Glassy polymer solutions: some morphology—property relationships

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The *in-situ* crystallization of low molecular weight crystalline organic compounds in general purpose and high impact polystyrene has been studied. Three modes of crystallization, namely needle-like, dendritic and tiny crystalline particles have been observed in these systems. Phase diagrams of tetrachloroxylene and tetrachlorobenzene with high impact polystyrene have been constructed. The effects of the crystalline additive, its concentration and morphology on some mechanical properties have been analysed. A significant difference between general purpose and high impact polystyrene was observed regarding their mechanical behaviour in the presence of the crystalline additives. Exudation and crystallization of the crystalline additives on the surface are also discussed. It is shown that these phenomena can be enhanced by annealing and stress crazing.

INTRODUCTION

Glassy polymer solutions consisting of an amorphous polymer as a solvent and a crystalline low molecular weight organic compound as a solute have been studied by several authors[1–5]. Such crystalline additives (CA) may play an important role in bestowing specific properties upon polymeric materials. The CA might, under certain conditions or with time, precipitate out as a separate phase distributed in the polymeric matrix or exude to the surface. At elevated processing temperatures true solutions were formed[4]. Upon quenching of these solutions, the following solid systems can be formed: transparent solid solution, transparent supersaturated solid solution, and opaque supersaturated solid solution containing discrete CA particles.

Other workers[1,2] have studied similar systems of amorphous polymer matrices and *in-situ* crystallized additives, shedding some light on the growth of the crystallites and their morphology, proving that their shape depends on the crystallization conditions. A somewhat different system is the one utilizing crystallizable polymers as the matrix phase[6,7,8]. A eutectic solidification was recognized in these systems due to the simultaneous crystallization of the CA and of the macromolecules.

The *in-situ* crystallization of the CA provides a method of producing polymer composites with fine and uniform dispersion of additives. Furthermore, forcing oriented precipitation of the CA might form unique anisotropic materials[1,5].

In this work, general purpose clear polystyrene (GPPS) and high impact polystyrene (HIPS) were chosen as matrices and 2,4,5,6-tetrachloroxylene (TCX) and 1,2,4,5-tetrachlorobenzene (TCB) as crystalline additives.

The objectives of the present work are the construction of phase diagrams and morphological investigation of these systems, and the correlation of tensile properties of these systems with their morphology.

EXPERIMENTAL

Polystyrene or high impact polystyrene (general purpose Galirene HP-55 and Galirene HT-88-5, respectively, both made by the Israel Petrochemical Enterprises Ltd) were mixed with various amounts of TCX or TCB (EGA – Chemie KG, West Germany). The melting points of these crystalline materials are 220° and 141°C, respectively, and their melting is accompanied by some sublimation. The mixtures were prepared in a Brabender Plasticorder (Model PL 3S) at 160°C. The additives were mixed slowly into the molten polymer and stirred for 10 minutes. Under these conditions TCX and TCB are soluble in the polymers at the proportions used. The TCB mixtures contained not more than 40 phr of TCB, and the TCX mixtures 30 phr. These ratios were found to be the limits above which a homogeneous solution of the polymer and crystalline additives could not be achieved under the working conditions. Precautions were taken to prevent any of the added CA form subliming during mixing. The concentrations of the mixtures are therefore considered to be the initial ones. Thin films (0.1 mm thick) and sheets (1.2 mm thick) were prepared by compression moulding at 160°C and subsequently slow-cooled to room temperature.

The thermo–morphological behaviour of the crystalline additives in the thin films was observed by heating and cooling samples in a hot-stage microfurnace (Mettler FP 52) installed in an optical polarizing microscope (Wild M21).

Softening points were measured on the thick samples using a Vicat softening point (VSP) instrument (Zwick Model 4204).

Tensile properties were measured on the thick samples with an Instron testing machine at a crosshead speed of 0.05 cm/min. All strains were monitored with a strain gauge extensometer.

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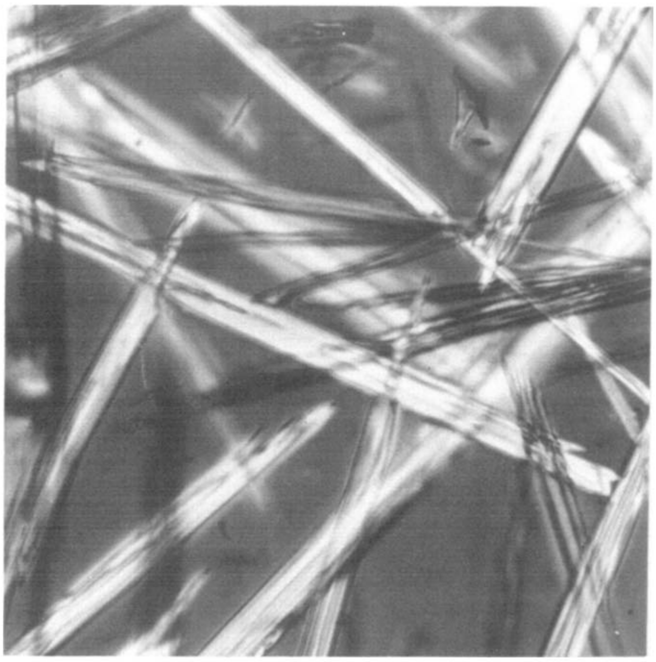

Figure 1 Needle-shape TCX crystallites precipitated out of a 20 phr GPPS/TCX system. Cooling rate, 3° C/min (Mag. 250X)

RESULTS AND DISCUSSION

Crystalline morphology

Previous work[3–5] has shown that at elevated temperatures a true solution of polymer and CA is formed, which upon fast cooling becomes either a glassy solution or a supersaturated glassy solution. At certain conditions (high CA concentrations, slow cooling, annealing, etc) the solute precipitates out, forming a separate phase distributed in the polymer matrix.

The morphology of the precipitated crystalline additives is of major importance to the understanding of the phenomenon of *in-situ* crystallization of a low molecular weight material in a highly viscous matrix. Commercial TCX and TCB crystals are needle-like in shape, however, when they crystallize out of a viscous matrix their shape may be different, depending on rate of cooling and temperature, i.e. on the viscosity of the medium at the crystallization temperature. The crystallization of TCX and TCB is diffusion controlled, depending on the viscosity of the medium. At higher cooling rates and lower temperatures the crystallization is thus hindered.

Figure 1 shows TCX crystallites which have precipitated out of a 20 phr mixture at a slow cooling rate of 3°C/min. At such low cooling rates the crystallization takes place at a relatively high temperature (150°C), at which the medium viscosity is rather low and the diffusing molecules are able to form well-shaped crystals. These needle shape crystallites resemble the regular TCX crystallites, although they are much smaller. When the cooling rate is faster (approximately 10°C/min) dendritic-shaped crystals are formed throughout the whole sample (*Figure 2*). Scanning electron micrographs of fracture surfaces show that feather-shape crystals grow throughout the sample in all directions.

TCB crystals precipitated out of a 30 phr system at the lower cooling rate of 3°C/min are already dendritic (dendritic–spherulitic). These crystals begin to form at 95°C, a temperature at which the system is already quite viscous and dendritic growth is thus enhanced. When the cooling rate is higher (10°C/min) not even dendrites are formed; rather, a large number of tiny crystallites appear. Electron micrographs of this sytem show a porous structure formed after the tiny TCB crystallites have sublimed during the *SEM* preparatory process (see *Figure 3*). Similar results were reported by other workers[8] dealing with the eutectic system pentaerythrityl tetrabromide – isotactic polypropylene. A similar mottled crystallization occurs in a quenched GPPS–TCX system. The quenching prevents formation of needle-like and dendritic crystals seen in *Figures 1* and *2*, which are formed at a higher crystallization temperature.

In summary, three modes of crystallization, namely needle-like, dendritic and tiny crystalline particles have been observed in PS–TCX and PS–TCB systems depending on cooling rate. As the cooling rate increases, or crystallization temperature decreases, the morphology of the crystals changes from needle-like through dendritic to tiny particles.

Figure 2 Dendritic-shape TCX crystallites precipitated out of a 30 phr GPPS/TCX system. Cooling rate, 10° C/min (Mag. 150X)

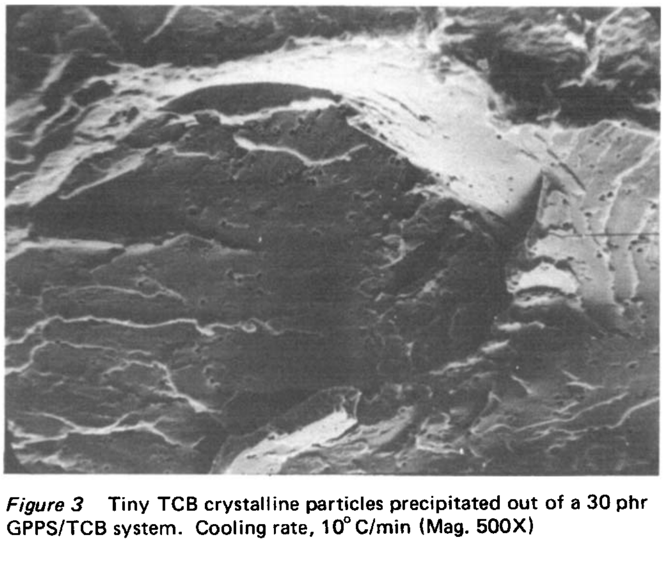

Figure 3 Tiny TCB crystalline particles precipitated out of a 30 phr GPPS/TCB system. Cooling rate, 10° C/min (Mag. 500X)

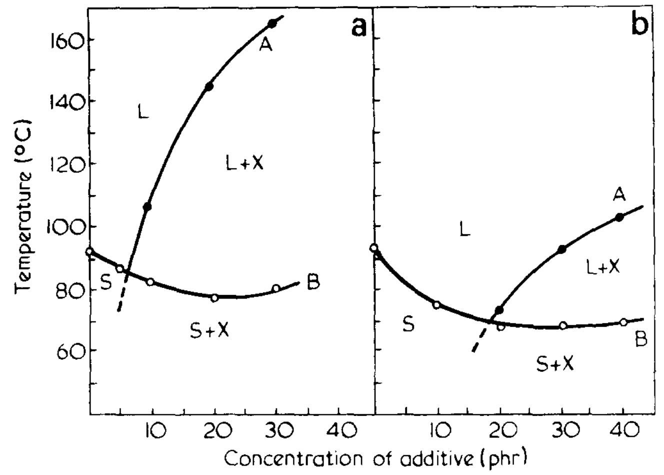

Figure 4 Phase diagrams of (a) HIPS/TCX and (b) HIPS/TCB showing: A, precipitation and B, softening curves

At the higher temperature the required conditions exist for the CA to crystallize regularly, whereas at lower temperatures the tendency towards dendritic growth increases as the crystallization becomes predominantly diffusion controlled. At even lower temperatures, the viscosity of the medium is so high that only tiny crystalline particles can develop. With the aid of phase diagrams, discussed below, we can design and control specific structures of such systems.

Phase diagrams

Phase diagrams were constructed with the aid of optical observations of the CA state, and thermal transition measurements (VSP) of the matrix. *Figure 4* shows the phase diagrams of HIPS–TCX and HIPS–TCB systems. Precipitation curves for the CA as well as softening curves for the whole system are used to construct the phase diagrams. The precipitation curve describes the temperature at which, upon cooling, precipitation of CA starts, as observed by optical microscopy, at various CA concentrations. The softening curve is a plot of the Vicat softening temperature as a function of CA concentration.

The softening points of both systems decrease at low CA concentrations as the concentration of CA is increased to 15–20 phr, above which the VSP increases. The softening of the system is strongly dependent on the solubility and the precipitation of CA from the matrix. The solubilized CA acts as a plasticizer causing lowering of the system softening temperature. When precipitation and crystallization occur, the precipitated material has a reinforcing and hardening effect on the system over its softening range, resulting in higher VSP values.

The precipitation curves in the phase diagrams shown in *Figure 4* represent temperatures at which, upon cooling, crystallization starts. Above these curves there exists only one phase – viscous liquid solution (designated L). A two phase system exists between the precipitation and softening curves (designated $L + X$). One phase is the pure crystalline additive and the other is viscous solution of some of the CA in the polymeric matrix. The precipitation and softening curves intersect at a point indicating the concentration below which the CA does not precipitate out and two phases are not formed. Below this concentration (~6 phr in the HIPS/TCX system and ~18 phr in the HIPS/TCB system) the liquid phase solidifies forming a single phase glassy solid solution (designated S). At higher CA concentrations, below the softening curve, a two phase system exists composed of a glassy matrix which might contain some dissolved CA and a second crystalline phase (designated $S + X$).

Tensile properties

Tensile properties including elongation at break, tensile strength and modulus as a function of CA concentration in GPPS and HIPS are shown in *Figures 5–7*. The elongation at break decreases linearly with CA concentration in the

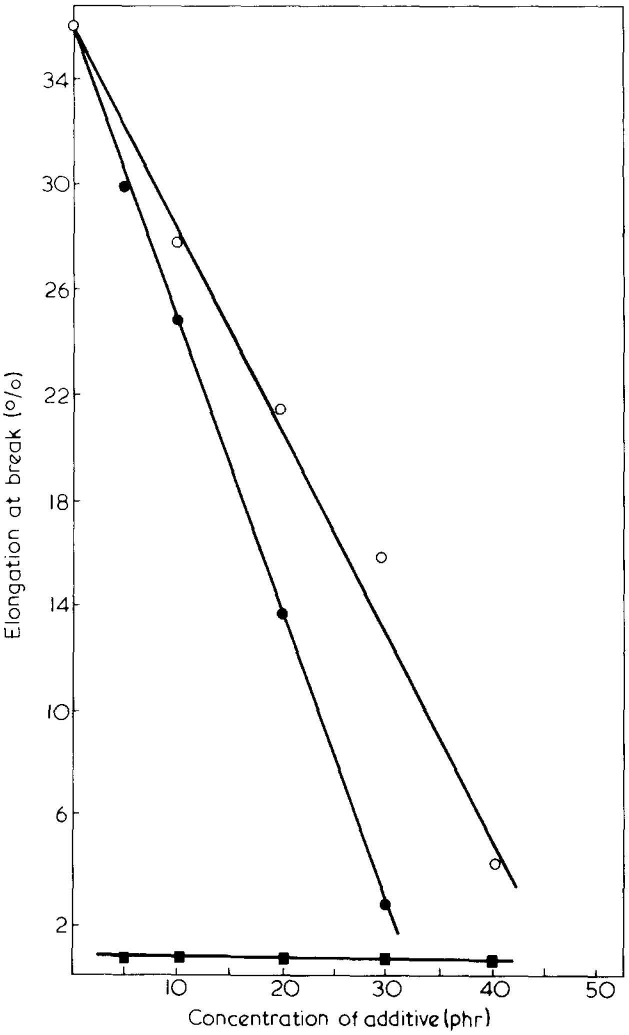

Figure 5 Dependence of elongation at break on concentration of HIPS/TCB (○), HIPS/TCX (●), GPPS/TCX and GPPS/TCB (■)

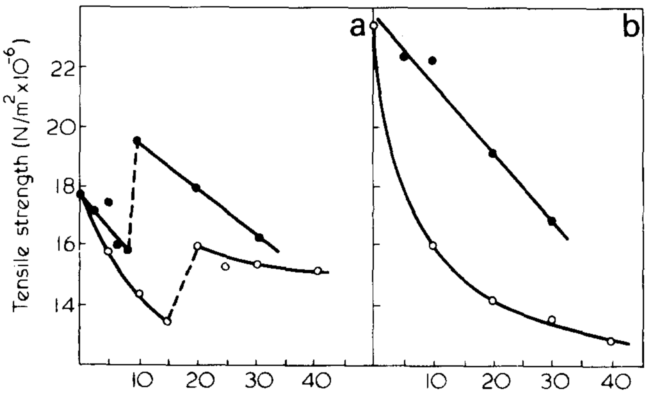

Figure 6 Dependence of tensile strength on concentration: A, ○, HIPS/TCB; ●, HIPS/TCX; B, ○, GPPS/TCB and ●, GPPS/TCX

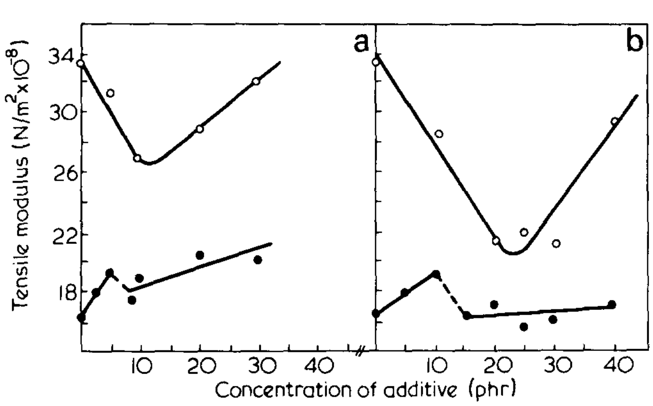

Figure 7 Dependence of tensile modulus on concentration: A, ○ GPPS/TCX; ●, HIPS/TCX; B, ○, GPPS/TCB and ●, HIPS/TCB

range studied for HIPS and GPPS. The dramatic reduction seen for HIPS is noteworthy. The tensile strength of GPPS decreases gradually with CA concentration showing a more pronounced reduction by TCB as compared to TCX. A more complex behaviour is exhibited by the HIPS/CA systems regarding the effect of CA on the tensile strength. This behaviour, shown in *Figure 6a,* where a discontinuity is present between two ranges in both of which the tensile strength decreases with CA concentration. Similarly, discontinuity indications can be seen in the tensile modulus curves of HIPS shown in *Figure 7.* A different behaviour is exhibited by the GPPS/CA systems, namely the modulus decreases in the lower concentration range, goes through a minimum and then increases. It should be emphasized here that the properties depend on the cooling rate during sample preparation, which affects CA concentration in solution, mode of dispersion, morphology, etc.

In the case of general purpose polystyrene one has to consider a system consisting of a glassy matrix in which some of the added CA is dissolved and some dispersed in a variety of crystalline shapes. The physical properties of such systems depend on numerous parameters including relative concentrations of the components in their various states and forms and their properties. As long as the additive is dissolved, it acts as a plasticizer whereas if dispersed it may function as a reinforcing material. This behaviour is exhibited by the tensile modulus *versus* CA concentration curves as shown in *Figure 7.* The CA concentrations at the curve minima (~12 and 23 phr for TCX and TCB respectively) correspond to concentrations at which the system turns from transparent to opaque due to massive precipitation. It is important to emphasize that at these very same concentrations the softening curves in the phase diagrams[5] also go through a minimum. Apart from the modulus which is a low strain property, the elongation at break (*Figure 5*) of CA/GPPS systems and their tensile strength (*Figure 6*) show continuous decreases in the whole range of CA concentration studied. Here, the dissolved as well as the dispersed CA affect the above mentioned properties in the same direction.

High impact polystyrene is a two phase material that consists of a rigid matrix of styrene homopolymer in which soft rubber particles are imbedded. These rubber particles present a site for craze initiation, a route for craze propagation and also assist in craze termination. Both phases, the glassy and the rubbery, could be affected by the addition of organic compounds. The effect of CA on glassy matrices has already been discussed. In the case of elastomers, reinforcement by crystalline organic fillers has been reported. For example, Stiehler *et al.*[9] report pronounced stiffening of rubber by adding small amounts of crystalline phenyl-β-naphthylamine (PBNA). The effectiveness of such a filler is determined mainly by its crystalline morphology. Microscope studies[9] reveal that as long as the PBNA is in the form of dendrites or clusters of needles it acts as an effective stiffener for the elastomer whereas granular crystals do not.

The differences between GPPS and HIPS as affected by CA are clearly shown in *Figures 5–7.* It is suggested that these differences may result from changes imparted by the CA to the rubber particles and their interfaces. Direct evidence for the effect of CA on the rubber particles imbedded in HIPS is not yet available. However, it is assumed that Stiehler's results for PBNA/elastomer systems could be implied to the CA/rubber particles in the present systems. Hence, at elevated temperatures some of the added CA is absorbed in the rubber particles and completely precipitated as crystals upon cooling. The CA crystallization in the rubbery phase results from the poor affinity between the two materials contrary to the higher chemical affinity between CA and polystyrene matrix. Since precipitation of CA in the rubber particles takes place already at high temperatures the CA morphology is expected to be needle-shape or dendritic, as described previously. Such a structure should stiffen the dispersed elastomeric phase which is indeed observed in the tensile modulus behaviour of HIPS (see *Figure 7*) in the lower CA concentration range. The observed stiffening is slight due to the low concentration of the rubbery phase in HIPS and limited to the low CA concentration range because of its poor solubility in the rubber. The behaviour of the glassy matrix regarding its modulus is essentially similar to that exhibited by GPPS (see *Figure 7*), i.e. softening followed by stiffening. It is suggested therefore that curves of tensile modulus of HIPS are the result of superposition of separate modulus curves of CA/glassy polystyrene and CA/rubber.

In the strength analysis of polymers we consider a fracture mechanism. In this respect GPPS is well known to behave as a brittle material whereas HIPS behaves in a ductile manner. GPPS may craze in some locations, while HIPS, as a two phase system, undergoes inhomogeneous deformation throughout the whole volume. The mechanism of the inhomogeneous deformation stems from localized stress concentrations, imparted by the rubber particles, leading to crazing and delayed cracking. It is necessary therefore to consider the various effects of CA on strength properties in view of the pronounced difference between fracture mechanisms prevailing in brittle GPPS and ductile HIPS. In the case of GPPS the CA causes plastification and introduces imperfections both acting to reduce the tensile strength. The presence of CA in HIPS results in a much more complex system. In addition to plastification and introduction of imperfections, changes in properties of the rubber particles and fracture mechanism in the continuous glassy matrix are possible. Some reinforcement of the rubber particles and plastification of the matrix may take place, reducing the moduli ratio of the two, thus decreasing stress concentrations. It is therefore necessary to consider at least three effects of CA on crazing, namely, changes in stress field, level of yield strength and interfacial characteristics. The pressure of CA crystals, precipitated massively in the glassy matrix, at various concentrations, size and shape should not be underestimated. These rigid crystals participate in load carrying; however, at a certain strain they might fail due to their brittle nature. Prior to failure they resemble short fibre reinforcement whereas upon failure they introduce new imperfections into the system. It should be noticed that the discontinuities in tensile

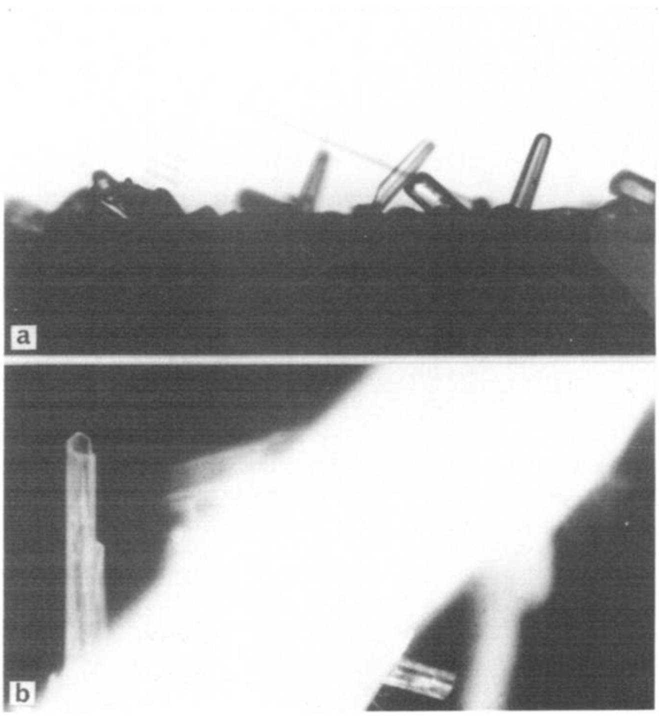

Figure 8 TCX crystallites protruding out of (a) a fracture surface (Mag. 20) (b) a stretched sample surface (Mag. 40X). Photographs taken several days after fracturing and stretching, respectively (30 phr HIPS/TCX system)

strength curves (see *Figure 6a*) occur at CA concentration ranges corresponding to concentrations at which massive precipitation takes place (intersection of precipitation and softening curves, in *Figures 4a* and *4b*). In summary, addition of crystalline additives into glassy and toughened plastics affects the systems' behaviour differently although concentration of the elastomeric dispersed phase is rather low.

Exudation and surface crystallization

Crystallization of CA on the polymer surface has been observed to be induced either mechanically or thermally. Surface crystallization has been observed under an optical microscope (see *Figure 8*) in samples of CA containing HIPS, some time after these samples were extended to break and stored at room temperature. It should be noted that when the surface is carefully observed, it is revealed that the protruding crystallites grow out from the interior of the sample and that many of them have a hollow profile. Crystallization has been observed to occur throughout the surface of the crazed sample. It is well known that crazing phenomena are accompanied by the formation of porous material in the crazes, and thus surface area increases. In the present system this structural change probably enhanced the exudation process by increasing the diffusion rate. It is important to point out that in those regions which did not undergo crazing (the wide part of the dog-bone sample) enhanced exudation could not be observed, thus crazing is an accelerating effect for exudation.

A similar phenomenon of exudation and on-surface crystallization has been observed upon annealing of samples above their glass transition temperature in a sealed container (sealing prevents sublimation of CA). No precipitation of crystallites on the container walls has been observed, rather the sample surfaces were densely covered with crystallites. The on-surface crystallization, upon heating, occurs in both HIPS and GPPS, whereas upon deformation it occurs only in HIPS, which undergoes enhanced crazing. In some well-wrapped samples slight crystallization on the surface could be observed even after storing at room temperature for long periods of time.

In summary, exudation is a diffusion controlled process, thus any effect enhancing diffusion such as surface area, temperature, etc, will help to accelerate exudation in polymeric systems containing crystalline additives.

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