Mechanical properties of miscible polycarbonate–copolyester blends

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Miscible blends of polycarbonate and the copolyester based on 1,4-cyclohexane-dimethanol and a mixture of terephthalic and isophthalic acids were melt processed into film and injection moulded into test bars. Wholly amorphous specimens of each type were mechanically tested directly after fabrication and after a variety of annealing conditions. As processed blends exhibited nearly additive responses *versus* blend composition for modulus, strength, elongation at failure, and notched Izod impact strength. Various annealing protocols caused maxima to appear in plots of modulus *versus* composition. Similar responses were observed for blend density, and good correlations were noted between density and modulus as both composition andhistory were varied. Sub-T_g annealing of injection moulded specimens was demonstrated to involve simultaneous relaxations of volume and molecular orientation. The individual effects of this combined process were separated by sequential super-T_g (or T_m) and sub-T_g annealing steps.

Keywords Mechanical behaviour; orientation; polycarbonate; copolyester; blend; relaxation

INTRODUCTION

In the last few years, it has become more widely appreciated that polymer–polymer miscibility can occur when there is an exothermic heat of mixing stemming from intermolecular interactions between segments of two polymeric components[1–4]. Much progress has been made in quantifying these interactions in polymer blends and in relating this information to the molecular structure of the component polymers[1–12]. These efforts have been concomitant with a rapid acceleration of discoveries of miscible polymer blends as seen in the recent literature. This logically leads to fundamental and practical interest in the physical property relationships exhibited by miscible polymer blends; however, knowledge and understanding in this area are rather limited.

A few papers have described the mechanical behaviour of miscible blends[13–19] and report that properties such as modulus and strength lie *above* the linearly additive line connecting the values of the pure components. In some cases, these properties exhibit a maximum value greater than that observed for either pure component. It has been suggested that such synergism is a result of the volume contraction, or densification, that accompanies mixing in these systems[17]. One paper[15] proposes a model to quantify this intuitively attractive hypothesis. Since the volume change or mixing is related to the energetics of mixing, this suggests an interesting interrelationship between properties and basic causes for miscibility[20]. The published literature contains little if any information on the equally important and interesting issues related to ductility, e.g. elongation at failure or impact strength, of miscible blends.

The purpose here is to add further information and insight about the mechanical behaviour of miscible blends by reporting results of a rather thorough study for mixtures of polycarbonate and a copolyester. An earlier paper[21] has shown this pair to be miscible for all blend compositons. Other papers will deal with the thermodynamics and chemistry of this system. The present observations were made while these blends were in the glassy state; hence, the properties depend on the processes used to fabricate the test specimens and their prior history. These issues are shown to be important factors in the property relations observed.

BLEND PREPARATION

The bisphenol-A polycarbonate used is a commercial product of the General Electric Co. designated as Lexan 131-111 which has $\bar{M}_n = 13.3 \times 10^3$ and $\bar{M}_w = 34.2 \times 10^3$. This polymer exhibits a glass transition of approximately 148°C by thermal analysis and does not crystallize when melt processed by conventional methods. The copolyester is a commercial product of Eastman Chemical Products, Inc., designated as Kodar A-150, and is composed of 1,4-cyclohexanedimethanol units with a mixture of terephthalic and isophthalic acid units. Approximate analyses[20] reveal that the isophthalic/terephthalic acid proportion is 20/80 and that $\bar{M}_n = 22 \times 10^3$. By thermal analysis, $T_g = 87°C$ and $T_m = 265°C$. Crystallization rates for this copolyester are relatively slow, and in normal melt processing operations it can be quenched to a completely amorphous state.

Blends were prepared in a single screw laboratory extruder with a barrel diameter of $\frac{3}{4}$ inch. Prior to extrusion, the pellets were dried at 70–75°C in an air oven for 24 h to ensure removal of any sorbed moisture. To aid pellet flow in the feed section, drying was followed by heating the pellets one hour at 150°C to crystallize the copolyester. The barrel temperature was set at an optimum temperature generally found to lie in the range 275° to 300°C which gave homogeneous blends with

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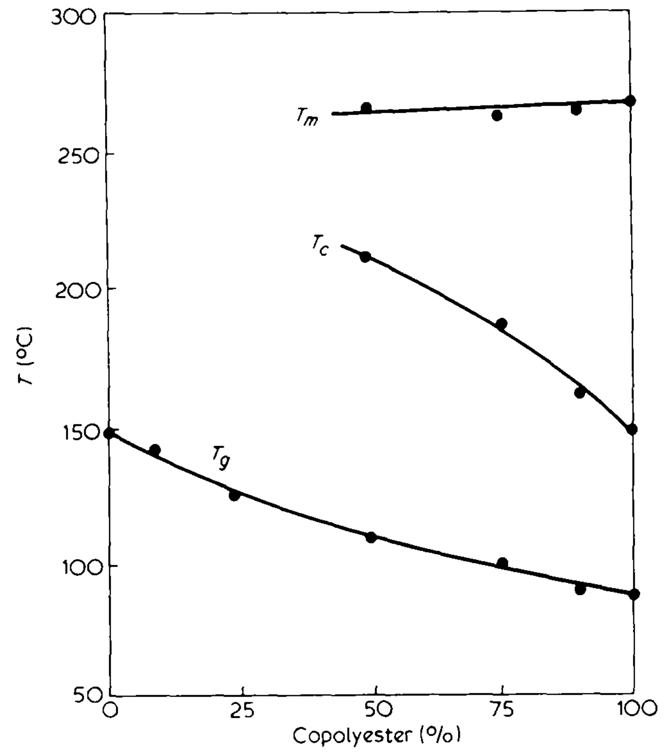

Figure 1 Glass transition, melting, and crystallization temperatures for polycarbonate–copolyester blends obtained on first heat by d.t.a. at 10°C min^{-1}

minimal degradation. The extruder was fitted with various dies depending on the intended use for the extrudate. Films were made at various draw ratios using either a film die with a cross-section of 6.25 × 0.044 in or a ribbon die with a cross-section of 3.25 × 0.050 in. Draw ratios were computed by comparing the cross-sectional areas of the die and the final extrudate. For the ribbon die, the extrudate was run through an ice water bath prior to takeup; while for the film die, the extrudate was fed directly to chilled rolls.

To prepare material for injection moulding, extrudate from a rod die (diameter $\frac{1}{8}$ inch) was pulled through a water bath prior to chopping into pellets. Just before moulding, the blend pellets were subject to the same drying and crystallization treatments described earlier. Test specimens in the form of dogbones (ASTM D-638) and Izod bars (ASTM D-256) were injection moulded using optimum machine settings and the barrel temperatures were generally similar to those used in extrusion.

THERMAL ANALYSIS

The blends were characterized by differential thermal analysis (d.t.a.). *Figure 1* summarizes the important thermal events noted on first heats using a heating rate of 10 C/min. There is a single, composition dependent glass transition as expected for a miscible blend system. Following the glass transition, a crystallization exotherm is noted as the quenched copolyester component crystallizes, and the peak temperature, T_c, of this exotherm is noted in *Figure 1*. Blends containing less than 50% of this component developed no crystallinity on heating in the d.t.a. The melting point of the copolyester is also shown in *Figure 1*. These results are substantially identical to those reported earlier for batch processed blends[21] and give some assurance that these continuous processing techniques result in well-mixed blends.

Figure 2 shows the relative area under the copolyester melting endotherm for samples with different processing and annealing histories. These results establish two important points. Given enough time, the copolyester will crystallize to approximately the same fractional extent regardless of blend composition[22]. The processing steps do not lead to significant interchange reactions between the two components[21] or such levels of crystallinity would not be possible.

Blends which were subjected to prolonged annealing below their glass transition temperatures developed endothermic peaks in the glass transition region and elevated apparent T_g's as has been noted for other glassy polymers[23].

MECHANICAL PROPERTIES OF AS-PROCESSED BLENDS

The mechanical properties of film and moulded blend specimens directly after processing without any further thermal history are given here. These specimens were completely free of copolyester crystallinity.

Film

Film specimens were prepared at different draw ratios by fixing the extruder output and varying the take-up speed which affects the extent of molecular orientation frozen into the sample by quenching. Test specimens were cut from the film that had a width of $\frac{3}{8}$ inch and a length sufficient to give a gauge length of 10 inches when installed

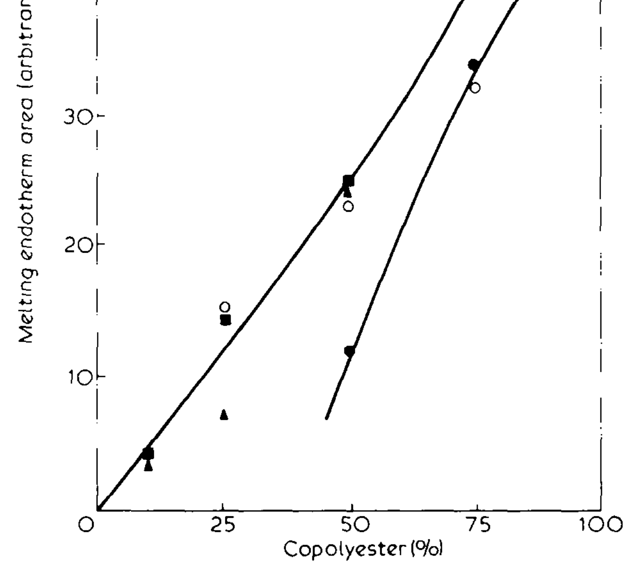

Figure 2 Area under melting endotherm for blend samples with various histories obtained by d.t.a. on first heat. Extruded pellets: ●, unannealed; ▲, annealed at 180°C for 2 h; ■, annealed at 180°C for 24 h. Injection moulded samples: ○, annealed at 125°C for 5 h

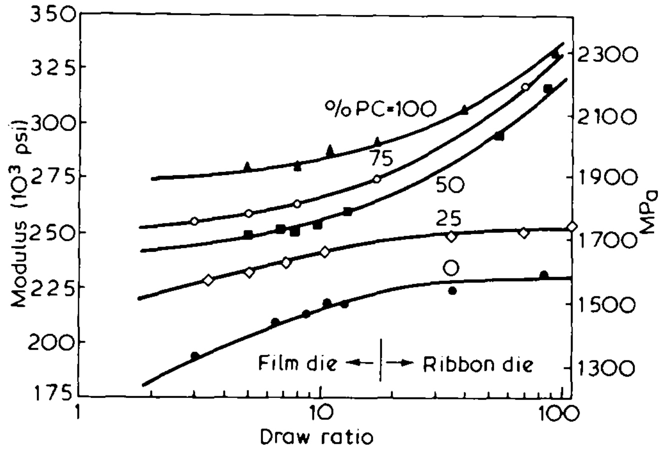

Figure 3 Effect of draw ratio on modulus of blend films

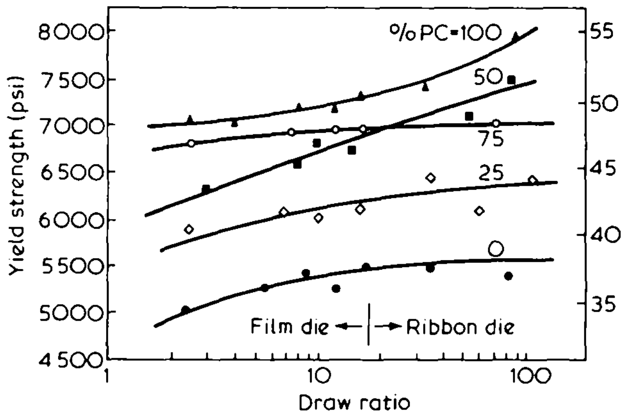

Figure 4 Effect of draw ratio on yield strength of blend films

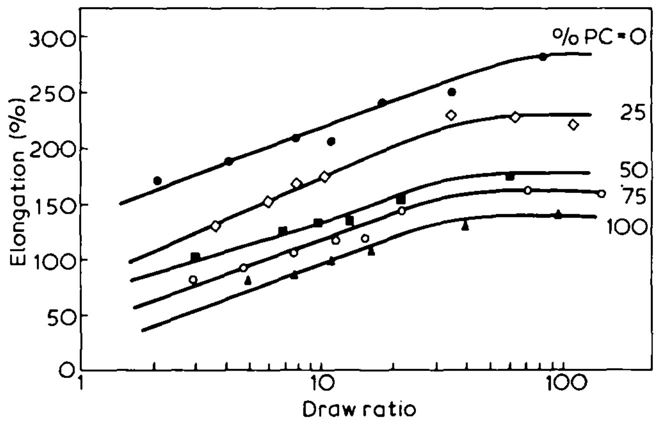

Figure 5 Effect of draw ratio on percent elongation at break of blend films

in the grips of the Instron. The testing speed was 0.5 inches/min for the modulus and was increased to 5 inches/min to obtain yield and failure properties.

The various tensile properties for all blends are shown as a function of draw ratio in *Figures 3–5*. The film and ribbon dies were used to obtain the wide range of melt draw ratios shown, and the data for the two regions match up well. As expected, the modulus and strength increase with draw ratio. The increase in modulus becomes more pronounced the higher the polycarbonate content owing to the much greater melt strength or resistance to relaxation of this component. The elongation at break also increases with draw ratio in all cases which is not general for all polymers but is typical for amorphous glasses[24]. As indicated by the magnitude of these values, both polymers are quite ductile.

Cross plots of these data at fixed draw ratios give a better indication of the property relationships for the blends and such plots and shown in *Figures 6–8*. The

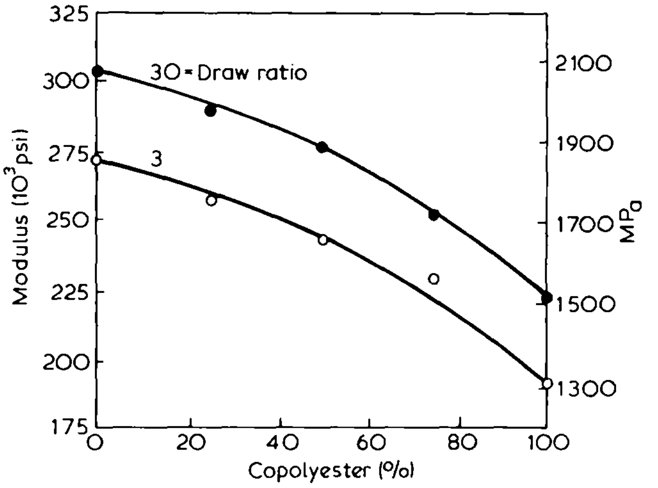

Figure 6 Modulus of film as a function of blend composition

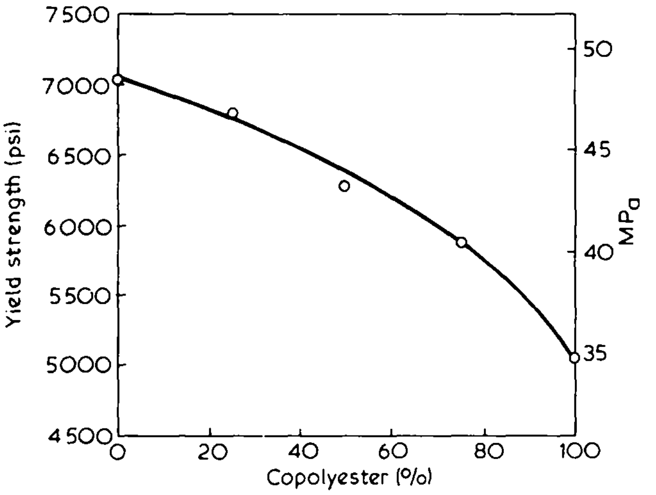

Figure 7 Yield strength of film as a function of blend composition. Draw ratio = 3

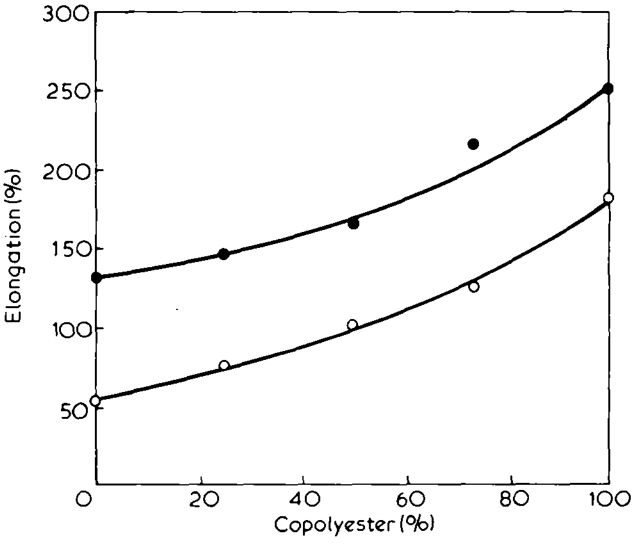

Figure 8 Percent elongation at break of film as a function of blend composition. Draw ratio = ●, 30; ○, 3

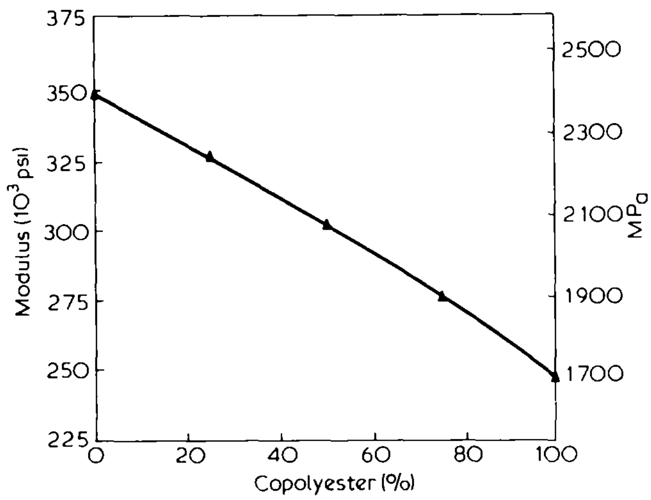

Figure 9 Modulus of injection moulded blends prior to annealing

trends are generally the same regardless of the draw ratio selected except for yield strength at high stretch levels owing to the apparently anomolous trend seen for the 50% blend. Interestingly, on this basis, the blends show properties which are intermediate to those of the pure compounds. The results do not lie on a linear tie line connecting the pure component values, but rather the modulus and strength lie slightly above such a line while the indicator of ductility, percent elongation at failure, lies below.

Injection moulded samples

Injection moulded dogbone specimens were tested using an Instron at a crosshead speed of 0.1 inches/min to obtain the modulus and at a speed of 2 inches/min to obtain failure properties. An extensiometer with a gauge section of one inch was used for the modulus determination. Deformation at failure was computed from the crosshead travel using the 4.25 inch length of the uniform section of the dogbone specimen. The Izod impact strength was determined on notched bars using a TMI tester with a 5 ft·lb hammer. The tensile and impact specimens were $\frac{1}{8}$ inch thick.

Figures 9 and *10* show the results of the tensile testing. All three properties show trends with composition similar to that observed with film specimens, *Figures 6–8*; however, the absolute values of modulus and yield strength are higher for the moulded specimens than seen for film. Elongations at break are similar in magnitude for the two methods of processing. The Izod impact strengths for the blends are shown in *Figure 11*. These results lie slightly below the tie line constructed between the values for the pure components and closely parallel the behaviour of the elongation at break. Note that both components are quite tough and the blends have intermediate values.

Discussion

The modulus and strength data for either film of moulded specimens shown here do not exhibit the synergism or maxima described in other reports for miscible blends[13–19]. The two preparation methods used here were comparable to industrial production methods; whereas, most of these previous reports used somewhat different methods of fabrication. It must be recalled that the extrusion and moulding techniques induce molecular orientation and may involve different states of molecular packing. Thus, it was decided that further investigations of these property relationships and sample characterization may be interesting and could add some insight to the differences with other studies that have been reported. These further studies are described in the following sections.

EFFECT OF ANNEALING ON BLEND MECHANICAL PROPERTIES

Thermal annealing of materials not already in equilibrium can allow a closer approach to this ultimate state; however, several phenomena may become involved. It is well known that annealing of glassy polymers at temperatures just below their T_g causes a reduction in

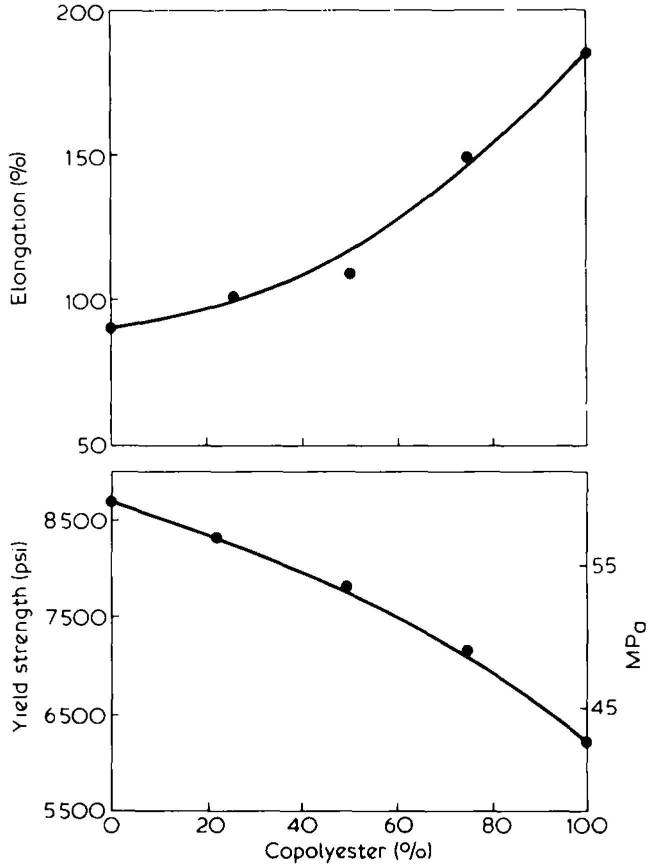

Figure 10 Percent elongation at break and yield strength of injection moulded blends prior to annealing

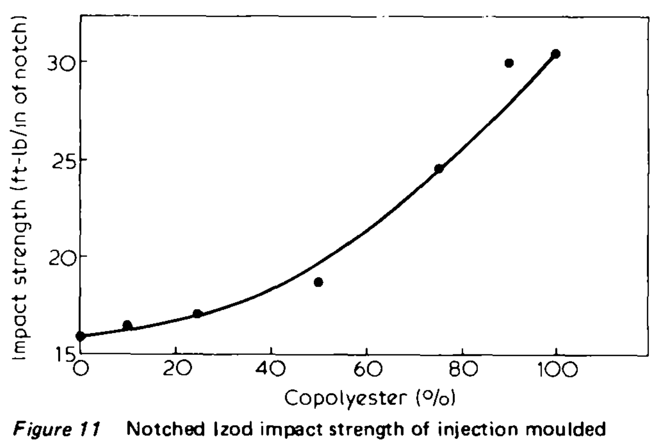

Figure 11 Notched Izod impact strength of injection moulded blends prior to annealing

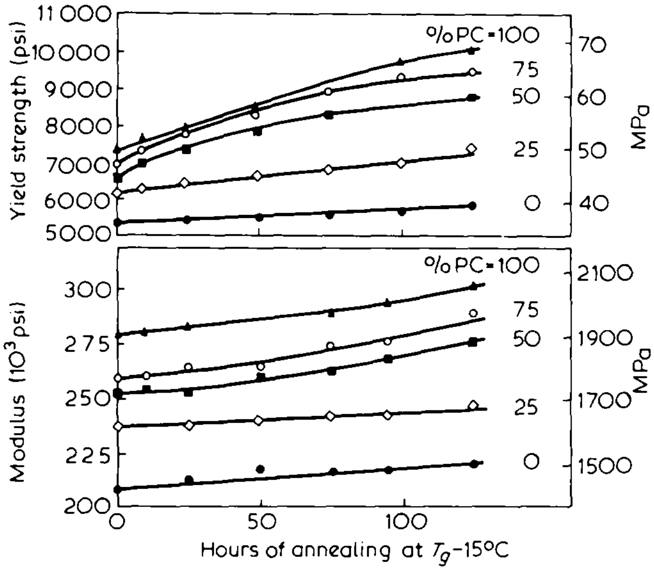

Figure 12 Effect of sub-T_g annealing on yield strength and modulus of extruded film

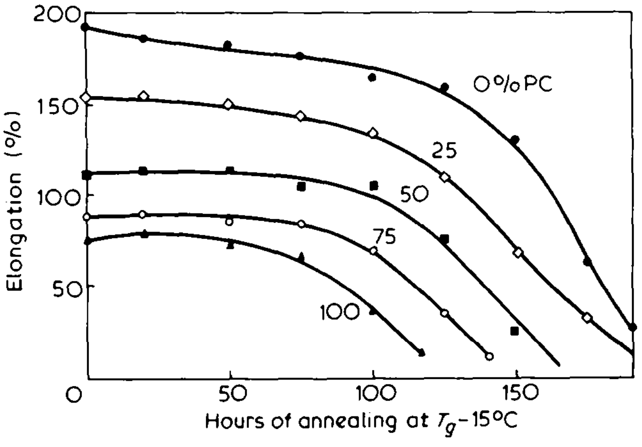

Figure 13 Effect of sub-T_g annealing on percent elongation at break of extruded film

both volume and enthalpy[23] as the material gradually relaxes toward the equilibrium state. Naturally, there are accompanying changes in mechanical properties with modulus and strength expected to increase; however, the more dramatic and serious change is the reduction in ductility, i.e., embrittlement[25]. These responses can be interpreted, at least qualitatively, as resulting from the loss in free volume during sub-T_g annealing[25]. However, the changes may not be simple when the glassy specimens have complex physical states, including frozen-in molecular orientation, generated in processes like injection moulding. The results shown below illustrate these effects in addition to revealing some interesting features of mechanical behaviour of miscible blends. It has proved instructive to decouple the various relaxation processes by also using annealing above the T_g (or the melting point as was necessary here). A subsequent section deals with changes in volume or density and will serve to unify some of the mechanical responses seen here.

Comparable sub-T_g annealing conditions for miscible blends involves the complication that T_g depends on blend composition. For this work, it was decided to anneal each composition at 15°C below its measured T_g. Of course, relaxation times may be expected to vary both with temperatures and composition, so this strategy does not ensure equivalent fractional degrees of relaxation for different specimens but it does permit a limited evaluation of the trends.

A special device was constructed for some of the annealing experiments with dogbone shaped specimens. This consisted of a $\frac{1}{8}$-inch thick plate into which cavities identical in shape to the test specimens were cut. This plate, with specimens installed in the cavities, could be placed between the plattens of a compression press. The plattens were fitted with heating elements and also a cooling water circulation system so that specimens could be held at a desired temperature and then rapidly quenched to room temperature at the desired time. In this way, specimens could be maintained in the dogbone shape (even above T_g or T_m) in an environment relatively free of oxygen and moisture.

Film

Film samples with a constant draw ratio of 5.5 were annealed in an air oven at T_g − 15°C for various periods of time. The mechanical properties following this heat treatment are shown in *Figures 12* and *13*. As might be expected, the modulus and yield strength gradually increase with annealing time. On the other hand, elongation at break drops precipitously after a certain period of time[25]. The changes seem to be more rapid for polycarbonate for all properties. In every case, the response of the blends is intermediate to that of the pure components.

Injection moulded samples

The injection moulded specimens were subjected to several annealing procedures. First, the as-processed samples were annealed at T_g − 15°C for varying periods of time in an air oven. The yield strength increased and the elongation at break decreased as expected. The Izod impact strengths also decreased dramatically (see *Figure 14*) in the manner observed by others[25]. As shown in

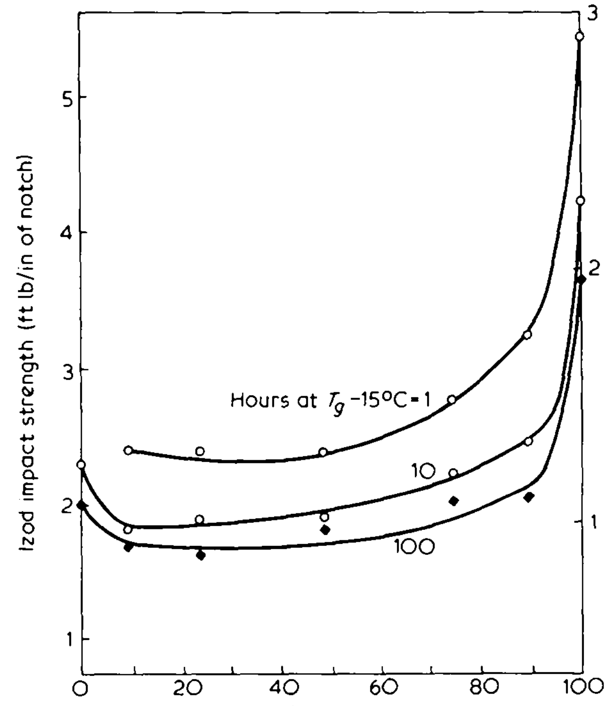

Figure 14 Effect of sub-T_g annealing in an air oven on impact strength of injection moulded samples

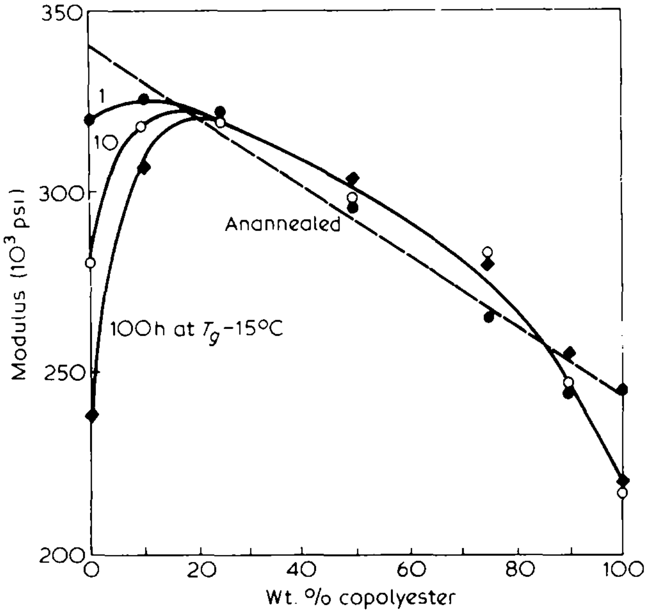

Figure 15 Effect of sub-T_g annealing in an air oven on impact strength of injection moulded samples

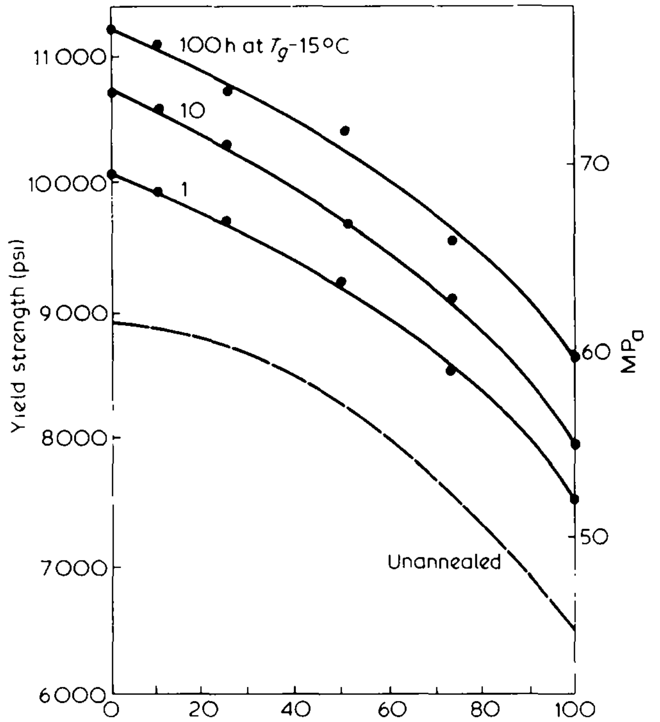

Figure 16 Effect of sub-T_g annealing in an air oven on yield strength of injection moulded samples

Figure 14, the blends appear to have suffered more embrittlement than the pure components. The most unusual change, however, was in the modulus. As *Figure 15* shows, sub-T_g annealing caused a small increase in the modulus of most blends, but there was a significant decrease in the modulus for both pure components. The latter is generally not expected; although, one other published report[27] shows a similar result. Interestingly, the net effect is that following this annealing procedure there is a pronounced maximum in the plot of modulus *versus* composition. The yield strength, on the other hand, does not exhibit such an effect as may be seen by the data in *Figure 16*. Obviously, the unexpected decrease in modulus of the pure components on annealing requires some explanation. It has been suggested that annealing in an air oven may lead to some hydrolysis of condensation polymers[28]. We were not able to detect any significant losses in molecular weight by dilute solution viscometry; however, this idea prompted another procedure for sub-T_g annealing as described next.

Moulded bars were annealed at $T_g - 15$°C in the device described earlier which isolates the specimen from any humidity that may exist in the air. Further, this device restrains the sample from dimensional changes. The effects of annealing in this manner on modulus are shown in *Figure 17* which displays qualitatively similar results to those in *Figure 15*; although, there are some quantitative differences perhaps owing to the constraints on the specimens. *Figures 18* and *19* show the change in failure properties for these specimens on annealing, and once again the trends are qualitatively the same as before. In this case, the data suggest that sub-T_g annealing may produce a maximum in the yield strength at $\sim 75\%$ polycarbonate. We conclude for injection moulded

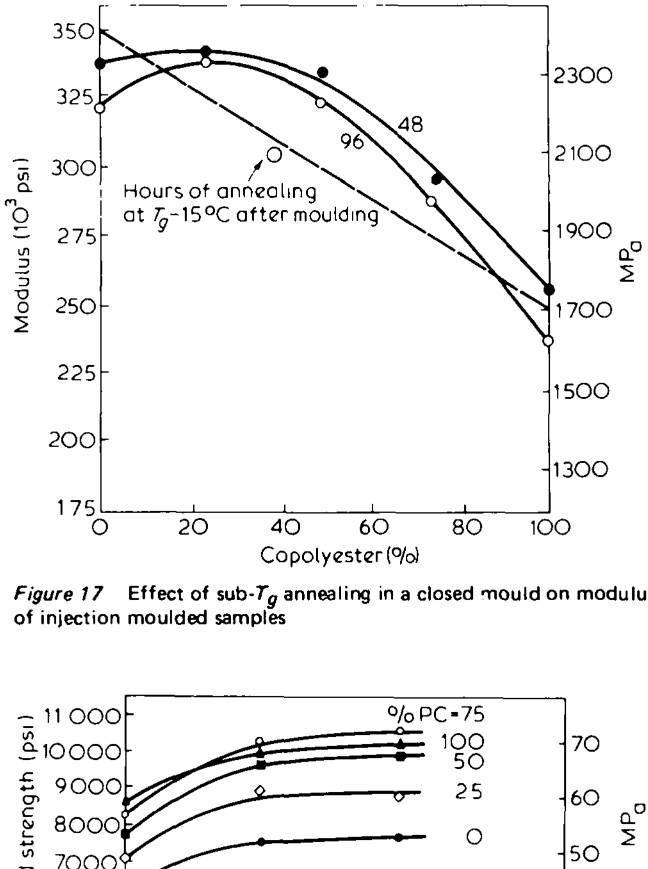

Figure 17 Effect of sub-T_g annealing in a closed mould on modulus of injection moulded samples

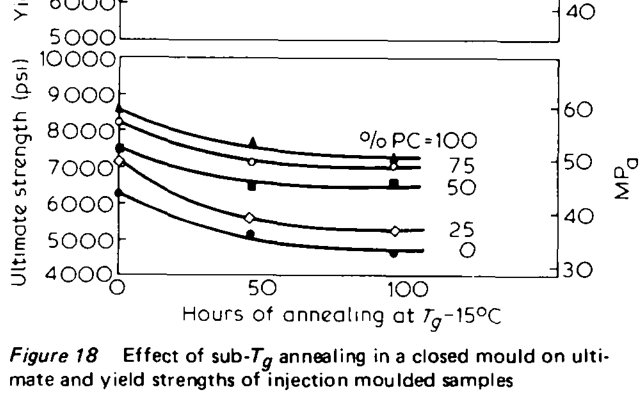

Figure 18 Effect of sub-T_g annealing in a closed mould on ultimate and yield strengths of injection moulded samples

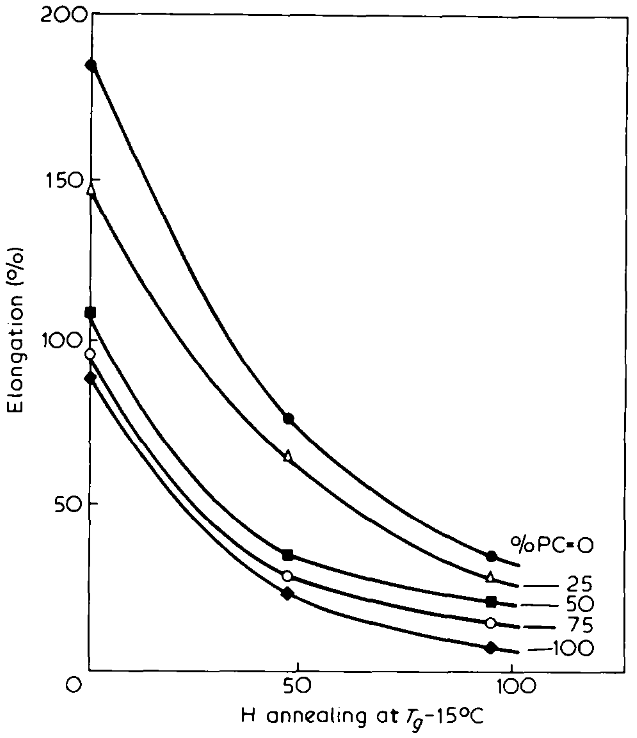

Figure 19 Effect of sub-T_g annealing in a closed mould on percent elongation at break of injection moulded samples

specimens that mechanisms for volume and orientation relaxation are simultaneously at work during sub-T_g annealing. Evidence for loss in orientation during annealing can be seen by examination of the specimen through crossed polarizers. As seen in *Figure 20*, prolonged annealing causes a break-up of the uniform birefringence pattern exhibited by processed specimens.

Next a procedure was devised which decouples the simultaneous relaxation of volume and orientation. This involves first annealing above T_g to get orientation relaxation; however, to avoid crystallization of the copolyester component, it was actually necessary to select a temperature above its melting point for this treatment. To avoid hydrolysis and bubble formation from absorbed moisture at this high temperature, the specimens were carefully dried at 75°C for 48 h. The samples were then heated in the device described earlier (necessary for shape retention) at 275°C for 4 min and then rapidly quenched to room temperature to avoid crystallization of the copolyester component. Super-T_m annealing in this way appeared to remove all molecular orientation with minimal molecular weight degradation. These specimens are roughly equivalent to what might be obtained by compression moulding. *Figures 21–23* show the mechanical properties of specimens annealed above T_m (data for as moulded samples from *Figures 9* and *10* are shown for comparison). Super-T_m annealing causes a drop in modulus, yield and ultimate strength, and elongation at break as might be expected by a loss of molecular orientation (see film data). Interestingly, these specimens show a pronounced maximum in the plot of modulus *versus* composition.

Samples annealed above T_m to relax out orientation were subsequently annealed below T_g to ascertain the effects of volume relaxation on purely isotropic specimens. The results are shown in *Figures 24–26*. The maximum in modulus is retained, but all values are shifted upwards following 48 h at T_g-15°C. Relative to the unannealed or as moulded materials, sequential super-T_m and sub-T_g annealing produces a similar pattern as seen in *Figures 15* and *17* where the as moulded samples are sub-T_g annealed directly. This is further confirmation that the latter trends are the result of simultaneous relaxation of volume and molecular orientation. *Figures 25* and *26* show the effect of volume relaxation on strength and ductility for orientation-free materials. The embrittlement

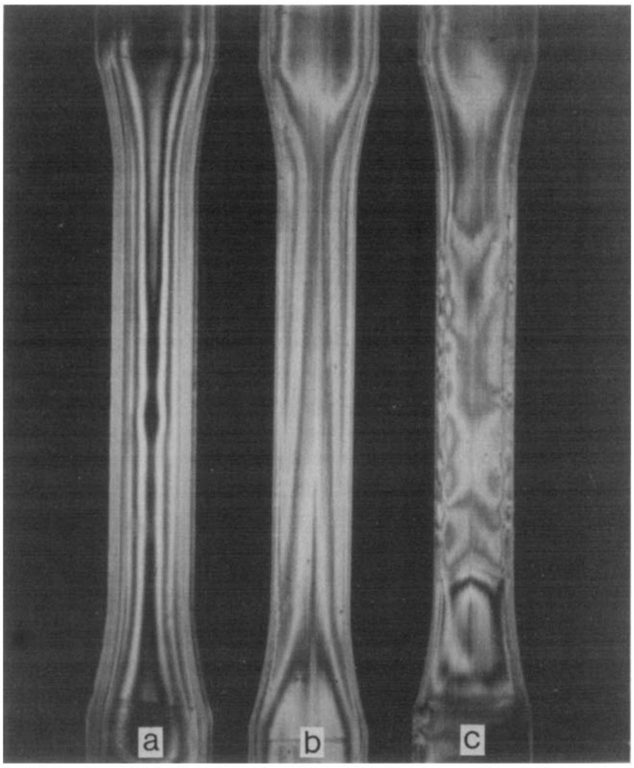

Figure 20 Examination of injection moulded polycarbonate bars between crossed polarizers prior to annealing (a) and after annealing at T_g −15°C in a closed mould for 1 day (b) and 4 days (c)

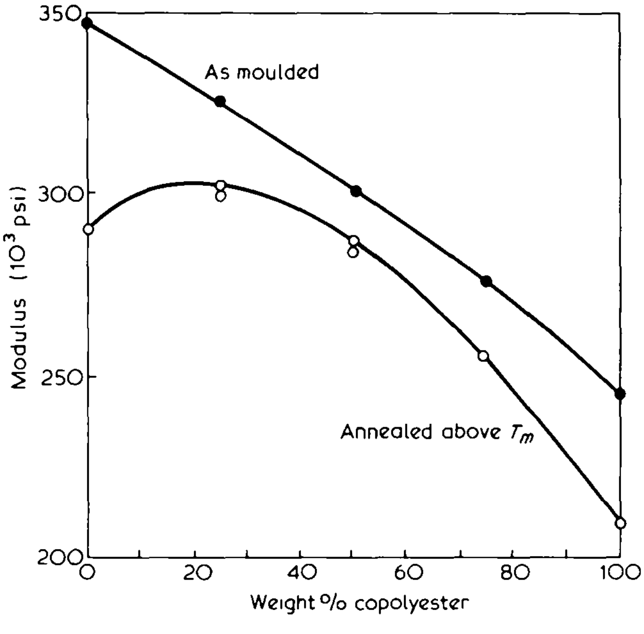

Figure 21 Modulus of injection moulded blends after annealing above T_m (open circles) as compared to moulded blends (closed circles)

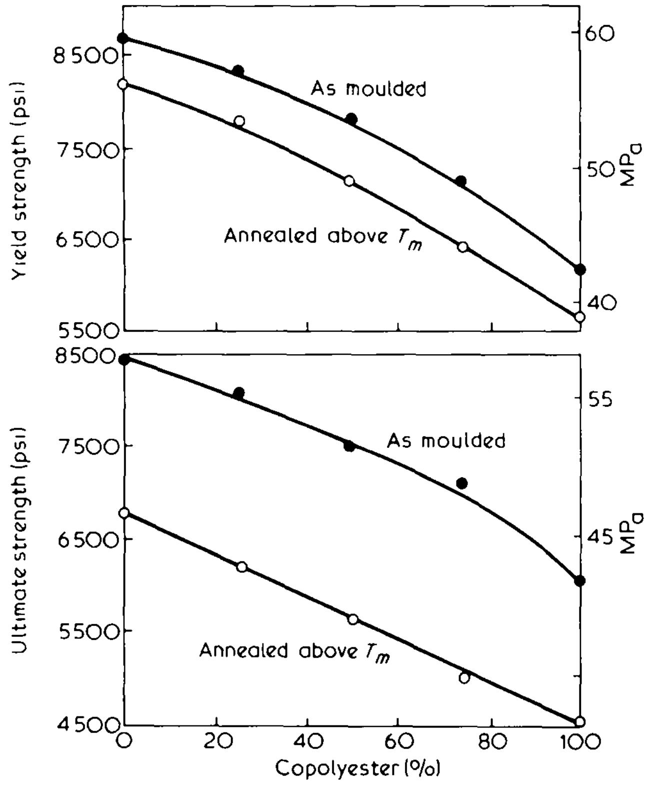

Figure 22 Yield and ultimate strengths of injection moulded blends after annealing above T_m (open circles) as compared to moulded blends (closed circles)

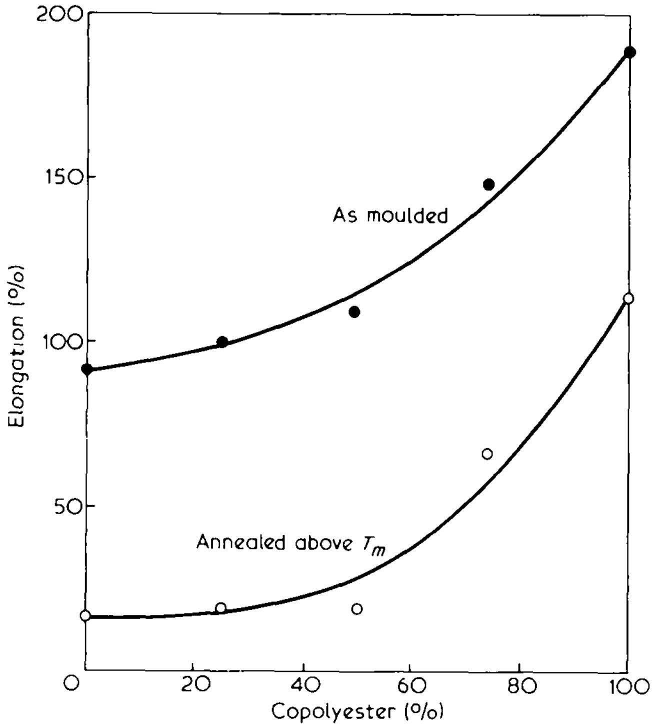

Figure 23 Percent elongation at break of injection moulded blends after annealing above T_m (open circles) as compared to moulded blends (closed circles)

seems to be more severe in this case than noted for specimens with orientation as seen by comparing *Figures 19* and *26*.

DENSITY CHARACTERIZATION

The above discussion has shown that the properties of these blends depend on previous thermal and mechanical

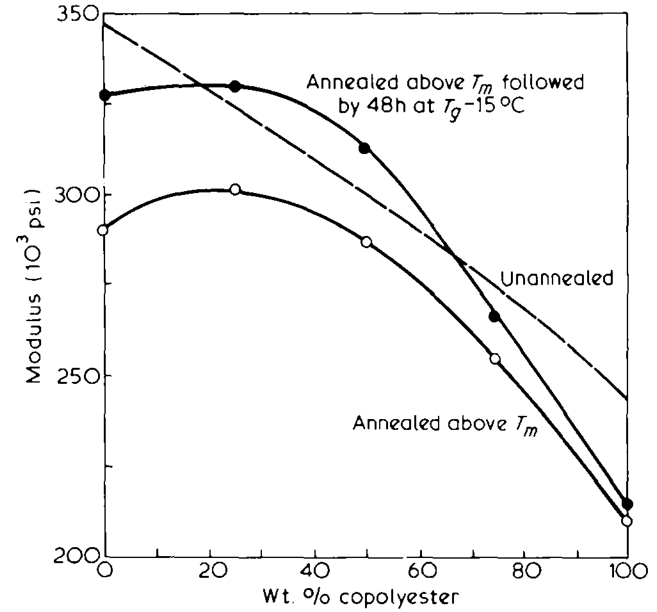

Figure 24 Effect of sub-T_g annealing in a closed mould on samples previously annealed above T_m. Data from previous figures shown for comparison

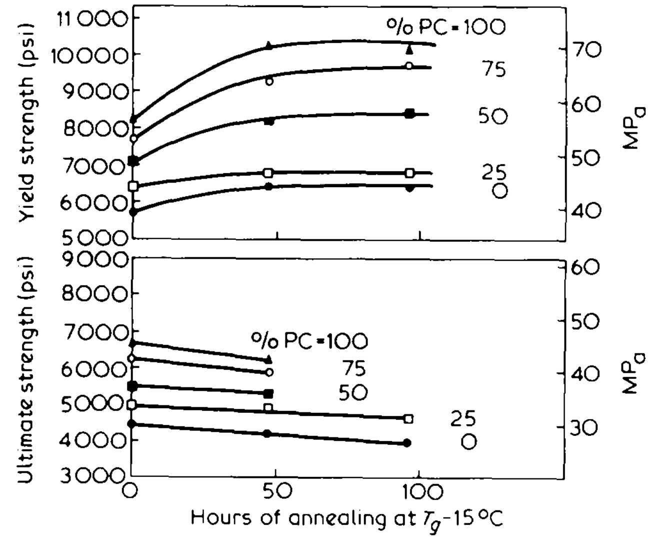

Figure 25 Effect of sub-T_g annealing in a closed mould on yield and ultimate strength for samples previously annealed above T_m

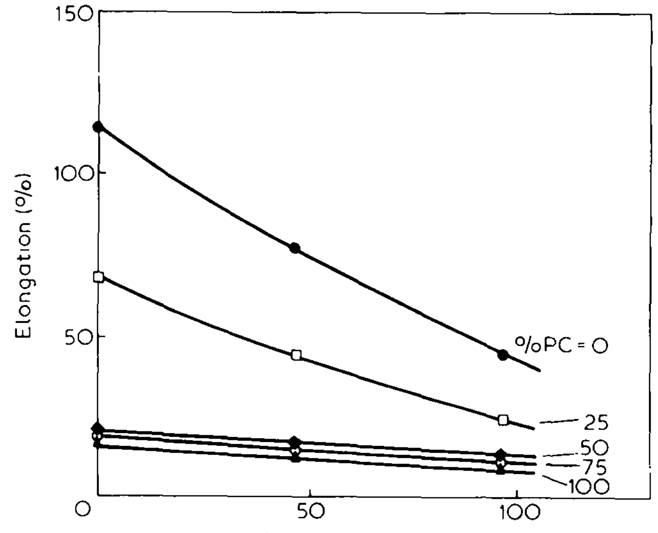

Figure 26 Effect of sub-T_g annealing in a closed mould on percent elongation at break for samples previously annealed above T_m

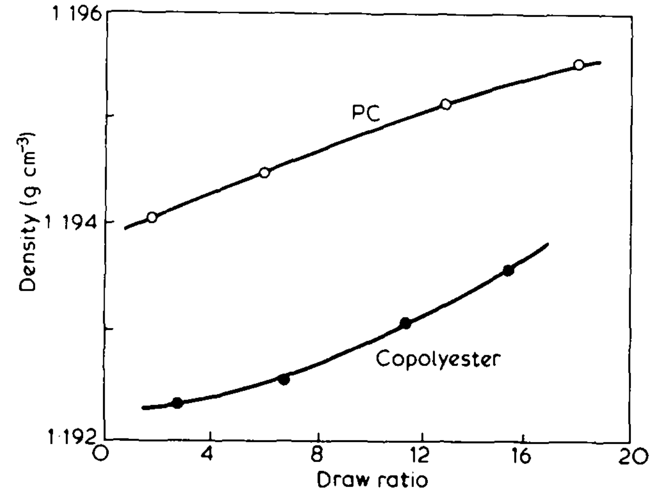

Figure 27 Influence of draw ratio on density of polycarbonate and copolyester film

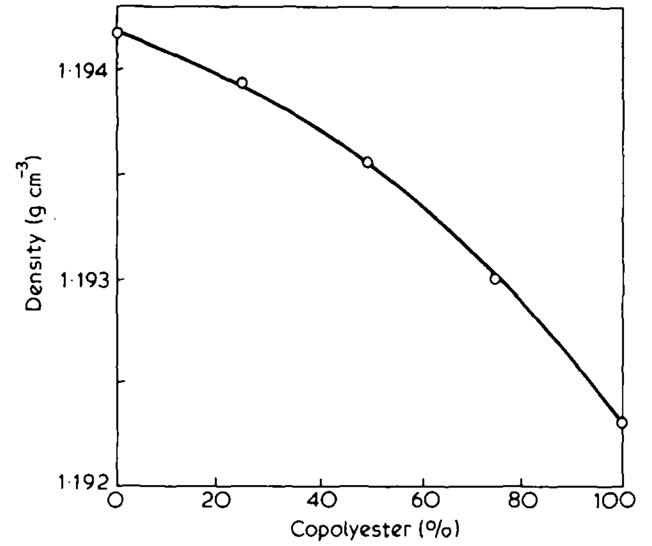

Figure 28 Film density as a function of composition. Draw ratio = 3

history as well as composition since they are non-equilibrium glasses. It was stated earlier that volume changes on mixing expected for miscible blends should be a factor in the property relationships observed; however, this effect, too, is likely to depend on history for glassy blends. We might expect characterization of various samples by density measurements to be informative. The density was accurately measured by comparative weighing of specimens in air and in heptane.

The densities of pure polycarbonate and pure copolyester film are shown in *Figure 27* as a function of draw ratio. Similar trends have been noted by others[29,30]. Apparently, the increase in density is the result of better packing of the chains as they become more aligned. *Figure 28* shows the density for blends at a fixed draw ratio, and there is a slight volume contraction on mixing since the data lie above the tie line. Note that owing to the similarity of densities for the two pure components, volume additivity is adequately represented by a linear tie line even though density and not specific volume is plotted.

The solid points in *Figure 29* give the density of injection moulded bars directly after fabrication. The trend is similar to that in *Figure 28* in that there is a slight trend toward volume contraction on mixing; however, the moulded bars are significantly more dense than the film owing to either more orientation or the pressure involved in moulding, or both. These plots of density look quite similar to the corresponding plots of modulus (*Figures 6* and *9*). *Figure 29* also shows the effect on density of sub-T_g annealing the as moulded bars. The blends become more dense while the pure components become less dense to produce a distinct density maximum. This is analogous to the changes in modulus seen in *Figures 15* and *17*.

The open circles in *Figure 30* represent densities of

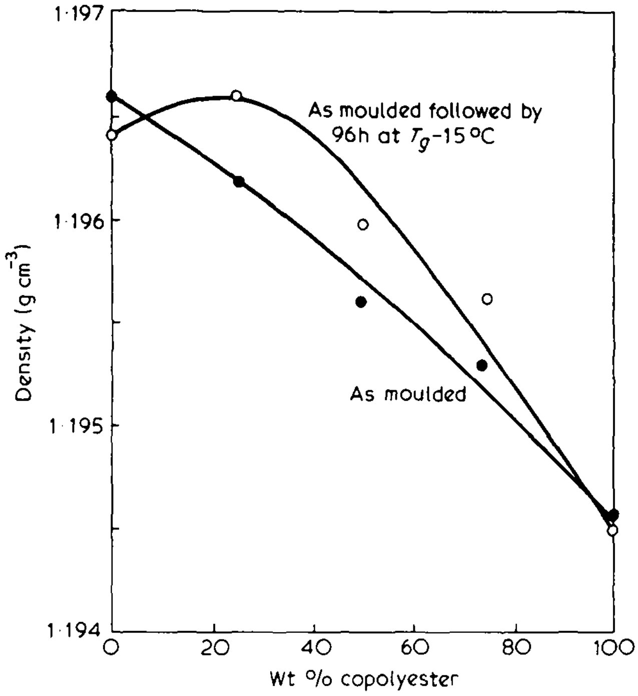

Figure 29 Density of injection moulded samples prior to and after sub-T_g annealing in a closed mould

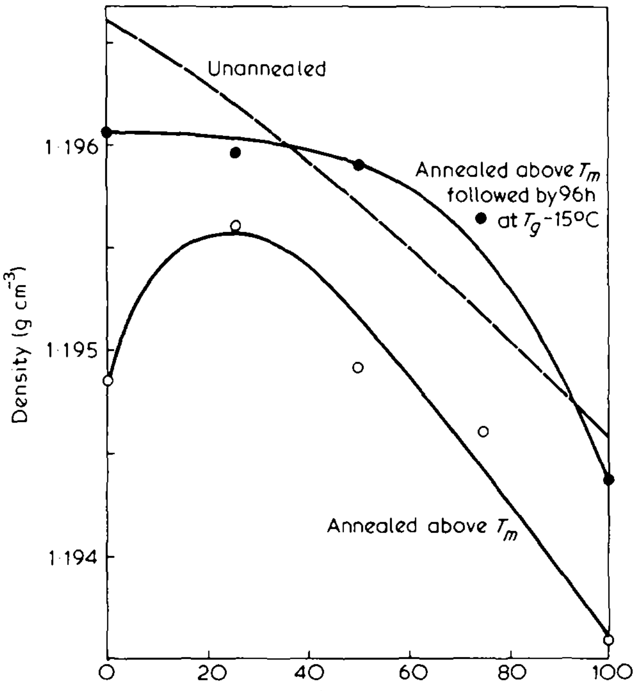

Figure 30 Effect of annealing above T_m and subsequent sub-T_g annealing on density

specimens which were annealed above T_m as described earlier. For every composition, the density decreases from that seen for the as moulded materials owing to relief of molecular orientation or of the packing caused by the moulding pressure. The resulting plot reveals a pronounced density maximum located at approximately 75% polycarbonate. The densities in this plot correspond to an isotropic state free of stress but not to equilibrium since the specimens are below T_g; however, each composition was cooled at the same rapid rate. Thus, one might be safe in saying this response is largely a result of the thermodynamic contraction in volume expected for a miscible blend.

Subsequent sub-T_g annealing causes an increase in density for all compositions as might be expected. The pronounced maximum disappears; although, there remains a substantial departure from volume additivity. A comparison of the super-T_m, sub-T_g annealed values to the as moulded results (dashed line in *Figure 30*) returns to a qualitatively similar pattern as shown in *Figure 29*. There is a remarkable similarity between the plots of modulus and density as may be seen by comparing *Figure 30* with *Figure 24*. We find a striking correlation of excess density with excess modulus as noted earlier by Kleiner, Karasz, and MacKnight[15] for PPO–polystyrene.

From these results, it appears that the unanswered question is not why annealing treatments cause development of synergisms in density and modulus but rather why do as-processed film and moulded specimens have almost linear responses of these factors with blend composition? The latter are the result of kinetic responses to these processing operations, and the fact that nearly additive relationships develop may be simply fortuitous.

CONCLUSION

Miscible blends of polycarbonate with a copolyester, based on 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids, were fabricated by continuous extrusion and injection moulding processes. Each technique resulted in homogeneous blends which were completely amorphous even though the copolyester is capable of crystallizing when sufficient time between T_m and T_g is allowed. The mechanical properties of these blends were extensively examined. All mechanical properties were found to lie near the simple additive values computed from the pure component properties when the blend samples were tested directly after processing. Stress related properties such as strength and modulus tended to fall slightly above the additive value, whereas, strain related properties such as elongation at break and notched Izod impact strength tended to fall slightly below the additive value.

Sub-T_g annealing of these materials increased the yield strength and severely reduced their toughness as expected. However, the modulus for injection moulded specimens was found to develop a maximum value at about 75% polycarbonate following this type of annealing. In the mid-composition range, annealing caused a slight increase in modulus but the pure components experienced a decrease contrary to simple expectations for densification by such a thermal history. This response was shown to be the result of simultaneous relaxation of volume and molecular orientation. These processes were decoupled by first relaxing out the frozen-in molecular orientation and pressure effects generated during moulding by annealing the specimens above the glass transition temperature (also above T_m to avoid crystallization) followed by rapid quenching to the glassy state. After this treatment, plots of density and modulus *versus* composition exhibited maxima. Subsequent sub-T_g annealing produced property changes expected from simple densification. The net effect of these two annealing treatments was a property relationship similar to that obtained by directly annealing the injection moulded materials below their T_g.

Some major conclusions are as follows:

(1) This work adds to a growing body of knowledge that shows miscible blend systems to exhibit nearly additive, and in some instances synergistic, mechanical property relationships to blend composition. The behaviour of miscible blends contrasts favourably with that for immiscible blend systems which often display minima in strength and ductility properties *versus* composition[31]. As a result, miscible blends offer an attractive approach for developing tailored polymer properties without the need for additional additives or chemistry. The present blend system is comprised of extremely tough components, and the property combinations that result may be quite useful for certain applications.

(2) The property relationships in the present systems are extremely dependent on the method of fabrication and previous history owing to the fact that they are glasses which do not achieve an equilibrium state. Similar behaviour is to be expected for other miscible blends below their glass transition temperatures. Additional factors such as the crystallization of one or both components may similarly complicate blend property relationships.

(3) Thermodynamic arguments suggest that the exothermic interactions generally responsible for miscibility in polymer blends should lead to a volume contraction on mixing. Simple notions of free volume further suggest that this effect ought to be manifested in certain physical properties. The results generated here confirm that such an effect does exist but demonstrate that it may not always be realized for systems not in equilibrium. For example, in the present system, injection moulded blends failed to develop significant departures from volume additivity for reasons not fully understood; however, the expected volume contraction for mixtures did develop after various annealing procedures and this was reflected in at least one property, the modulus.

(4) Kleiner, Karasz, and MacKnight[15] have proposed a model for miscible blends which quantitatively relates deviations from additivity of the elastic modulus to similar deviations from additivity of molecular packing or density. The present results are in excellent qualitative agreement with their model as seen by the striking similarity between our plots of modulus and density *versus* composition for a variety of process and thermal histories. However, *Figure 31* summarized from these data shows that excess modulus is not uniquely a function of excess density.

(5) It seems physically reasonable to attribute the trend for modulus and strength of miscible blends to lie *above* the additive tie line to a loss in free volume on mixing. Likewise, the noted tendancy for elongation at break and Izod impact strength, which are sensitive to irreversible deformation processes, to fall below the tie line may be interpreted to occur for the same reasons. It will be

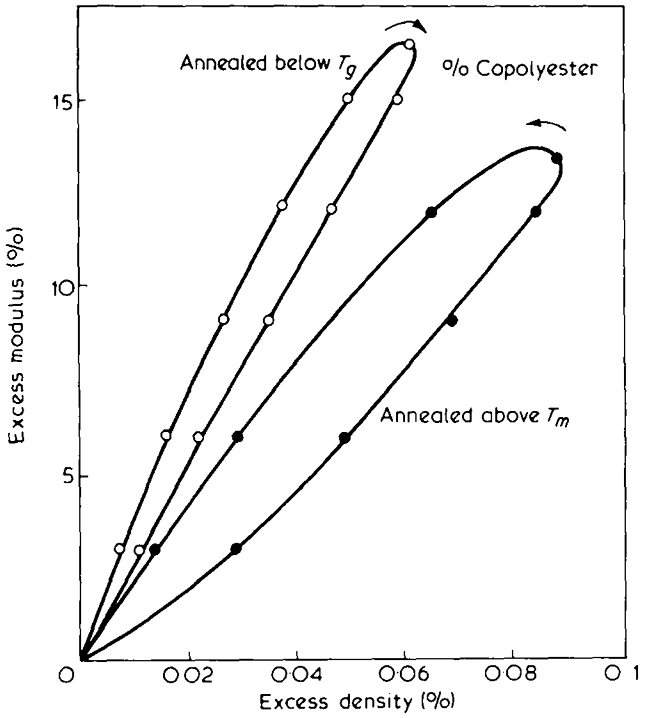

Figure 31 Correlation of excess modulus with excess density for blends with thermal histories shown

interesting to see these proposed free volume effects tested more thoroughly using more fundamental experiments such as creep, stress relaxation, or the kinetics of physical ageing[26].

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