

Precipitation from Glassy Polymer Solutions

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Synopsis

Solid solutions of general-purpose polystyrene containing crystalline tetrabromoxylene, tetrachloroxylene, or tetrachlorobenzene were prepared. The effects of the low molecular weight crystalline additive concentration and the thermal history on the thermal properties of the system have been studied. The system solubility, rejection of solute, etc., were characterized by such techniques as rheology, thermal analysis (DSC), and Vicat softening point.

INTRODUCTION

Literature reports strongly indicate that systems consisting of several phases which are formed by precipitation from a solid solution have important technological potential and are of scientific and engineering interest.^{1,2}

A polymer solid solution consists of a polymer as a solvent and a high molecular weight thermoplastic polymer or a crystalline low molecular weight organic compound as a solute. At elevated processing temperatures, a true solution is formed which upon fast cooling becomes either a solid solution or a supersaturated solid solution. At certain conditions, the solute precipitates out, forming a separate phase distributed in the polymer matrix. A necessary condition for precipitation is that the system in question becomes thermodynamically unstable and tends to decompose into other phases of different compositions. The precipitation process should depend strongly on such factors as degree of supersaturation, coherence between precipitate and matrix, solution thermal and mechanical history, and aging conditions. Such factors will affect the structure, shape, and orientation of the precipitate and thus the system physical properties. For example, a higher temperature solution should result in a more homogeneous system; the quenching program of solution should affect the structure of the supersaturated solid solution and the internal stresses frozen in. The aging program of the solid should control precipitation rate and fineness of dispersion.

Recently, the *in situ* crystallization of low molecular weight organic compounds from amorphous polymers was evaluated as a method for fabrication of composite materials³ or fire retardant materials.⁴ Joseph et al.³ have studied the effect of the dissolved material and its concentration on the polymer glass transition,

using this property to determine phase diagrams and crystallization kinetics. Siegmann et al.⁴ have studied such systems by the Vicat softening point technique and have observed dependence of mechanical properties on the system composition and its thermal history. The initial composition of the solid solution and the annealing temperature were found^{5,6} also to affect the morphology and *in situ* crystallization kinetics of a crystalline polymer precipitated from an amorphous polymer. It is well known that the mechanical response of nitrocellulose–camphor systems depends on the dispersion mode of the camphor in the polymer.⁷ Nitrocellulose–camphor complex is formed up to the saturation concentration, and all excess camphor is unbound. Crystalline solid plasticizers, also reported in the literature,⁸ tend to crystallize when used in high enough proportions to exude from the plastic matrix. The influence of the presence of thermoplastic materials on physical properties and performance of thermosetting polyester moldings has been studied.^{9,10} It was observed that the degree of shrinkage of the molded material depends on the properties of the thermoplastic phase which precipitates from the polymer solution upon cooling.

The objective of the present research is the investigation of basic processes and phenomena involved in precipitation of low molecular weight organic compounds from glassy polymer solid solutions. Polystyrene was chosen as the glassy polymer, and the crystalline additives (CA) were tetrabromoxylene (TBX), tetrachloroxylene (TCX), and tetrachlorobenzene (TCB); these three additives are chemically similar. In such systems, the solubility is rather high at elevated temperatures (processing conditions) and limited at room temperature, which enables the studying of the precipitation phenomena from supersaturated solutions.

EXPERIMENTAL

Polystyrene pellets (general-purpose Hostyrene A1301 Hoechst) were mixed with various amounts of TBX (Bromine Compounds, Ltd., Israel), TCX, or TCB (EGA-Chemie KG, West Germany). The melting points of these crystalline additives (CA) are 250°, 220°, and 150°C for TBX, TCX, and TCB, respectively. The mixtures were prepared in a Sigma blade kneader (Werner and Pfliederer, Germany) at 220°C. The CA were added into the molten polymer and mixed for 10 min. After cooling to room temperature, the solid mixtures were granulated (Dreher granulator, Germany). ASTM specimens for testing of mechanical and physical properties were injection molded with an Esgo laboratory-scale injection molding machine at 220°C (mold at room temperature). Some samples were annealed slightly above the T_g of the polymer in an air oven.

Vicat softening point (VSP) was measured by using the Zwick Model 4204 tester. Melt viscosity at a constant shear stress, $\tau = 7 \times 10^4$ dynes/cm², was measured with a melt flow indexer (Tinius Olsen Thermosyne). Differential scanning calorimetry (DSC) thermograms were obtained with the du Pont 990 thermal analyzer (running conditions will be specified).

RESULTS AND DISCUSSION

The Vicat softening point (VSP) is a useful property for quantifying the effects of a solid additive in thermoplastic systems. If the additive dissolves in the

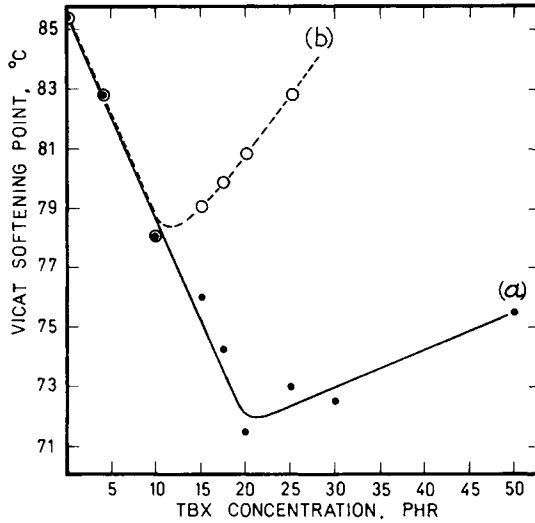


Fig. 1. Vicat softening point of GPPS containing various amounts of TBX before (●) and after (○) annealing.

thermoplastic, forming a solid solution, the VSP decreases; while if the additive disperses as a second phase, the VSP increases. It is important to note that at the VSP the polymer undergoes an enhanced softening (which is closely related to the glassy-rubbery transition), while the dispersed solid additive retains its

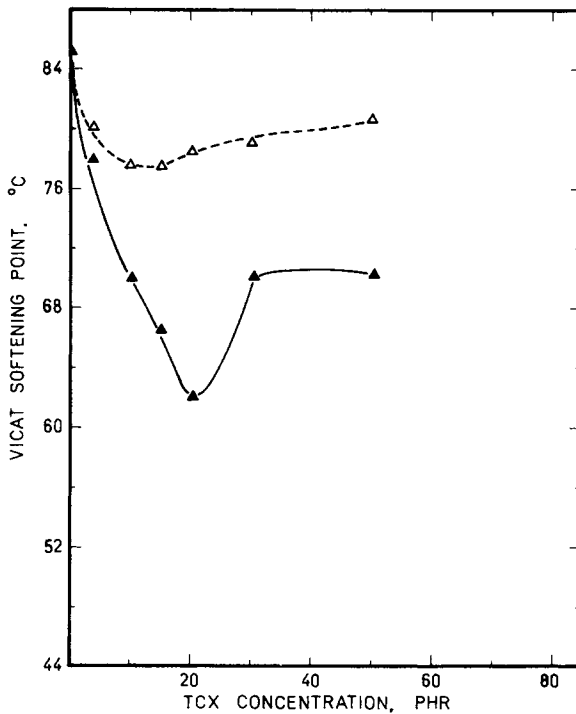


Fig. 2. Vicat softening point of GPPS containing various amounts of TCX before (▲) and after (△) annealing.

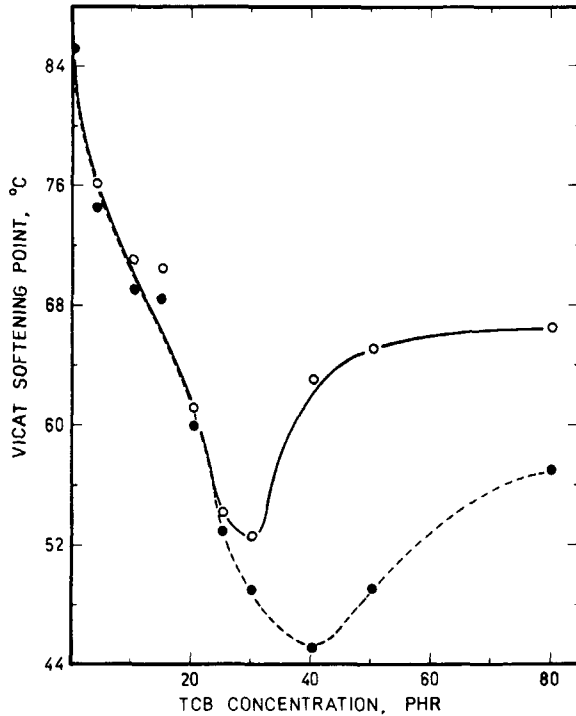


Fig. 3. Vicat softening point of GPPS containing various amounts of TCB before (●) and after (○) annealing.

rigidity. During the routine VSP test, the material is heated from the glassy state. In the glassy state there is no change in the state of dispersion of the composite system. Above the VSP, enhanced mobility of polymer chains and the reduction of the system viscosity enable physical changes to occur. Rejection or solvation of the additive will take place depending on the system composition and preparation conditions. The occurrence of such processes can be visually demonstrated since supersaturated transparent films at room temperature will turn opaque above the VSP if solute rejection occurs, while opaque films will turn transparent upon heating if solvation occurs.

The effect of TBX on VSP of general-purpose PS is shown in Figure 1.⁴ The softening temperature decreases with TBX content, attains a minimum at about 20 phr (parts per hundred), and then increases gradually. All samples prepared for the VSP test by injection molding were visually transparent up to a content of 17.5 phr TBX, while samples containing 20 phr and above were opaque. Upon annealing of PS-TBX samples below their T_g , no changes in VSP were found. However, upon annealing at 100°C (i.e., above T_g), samples containing more than 10 phr TBX became opaque and their softening temperature increased as shown in Figure 1. The VSP of polystyrene containing TCX and TCB is shown as function of their concentration in Figures 2 and 3, respectively. In the PS-TCX system, the VSP of the as-prepared samples decreases with TCX content. A minimum of 62°C (23°C below the VSP of the pure polymer) is found at TCX content of 20 phr, followed by a gradual increase. Annealing PS-TCX samples

containing more than roughly 5 phr TCX above their T_g results in significantly higher VSP values; the minimum VSP of annealed samples is about 77°C, which is only 8°C below that of the pure polymer. In the PS-TCB system, the VSP of the as-prepared samples decreases with TCB concentration down to a minimum of 45°C at 70 phr, which is 40°C below that of PS. Above a TCB content of 40 phr, there is a gradual increase of the VSP. Annealing of samples containing up to about 25 phr TCB does not affect their VSP, whereas samples containing higher TCB concentrations exhibit significantly increased VSP values. The minimum VSP obtained for annealed samples is about 53°C.

The behavior shown in Figures 1-3 suggests that at concentrations of the crystalline additive below that corresponding to the minimum VSP, the system, as prepared, is a solid solution, whereas at higher loadings it is a two-phase heterogeneous mixture. The solute decreases the VSP, whereas the presence of a dispersed, rigid phase increases the VSP. The concentration at the minimum in VSP corresponds approximately to the transition concentration from visually transparent to opaque systems. The room temperature solubilities of the crystalline additives in styrene monomer are in the following descending order: TCB > TBX > TCX (15%, 5%, and 1%, respectively). All are much lower than the solubility concentration corresponding to the minimum VSP. As was previously suggested,⁴ under the sample preparation conditions, i.e., injection molding of a hot, molten mixture into a cold mold, a solid solution or a supersaturated solid solution is formed. At the processing temperature and pressure, the crystalline additives (in the concentration range studied) are completely dissolved; and upon quenching, glassy solid solutions are obtained. The solid solutions are considered here as supersaturated for TCX, TBX, and TCB contents higher than roughly 1, 5, and 15 phr, respectively. The supersaturated solutions may approach their equilibrium composition upon thermal treatment. In our studies, samples were annealed at 100°C, i.e., above T_g , for 1 hr. As can be seen in Figures 1-3, annealing causes a shift of VSP to higher values. The shifted values reflect the amount of crystalline additive which is rejected from the solid solution, forming a second discrete crystalline phase. This process has a multiple effect on the VSP, namely, stiffening by reducing the solute concentration in solution and simultaneously adding rigid particles as a second phase. It is important to note that the solubility at the annealing temperature is considerably higher than that at room temperature.

Comparison of Figures 1-3 shows the same general behavior; however, two additional points are noteworthy: (a) By plotting the VSP versus molar concentration of the crystalline additive (mole CA per 100 g polymer) in the single-phase region, a common curve is obtained (not shown). This suggests that in a single-phase solid solution, the plasticization effect of the three chemically similar additives is practically the same on a mole per unit weight basis, hence this is a molecular effect. (b) The VSP curves of the annealed samples coincide with the nonannealed ones up to CA concentrations corresponding approximately to their solubility in the polymer. The solubilities of TCB, TBX, and TCX in the annealed polymer are about 30, 10, and 5 phr, respectively, of the same order as the room-temperature solubility in the monomer. Above these concentrations, upon annealing, a second discrete phase of CA is formed, resulting in higher VSP values, as exhibited by the upper curves. The VSP of the two-phase system should depend on the volume fraction of the dispersed CA as well as on the size,

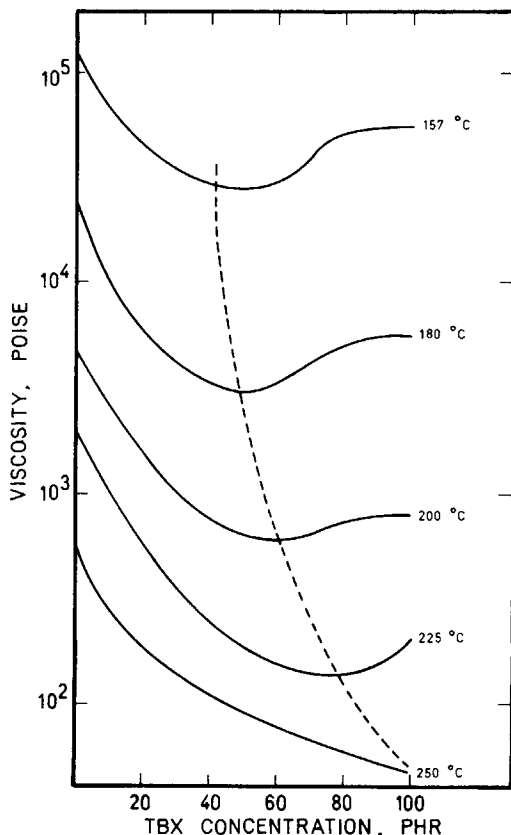


Fig. 4. Melt viscosity of GPPS containing various amounts of TBX at five temperatures (constant shear stress of 7×10^4 dynes/cm²).

shape, mode of dispersion, and rigidity-temperature relationship of the dispersed crystallites.

The crystallites found in the two-phase systems were always crystallized from solution during either the quenching process or the annealing stage and were not residuals of the original CA crystals. This has been proven by solubility determinations at elevated temperatures including the processing temperature. The solubility was indirectly estimated from melt viscosity-CA concentration curves. The principle behind the rheological study is that soluble CA reduces the melt viscosity, whereas dispersed CA crystallites increase the system viscosity. A minimum is thus expected at the saturation solubility. As can be seen, for example, in Figure 4, viscosity-TBX content curves exhibit clear minima, the values of which shift to higher concentrations as the temperature increases. In the temperature range of 157° to 250°C, the saturation solubility increased from 40 to ca. 100 phr TBX. At 220°C (sample preparation temperature), the TBX solubility is about 80 phr, whereas the maximum TBX concentration used in this work was 50 phr only. Hence, in all the experiments the starting system was a single-phase, true solution.

The changes occurring in these systems, namely, glass transition, precipitation, solvation, and melting, can be followed by using the DSC technique. Typical

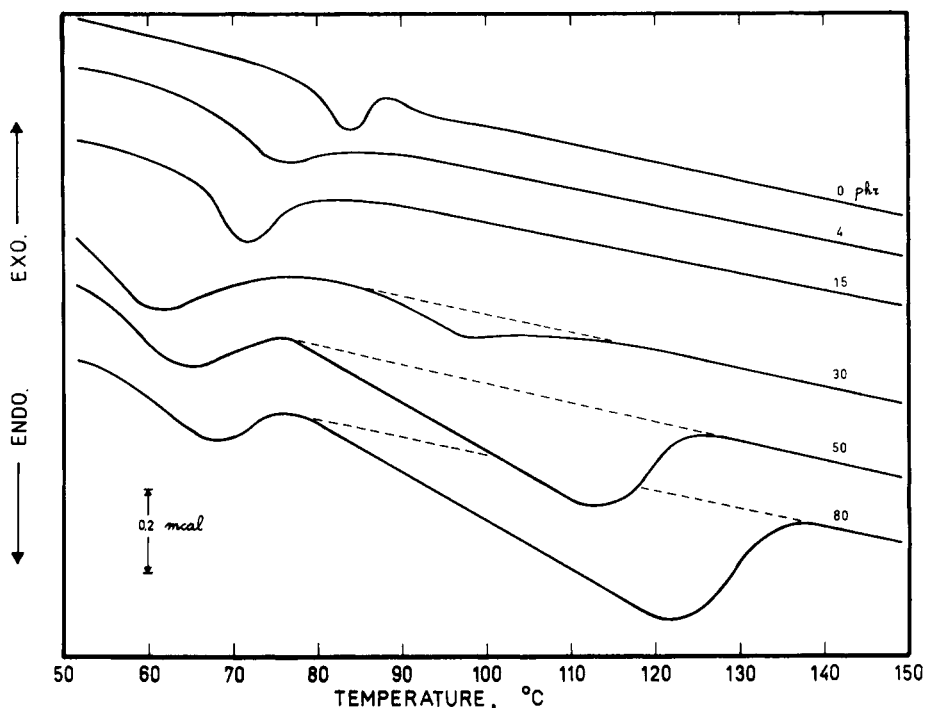


Fig. 5. DSC thermograms of GPPS containing various amounts of TCB (heating rate, $10^{\circ}\text{C}/\text{min}$).

thermograms for PS containing TCB are shown in Figure 5. The glass transition temperature, exhibited by the first peak in the thermogram, decreases with increasing TCB concentration up to 30 phr and then increases. This behavior is consistent with the VSP results of the nonannealed samples. The TCB in solution acts as a plasticizing additive, whereas in dispersion (discrete crystalline phase) it acts as a rigidizing species. TCB broadens the peak in the T_g region which is expected in multicomponent systems. At temperatures above T_g for samples containing less than 15 phr TCB (corresponding to R.T. solubility), no energetic changes occur, and therefore smooth thermograms (no peaks) are obtained. This shows that in this concentration range, the two components form single-phase systems which will not reject the solute upon heating above T_g . For higher TCB concentration, the endotherms at elevated temperatures, as shown in Figure 5, are apparently the net result of two thermodynamically opposing processes, namely, rejection and solvation of the additive. The endotherms start just above the T_g peaks at approximately 80°C . As expected, changes in the system start to take place in the vicinity of T_g where the polymer undergoes dramatic plasticization, enabling rearrangement of the CA.

As the TCB concentration (studied range 15 to 80 phr TCB) increases, the endotherm peak temperature and the peak end temperature increase from 97° to 123°C and from 110° to 137°C , respectively, which are always below 147°C , the melting point of pure TCB. Characteristic to such a system is the asymmetric shape of these endotherms, namely, a gradual decline to the peak minimum followed by a rapid incline. Such a behavior shows that the rate of the process

investigated increases with temperature resulting from both enhanced solubility and reduced polymer viscosity. Solubility-temperature data can be extracted from the thermograms; thus, at 110°, 127°, and 137°C (peak end temperature), the saturation solubilities are 30, 50, and 80 phr TCB, respectively, and the endotherms area, representing the total heat absorbed, increases with TCB concentration.

One can conclude that within the experimental range of CA concentration, true solutions are formed at elevated temperatures (rheological evidence). 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. Annealing above T_g enables the thermodynamically unstable system to approach its equilibrium state, thus changing the CA dispersion mode. The thermal and mechanical behavior of the studied systems was found to be sensitive to the CA type, concentration, and dispersion mode.

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