulated from a 2 wt % 30/70 PBZT/PEEK solution by humidity and (c) PEEK.

from the pure PEEK sample in a nitrogen atmosphere up to 700 °C (curve (c)). The total weight remaining was approximately 60 wt % for the gel which contained both the PBZT and PEEK residues (curve (b)). The TGA scans suggest that the gel contained nearly the same PBZT/PEEK composition as in the initial solution.

Slow coagulation of the ternary solutions of PBZT/Nylon 6,6/MSA by humidity showed that pure PBZT can precipitate out of the composite solutions first, as evidenced by DSC, TGA, and elemental analysis. Long after the PBZT was coagulated, the Nylon 6,6 was still dissolved in the solution. Similarly, for PBZT/Zytel®330/MSA system, PBZT appeared to precipitate first without the interference of Zytel®330. Subsequently, Zytel®330 precipitated as its solubility limit was reached. For the PBZT/PEEK/MSA system, co-precipitation of PBZT and PEEK was observed. These results indicate that the phase separation of rod and coil polymers is bound to occur during precipitation if they have different solubilities and the coagulation of the composite solution is controlled by diffusion. Therefore, the solubilities of PBZT, nylons and PEEK in the mixture of MSA/water warrant further study.

3.2. Solubility

The four polymers studied here have very different solubilities as shown in Table I. Nylons are much more soluble in MSA/water mixtures in comparison to PEEK or PBZT. As a consequence, for the case of PBZT/nylon/MSA solutions, PBZT was observed to precipitate first followed by precipitation of nylon (either Zytel®330 or Nylon 6,6) when MSA was further diluted as demonstrated in slow coagulation experiments. For PBZT/PEEK/MSA solution, both polymers precipitated at about the same dilution of MSA since PBZT and PEEK exhibit similar solubilities.

It should be noted that the solubility limit of the polymers indicates only a thermodynamic possibility for precipitation, and does not guarantee the realization of fibre formation. In fact, Nylon 6,6 fibres cannot be formed from MSA solutions at concentration less than 10 wt % polymer. In contrast, dilute solution of

TABLE I Coagulation values of water for 2% of polymer solutions

| Polymer | Coagulation value at room temperature (20 to 23 °C) (cc water/cc polymer solution) |
|-----------|--|
| PBZT | 0.15 |
| PEEK | 0.20 |
| Zytel®330 | 0.80 |
| Nylon 6,6 | 2.80 |

PBZT can be spun into fibres at concentrations as low as 0.05 wt % [20]; this is consistent with the tendency for PBZT to form a microfibrillar structure in the processing of the composite materials.

3.3. Rapid coagulation by immersion

It has been shown that slow coagulation can extract PBZT out of a PBZT/Nylon 6,6/MSA solution, and rapid coagulation is required to retain the PBZT/Nylon 6,6 gel composition from a ternary solution. As shown in Fig. 2, composite solutions of different compositions rapidly precipitated by immersion coagulation with water retain the original ratios of PBZT/Nylon 6,6. However, the immersion coagulation is not insurance for a simultaneous coprecipitation if the two polymers in the solution have different solubilities or coagulation rates. Furthermore, the term rapid needs to be quantified.

The rate of immersion coagulation can be characterized by the parameter Σ defined in the Equation 1. This quantity is commonly used in the study of fibre coagulation during spinning by plotting the data in the form of x^2 versus t , where x is the penetration distance of the coagulant and t is time [18]

$$\Sigma = \frac{1}{4} \lim_{t \rightarrow 0} \left(\frac{dx^2}{dt} \right) \quad (1)$$

The movement of the interface position, x , was recorded as a function of time. A linear square-root-of-time dependence of the interface location (measured from the edge of the gel) was found, for $x/R < 0.1$ (where R is the radius of the circular slide in model experiments), for all of the polymer solutions studied, as shown in Figs 5 and 6. An upward curvature was observed for $x/R > 0.1$ due to a circular geometry.

Some of the difficulties which cause serious complications for any transport analysis of coagulation are listed below; all of them are involved in coagulation of the polymer solutions of interest here.

1. The diffusion takes place in a quaternary system with possible coupling effects among the diffusion coefficients for each species, with polymers comprising two of the components.
2. The two polymers undergo a phase change at different solubility limits.
3. The diffusivities in the coagulated gel and the polymer solution are likely to be different.
4. There are thermal effects due to the heat of mixing of solvent and coagulant.
5. The boundaries and the volume of the system are not fixed.

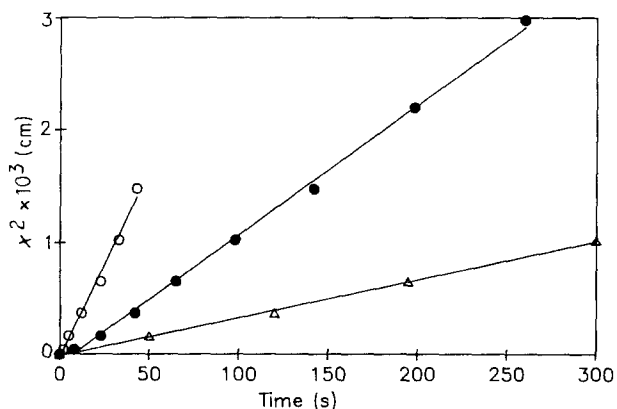


Figure 5 Rate of coagulation of pure polymer solutions; (○) 2% PBZT; (●) 2% Zytel@330; (△) 2% Nylon 6,6.

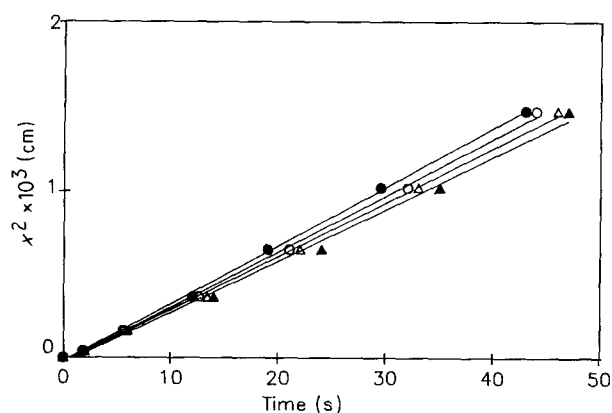


Figure 6 Rate of coagulation of pure PBZT and composite solutions; (○) 2% 50/50, PBZT/Zytel@330; (●) 4% 50/50, PBZT/Zytel@330; (△) 4.2% 10/90, PBZT/Zytel@330; (▲) 1% PBZT.

A great simplification is made with regard to item 1 by treating the mixture as a *pseudo*-binary system and considering only the diffusion of water and MSA since only a few weight per cent of polymer is contained in the solution. Paul [9] used the following reasoning to justify such a simplification. As the polymers change phase, they go from a molecularly dispersed solution to a porous, fibrillar network (gel). This means that on one side of the interface the solvent and the coagulant diffuse through a fibrillar network of coagulated polymer. Local diffusion of polymers is necessary to accomplish this change of morphology, but is not considered in a macroscopic description of the process. The easiest way to describe the phase change, concerning item 2, is to treat it as happening instantaneously as soon as the solubility limit of the polymer is reached (the concentration of water at which polymer precipitates, C^*). When the rate of phase change inside the fibre is very fast compared to the rate of coagulation, a distinct boundary between the coagulated gel and the un-coagulated solution forms and travels inwards as diffusion proceeds. Furthermore, a sudden desolvation of polymer in the outer layer of the fibre occurs at the exit from the spinneret. This layer acts as a semi-permeable membrane so that very little nylon (with higher solubility) diffuses out. Since the polymer content in the solution is low (2 wt %) the diffusion coefficient of water in the

coagulated gel and in the polymer solution is assumed to be unchanged (item 3). The thermal effects and small volumetric change are ignored. The thermal diffusivity is in general several orders of magnitude larger than the molecular diffusivity in liquids.

With the above assumptions, the penetration of coagulants into the polymer solutions can be treated as diffusion in a semi-infinite medium (as long as $x/R < 0.1$, which is the case in our experiments), shown schematically in Fig. 7. Note that when $x/R < 0.1$, the solution for a cylindrical geometry can be approximated by the solution in a semi-infinite geometry. Such a model seems to describe the experimental data rather well. The initial water content in the polymer solution, C_0 , is zero. The bath at the coagulating surface is assumed to be at a constant concentration C_1 (55.6 mol l^{-1}) since the polymer solution is coagulated in a large water bath. The penetration distance, x , and the concentration of water, $C(x, t)$ at the interface can then be related by

$$\frac{C_1 - C(x, t)}{C_1} = \text{erf}\left(\frac{x}{2(Dt)^{1/2}}\right) \quad (2)$$

where erf is the error function:

$$\text{erf}(\theta) = \frac{2}{\sqrt{\pi}} \int_0^\theta e^{-x^2} dx$$

This has the consequence that the concentrations and fluxes of solvent and coagulant depending only on the combination of x and t in the argument of the error function. Although x changes with t , the data in Figs 5 and 6 show that the ratio $x/(t)^{1/2}$ is essentially constant. Since the diffusivity is approximated as a constant the right hand side of Equation 2 is likewise. This requires a constant water concentration at the interface, i.e., $C(x, t) = C^*$.

The slopes obtained from Fig. 5, x^2/t , and C^* , were used to estimate an apparent diffusion constant of water in the polymer solutions. The results are shown in Table II. The rate of coagulation (x^2/t) for the isotropic composite solutions is not a strong function of composition and concentration, and is close to neat PBZT solution, as shown in Fig. 6. After the thin composite film is completely coagulated (the moving boundary reaches the centre of the glass slide) and removed from the microscope slide, a thin layer of nylon can be seen on the microscope slide. It appears that some degree of separation has already occurred.

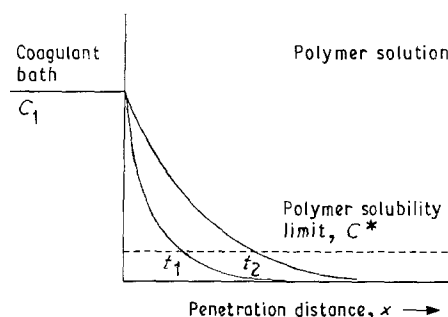


Figure 7 A diffusion schematic for the coagulation of polymer solutions. The interface is formed when the solubility limit (C^*) is reached.

TABLE II Diffusion constants for different polymer solutions calculated from the diffusion model

| 2% Polymer solution | $\frac{C_1 - C(x, t)}{C_1} = \operatorname{erf}\left(\frac{x}{2(Dt)^{1/2}}\right)$ | | | | |
|---------------------|--|-------------------------|--------------------------------------|------------------------------|---|
| | C^* (mol l ⁻¹) | $\frac{C_1 - C^*}{C_1}$ | $\left(\frac{x}{2(Dt)^{1/2}}\right)$ | $\left(\frac{x^2}{t}\right)$ | D (cm ² s ⁻¹) |
| PBZT | 7.2 | 0.871 | 1.072 | 3.5×10^{-5} | 7.6×10^{-6} |
| Nylon 6,6 | 40.9 | 0.264 | 0.238 | 3.3×10^{-6} | 14.4×10^{-6} |
| Zytel®330 | 24.7 | 0.556 | 0.552 | 1.1×10^{-5} | 9.1×10^{-6} |

Note: C^* is the concentration of water at the solubility limit of polymer determined from coagulation value experiment.

The quantity Σ in Equation 1 has the same dimensions and typically the same order of magnitude as the binary diffusion coefficients (10^{-7} to 10^{-5} cm² s⁻¹). It depends only on the rate of mass transfer, phase and structural transitions in the polymer-solvent-coagulant system in the same way as the coagulation rate in the actual wet-spinning process [18]. In fact, the diffusivities, calculated from the diffusion model, in Table II are of the same order of magnitude as the binary diffusion coefficient of water in sulphuric acid [21]. This also justifies the assumptions in the diffusion model. The rate of coagulation, for the polymeric solutions studied here, appears to depend on the solubility of the polymer in the solvent-coagulant mixture. The lower the solubility the earlier the polymer reaches its solubility limit for a nearly constant diffusivity (the faster the polymer precipitates), yielding a higher rate of coagulation. The diffusion coefficient is dependent on the solvent-coagulant pair and viscosity, and seems to be insensitive to the nature of polymer itself.

3.4. Coagulation time

According to the diffusion model, counter-diffusion of solvent and coagulant causes the polymer solution to reach the solubility limit and precipitate at a distance from the fibre axis as a function of time. Furthermore, it is possible to determine the coagulation time, i.e., the time required for the solidified layer to reach the centre of the fibre. With the general diffusion equation for an infinitely long cylinder, it was shown that the dimensionless group Dt/R^2 determines the characteristics of the coagulation process [21]. If a diffusion process in a cylinder of radius R_1 requires a time t_1 to progress to the centre, the corresponding time t_2 for a cylinder of radius R_2 is given by

$$\frac{t_2}{R_2^2} = \frac{t_1}{R_1^2} \quad (3)$$

The coagulation time for the actual wet-spinning process was estimated to be 4.8 s by extrapolating the model experiments to the actual die diameter (330 μ m) using the normal diffusion approximations, as shown in Fig. 8.

The analytical solution for an infinitely long cylinder was given by Crank [22]. Using the diffusivities obtained from the model, the time calculated to

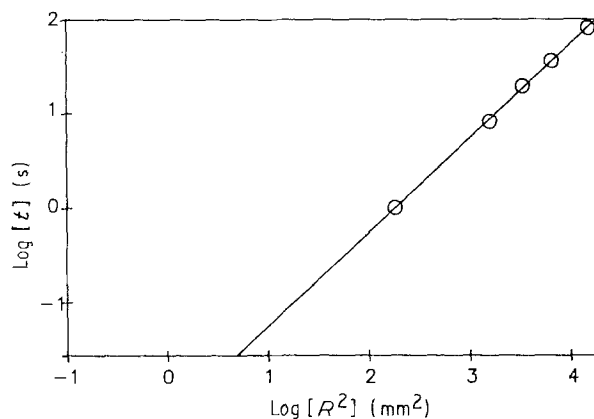


Figure 8 Estimation of actual coagulation time by extrapolation of model experiments of different diameters to the actual die diameter.

coagulate a pure PBZT fibre, spun from a 2 wt % solution in MSA, of 330 μ m would be 3.4 s. This time compares well with the actual coagulation time extrapolated from model experiments (4.8 s). In the actual spinning process, for a 2 wt % PBZT solution in MSA spun from a die diameter of 330 μ m, wet samples were removed from different positions of the partially coagulated fibre. The diameter of the minimally coagulated samples, removed from the spinning bath after 3 s, becomes 450 μ m in diameter one week after being taken out of the bath. The diameter increases with time because the residual acid in the fibre absorbs water which swells the fibre. A more fully coagulated sample taken out of the spinning bath after 20 s, collapses to approximately 150 μ m rather than expanding as the minimally coagulated sample does. A completely coagulated fibre, washed for 24 h in the water bath, has a wet diameter of 330 μ m. After drying in air without constraints for 1 h the fibre shrunk to a constant diameter of 95 μ m, due to the volatilization of water.

The coagulation time calculated above (3.4 s) was only for PBZT/MSA solution, while fibre could not be formed for a solution of 2 wt % Nylon 6,6 by itself in MSA. In other words, some nylon was still soluble in the mixture of MSA and water, while PBZT has completely solidified from the composite solution of PBZT/nylon/MSA. It appears impossible that PBZT and nylon would precipitate simultaneously to achieve a molecular level mixing during the immersion coagulation.

3.5. Implication for the preparation of composite fibres

Phase equilibria and kinetics of phase separation are the two decisive factors in determining the composite fibre morphology and physical properties. In wet-spinning, the solution undergoes a change in composition that is dependent on the fluxes of solvent and non-solvent. Precipitation of polymer takes place when the solubility limit is reached. This process happens step-by-step from the outer layer of the fibre towards the core, and appears to be a diffusion-limited process. At the outlet from the spinneret, a sudden desolvation of the outer layer of fibre occurs forming a skin of coagulated polymer. Nylon at the surface can coprecipitate on the surface of the fibre or diffuse into the coagulant bath, depending upon the instantaneous dilution of MSA. Across the thin skin, a counter-diffusion of MSA and water takes place. Because the skin acts as a semi-permeable membrane, very little polymer diffuses out, so that the mass of polymers remains almost constant (Fig. 2). Inside the skin of the fibre, it seems that PBZT would precipitate first consequently forming its preferred continuous network structure; nylon would precipitate later due to its higher solubility.

4. Conclusions

The slow coagulation of the ternary solutions shows that pure PBZT either precipitates from the solutions first or coprecipitates with the thermoplastic depending upon their relative solubilities. The immersion coagulation is required to retain the composition of PBZT/nylon precipitate from a ternary solution, but the immersion coagulation is not a guarantee for simultaneous coprecipitation into a single phase. Phase separation occurs during immersion coagulation, a diffusion-controlled process, due to the different solubilities. The relative solubilities of solution spun polymer pairs will directly affect the morphology of the coagulated products. The concept of a molecular composite of rigid rod and flexible coil polymers is attractive, but does not seem realistic based on the materials investigated here.

Acknowledgements

This research was supported by E. I. du Pont de Nemours, Inc. We thank C. Shambelan, G. M.

Prilutski and W. C. Uy for providing some of the materials.

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Received 24 July

and accepted 22 November 1989