The Apparent Domain Structure of Polystyrene as Revealed by Liquid and Vapor Crazing*

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Several investigators[1-5] have suggested the presence of domains in high polymers. Sauer and Hsiao[6] have indicated that the crazing of polystyrene is related to a domain structure. In this paper, additional evidence is presented for the existence of domains in polystyrene and similar materials which craze.

Some writers on the subject have been quite vague as to the definition of a domain in high polymers and what constitutes a domain, or how domains can be seen or studied. As used here, a domain will not necessarily mean a definite homogenous region surrounded by other homogeneous regions with some kind of a boundary between them. Instead, domains will be related to various types of imperfections and inhomogeneities the boundaries of which may differ in their distinguishability. Thus, small domains may exist inside of larger domains, so the size and type of domains which one may observe are dependent upon the type and intensity of treatment given the polystyrene in order to make the domains visible.

Two general types of domain structure can be shown to exist in polystyrene. The first type manifests itself in the usual craze cracks which develop in a polystyrene to which a large tensile force is applied or which is subjected to certain liquid environments. The second type of domain appears as a white, roughened surface in a polystyrene treated with certain liquids.

EXPERIMENTAL RESULTS

Domains as Revealed by Craze Cracks

Polystyrene may be crazed by first being soaked in a nonsolvent, such as methanol or ethanol, and then being exposed to the liquid or vapors of a solvent or partial solvent. For instance, the cracks shown in Figure 1 were produced by soaking a compression-molded bar of polystyrene in
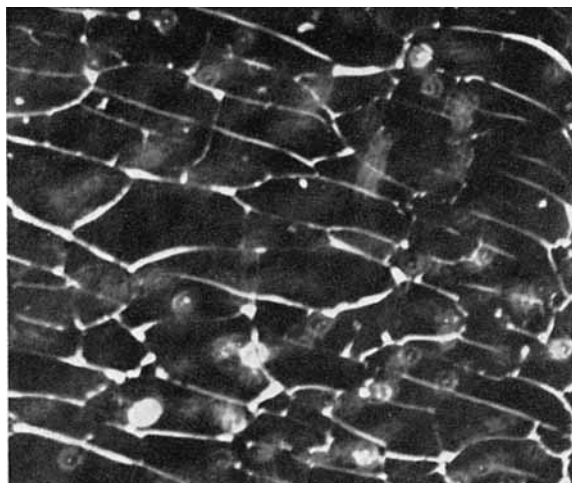
Fig. 1. Craze cracks in unoriented polystyrene produced by immersion in methanol and then hexane vapors. Magnification approximately 30×.

methanol for a day and then exposing the bar to the vapors of Skellysolve B[7] (mostly hexanes) for a few seconds. The craze cracks develop with amazing rapidity, in a manner similar to the appearance of the image during the development of a photograph. Figure 1 is typical of the results found with polystyrene when there is no orientation of the long-chain molecules. The number of the domains can be increased by increasing either the exposure to methanol or to Skellysolve vapors. Similar results are obtained if ethanol is used instead of methanol, but the soaking period required for comparable results is much longer with ethanol. Likewise, Skellysolve B (liquid or vapor) can be replaced by the vapors of such solvents as benzene, xylene, chloroform, and methyl ethyl ketone.

The ease and intensity of crazing can be increased by decreasing the molecular weight of the polystyrene or by addition of such materials as monomer. A carefully annealed bar of polystyrene has much less tendency to craze than one which has been quenched from the melt, even though no molecular orientation can be observed by bire-
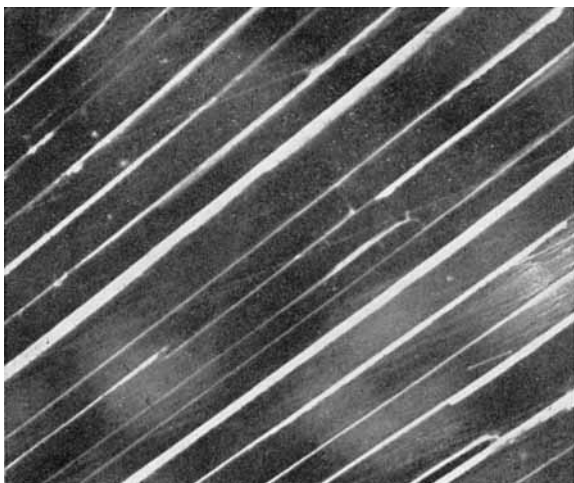
Fig. 2. Craze cracks in an injection molded polystyrene bar produced by immersion in methanol and then hexane vapors. Main cracks follow flow lines.
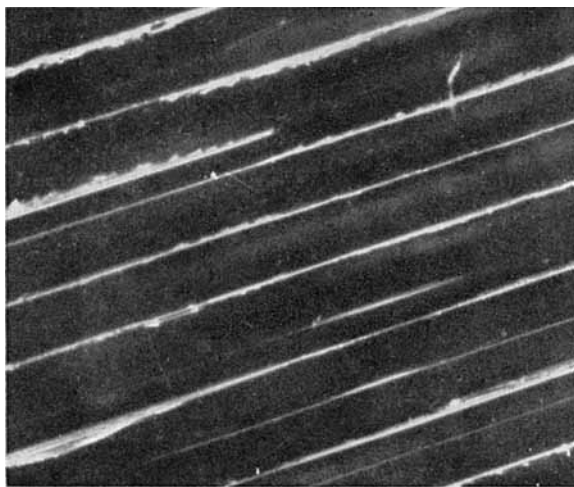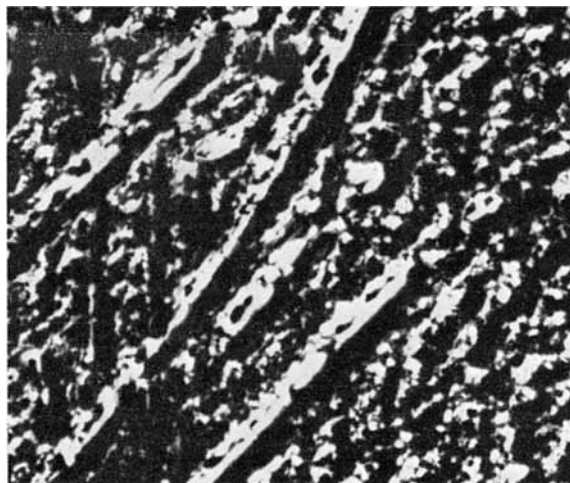

Fig. 4. The white, roughened surface-type of crazing of an injection-molded bar of polystyrene produced by a mixture of benzene and methanol. Magnification approximately 30×.

Fig. 3. Craze cracks similar to those in Fig. 2 except for shorter immersion time in methanol and hexane vapors.

fringence. These results agree with field experience on the crazing of polystyrene.

Films which have been stretched in the molten state and injection-molded bars may also be crazed by the above technique. Birefringence measurements indicate the molecules have been oriented preferentially in one direction. Figure 2 shows the craze cracks in an injection-molded bar. The cracks are parallel to the direction of orientation. Occasionally, cracks develop at right angles to the direction of orientation to give the appearance of rectangular domains. Less drastic treatment with methanol and solvent vapors gives cracks such as those shown in Figure 3. Here, the cracks parallel to the molecular orientation are visible, but the perpendicular cracks do not appear.

Domains Revealed by Solvent-Nonsolvent Mixtures

An entirely different type of domain structure may be revealed in polystyrene by giving it a one-stage treatment with certain mixtures of solvents and nonsolvents. A great many combinations may be used. Best results are obtained when enough solvent is added to a nonsolvent to swell polystyrene and to soften it. A few of the combinations tested were benzene and methanol, chloroform and methanol, benzene and heptane, and toluene and Nujol. In Figure 4 is shown the result of treating an injection-molded bar with a drop of a mixture consisting of 11 ml. benzene and 25 ml. methanol. Within a few seconds after the drop touches the polystyrene, the surface of the bar turns white and becomes rough. Craze cracks of the type shown in Figures 1–3 do not occur. The coarse cracks or cuts which do appear in general run perpendicular to the direction of overall molecular orientation.

Carefully annealed polystyrene will not show the white, roughened- surface type of domain structure; the liquid mixtures soften the polymer, but, when the liquid evaporates, the polystyrene remains smooth and transparent. Polystyrene films cast from solvents and stretched above the glass temperature to orient the molecules are not capable of producing this type of domain structure either. Polystyrene quenched from the melt, likewise, does not give a whitened surface as long as the birefringence is zero or uniform throughout a small area. The phenomenon shows up best on injection-molded objects where the surface birefringence of the material varies radically from point to point;

that is, where the surface layer is heterogeneously oriented in both intensity and direction.

DISCUSSION

Two factors important in determining the domain structure of a material are: (1) stresses, internal and external, and (2) inhomogeneities and imperfections of various kinds in the material. Internal or frozen-in stresses may result from molecular orientation or from "thermal" stresses resulting from the rapid cooling of the polymer. Inhomogeneities and imperfections in a polymer may include: (1) ends of polymer molecules, (2) monomer and other low molecular weight materials which are soluble in liquids such as methanol, (3) density fluctuations, (4) cracks and voids, (5) spacial inhomogeneities resulting from differences in molecular weight of polymer or from differences in concentration of low molecular weight materials such as monomer in different parts of the piece, and (6) heterogeneity of molecular orientation as measured by nonuniformity of birefringence from place to place.

The crack crazing of polystyrene may be understood by a simple theory, which was first proposed by Hopkins, Baker and Howard[8] to explain a somewhat different phenomenon. Because of the voids and various types of imperfections in polystyrene, gases and vapors of nonsolvents such as methanol can readily penetrate or diffuse into the polymer. The vapors will concentrate in the regions of the imperfections and will adsorb on the surfaces of cracks and voids. These adsorbed molecules will exert a two-dimensional gas pressure, such as that measured by a Langmuir trough. The two-dimensional pressure is probably equal to or greater than what would be estimated by the simplified equation of state:[9] $FA = nRT$, where F is the force exerted by a surface film compressed to an area A and composed of n moles of adsorbed molecules, T and R being the absolute temperature and the gas constant, respectively. Nonsolvent molecules, such as methanol, are not strongly adsorbed by polystyrene (n is small), so that methanol will craze polystyrene slowly, if at all. However, when polystyrene that has been soaked in methanol is exposed to the vapors of a solvent, the solvent vapor molecules are strongly adsorbed and n greatly increases. The surface film then exerts a force greater than the tensile strength of the material, so crack develops. The treatment with methanol is essential to keep the solvent molecules from dissolving in the polystyrene and softening it. Dissolved molecules do not exert a two-dimensional gas pressure, and, even if they

did, a crack would not develop in the soft rubbery material resulting from the lowering of the glass temperature by the solvent. Although we have no experimental values for the magnitude of n, it is easily shown that sufficient force might be built up in polystyrene to exceed the tensile strength. If a Langmuir surface pressure F of 25 dynes/cm. (an attainable experimental value) is assumed to be acting through a surface film of 5 A. a pressure of 7250 psi would exist on a molecular scale; this is greater than the tensile strength of normal polystyrene, even if one neglects any stress concentration factors that may exist.

It has been established that adsorbed molecules may give rise to large enough forces to expand the solid adsorbing phase. For instance, it is known that charcoal expands when it adsorbs benzene.[10] It seems probable that a similar thing occurs in the crazing of polystyrene by liquids or vapors.

On the basis of this theory, most crazing phenomena are easily understood. Quenched samples should craze more easily than annealed samples because of the greater void space and frozen-in stresses of the quenched material. Low molecular weight polystyrene crazes, more easily than higher molecular weight material because of the imperfections and void spaces created by the endgroups. Craze cracks run parallel to flow lines or the direction of molecular orientation preferentially because polystyrene has less strength perpendicular to the direction of orientation than parallel to the orientation.[11] Intensity of crazing increases with length of immersion time in methanol because of the time dependence of n; it takes time for the molecules of methanol to diffuse through the polystyrene and reach an equilibrium condition.

The white, roughened-surface-type of domain sturcture also appears to have a fairly simple explanation. The surface of injection-molded objects is generally highly oriented, but in a random manner on a microscopic scale. One small volume element of material is oriented at an angle with respect to another. When the surface is softened by a liquid, the oriented elements snap back to an unstretched state; this decreases their length, but increases their thickness. This gives rise to the roughened surface. The surface appears to be white for the same reason that powdered glass is white. The role of the nonsolvent in the liquid mixture is to harden the plastic as the solvent evaporates. If no nonsolvent were used, the solvent would give the white surface at first, then the polymer would remain soft for so long that the nonuniformities would disappear by flow and fusion of the polystyrene surface. This

was proved by treating polystyrene surfaces with a good solvent such as benzene for a fraction of a second before removing the solvent with a blast of air. Under such conditions, benzene alone behaves like solvent-nonsolvent mixtures.

As expected from the above explanation, homogeneous materials which have been quenched or uniformly oriented will not give a milky surface when treated with solvent-nonsolvent mixtures. Likewise, the interior of injection-molded objects shows very little effect compared to the surface of such objects.

Although the crazing phenomena reported here may be described in terms of a domain structure in polystyrene, this does not seem to be a very fruitful approach. The so-called domains must not have definite boundaries, since their size and appearance depend very strongly on the type of treatment used to make them visible. Theories based on imperfections and heterogeneities in polystyrene seem to give more reasonable interpretations of the results than do explanations based on well-defined domains.

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Synopsis

Domains, or areas of inhomogeneities and imperfections, may be made visible in polystyrene by treatments of the plastic with certain liquids and vapors. Different types of domains are revealed by different techniques, depending upon the solvent power of the liquids and vapors. One type of domain reveals itself as craze cracks when polystyrene is first soaked in a nonsolvent such as methanol, and then exposed to the vapors of a solvent such as hexane or benzene. A second type of domain may be revealed by exposing polystyrene to certain mixtures of solvents and nonsolvents which produce a rough, whitened surface on the polystyrene. For the first type of crazing, the size of the domains is influenced by the frozen-in thermal stresses, and the shape of the domains is influenced by molecular orientation. The domains of the second type are due to heterogeneity of molecular orientation and are not found in annealed specimens. A theory has been proposed which explains crack crazing in terms of adsorbed vapors in cracks and areas of imperfections in the polystyrene.

Résumé

Des domaines ou des régions d'inhomogénéité et d'imperfection peuvent être rendus visibles dans le polystyrène par le traitement de ce plastique avec certains liquides ou vapeurs. Différents types de domaines ont été révélés à partir de différentes techniques, selon la force solubilisante des liquides et des vapeurs. Un type de domaine se montre sous forme de fines craquelures, quand le polystyrène est trempé dans un non-solvant, comme le méthanol, et ensuite exposé aux vapeurs d'un solvant, comme l'hexane ou le benzène. Un autre type de domaine peut être répéré quand on expose le polystyrène à certains mélanges de solvants et de non-solvants, qui produisent sur le polystyrène une surface blanche et rude. Quand au premier type de craquelures, la grandeur des domaines est influencée par des tensions thermiques internes et la forme des domaines par l'orientation moléculaire. Les domaines du second type sont dus à l'hétérogénéité de l'orientation moléculaire et ne se retrouvent pas dans les échantillons préparés dans des conditions modérées. Une théorie a été proposée afin d'expliquer les craquelures fines en termes d'absorption de vapeurs dans les craquelures et dans les régions imparfaités du polystyrène.

Zusammenfassung

Inhomogene und fehlerhafte Stellen können in Polystyrol durch Behandlung mit gewissen Flüssigkeiten und Dämpfen sichtbar gemacht werden. Durch verschiedene Methoden werden, entsprechend dem Lösungsvermögen der Flüssigkeiten und Dämpfe, verschiedene Arten solcher Stellen kenntlich gemacht. Eine Art von Stellen macht sich selbst als Spaltrisse bemerkbar, wenn Polystyrol zuerst in ein Nicht-lösungsmittel, wie Methanol, eingelegt und dann den Dämpfen eines Lösungsmittels, wie Hexan oder Benzol, ausgesetzt wird. Eine zweite Art von Stellen kann dadurch erkannt werden, dass Polystyrol mit bestimmten Mischungen von Lösungs- und Nicht-lösungsmitteln in Berührung gebracht wird, die eine rauhe, weiss erscheinende Oberfläche des Polystyrols erzeugen. Bei der ersten Art von Rissigwerden, wird die Grösse der Stelle durch die eingefrorenen thermischen Spannungen, ihre Gestalt durch die molekulare Orientierung beeinflusst. Die Stellen der zweiten Art werden durch die Heterogenität der molekularen Orientierung verursacht und werden in getemperten Proben nicht angetroffen. Eine Theorie zur Erklärung des Rissigwerdens die die in den Rissen und Fehlstellen im Polystyrol adsorbierten Dämpfe berücksichtigt, wurde vorgeschlagen.