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Styrene Diffusion in Crosslinked Unsaturated Polyester Networks

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Laminates of fiber reinforced polyesters are often exposed to aqueous or organic liquids or vapors in their applications as storage tanks or boat hulls. It has been observed that the long term exposure to such liquids degrade the mechanical properties of the laminate. Hence for design purpose and to ensure the successful performance of the product, it is necessary to have knowledge of the diffusion behavior of these liquids in the crosslinked network. Polyester samples of various crosslinking densities were exposed to liquid styrene and the diffusion process was characterized by weight gain measurements, and by microscopic observations of the cross section of the sample. The crosslinking density had significant effect on the diffusion mechanism and on the magnitude of the swelling stresses induced during diffusion. The diffusional swelling stresses were quantified in terms of strain birefringence, the magnitude of which was observed to depend on the degree of crosslinking of the network. The birefringence profile of the cross section indicated relaxation of the network behind the tip of the diffusion front. The prolonged exposure to styrene led to degradation by crazing and cracking. The initiation and growth pattern were also dependent on the crosslinking degree of the network.

KEY WORDS Unsaturated polyester, degree of crosslinking, diffusion, birefringence, crazes.

INTRODUCTION

Unsaturated polyesters are widely used as matrix materials for fiber reinforced composites,¹ and as structure materials they are often exposed to aqueous or organic liquids or vapors in many applications such as storage tanks or boat hulls.² The exposure of polyester laminates to organic liquids have been found to change the mechanical properties of the polymer. Hence for successful long term performance of the laminate, it is necessary to have knowledge of the diffusion of these liquids or vapors into the polyester network.

Unsaturated polyesters have crosslinked networks which are formed by the copolymerization of the polyesters and styrene monomer.³ The crosslinking density of the network depends on the curing reaction conditions and resin composition. It is known that the degree of crosslinking of the polymer affects the penetrant

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transport into the polymer.^{4,5} The diffusion of the solvent causes plasticization and swelling of the network.⁶ These structural changes require rearrangement, i.e. relaxation, of polymeric segments.⁷⁻⁹ The transport of penetrants in rubbery polymers follow Fickian (case I) behavior due to rapid relaxation while the slow relaxation of many glassy polymer molecules result in anomalous or non Fickian (case II) diffusion. During the diffusion process, significant stresses develop within the polymer network due to the resistance to deformation, and also due to uneven swelling of the network.^{10,11} The stresses exceeding the ultimate strength of the polymer leads to the degradation by crazing or cracking.^{12,13} The degree of crosslinking also influence the onset and the type of crazes in the polymer.¹⁴

In this paper, we examine the diffusion of styrene in a polyester network as a function of different degrees of crosslinking; quantify the swelling stresses, and define the conditions for crazing in a wide range of samples.

EXPERIMENTAL

Materials

General purpose orthophthalic polyester resin was obtained from Aristech Chemical Co., and was used without removing the added inhibitor. The catalyst system of Benzoyl Peroxide (Cadox 40E, Akzo Chemicals) as the initiator and N,N-dimethyl aniline (Eastman Kodak, Rochester, NY) as the promoter was used. The styrene monomer used as the penetrant was purchased from Aldrich Chemicals (Milwaukee, WI), and was used as received.

Methods

Polyester casting preparation. Polyester sheets were cast between mylar film (Dupont[™]) lined glass plates. Shims were used to control the sheet thickness of 40 mils (1.03 mm). Crosslinking of liquid resin was initiated by adding fixed amounts of promoter and initiator. The chosen amounts obtained resin gel times of 10, 22, and 45 minutes. Every casting was cured for 24 hours at room temperature. However, to get a casting of lower crosslinking first a casting was made at room temperature and after 1 hour it was put at very low temperature for few hours to prevent subsequent curing. Thus, polyester samples with four different degrees of crosslinking were obtained. These samples are designated as A, B, C and D, with an increasing degree of crosslinking. Thus, system A represents the lowest degree of crosslinking and system D has the highest degree of crosslinking.

Penetration front measurements. Polyester samples were cut into 1" by 1" [2.54 * 2.54 cm²] squares and the thickness of each sample was measured with a micrometer. The square polyester samples were immersed in styrene in tight bottles. At successive times, a sample was removed and a thin section from the center of the sample was cut perpendicular to the top using the diamond saw. This thin section was observed in plane and polarized light in a Leitz optical microscope. The distance of the diffusion front to the surface of the swollen polymer and the thickness of the glassy core were measured.

Weight gain experiments. Preweighed samples were immersed in styrene at 25°C temperature. Periodically these samples were taken out and weighed. The total time the sample was out of styrene was less than 30 seconds. The experiment was performed with 3 samples having the same dimensions. The dimensions of the samples were chosen such that the surface area was maximized with respect to thickness. The time at which the samples began to crack or craze was also noted. The experiment was continued until the polyester samples started to warp and break as the sample began to shed fracture particles, and the weight gain data became meaningless. This period was different for samples with different degrees of crosslinking.

Birefringence measurements. To evaluate the swelling stresses generated by the penetration of styrene in the sample, the same thin section was observed in polarized light and a birefringent zone was observed in the diffusion zone. The birefringence was quantified using a compensation technique. A Berek compensator was inserted in the microscope at 45° to both the polarizer and analyzer. The vibration directions of the birefringence were determined following the procedure explained in detail elsewhere.¹⁵⁻¹⁷ The rotation of the compensator crystal introduced a phase difference of the opposite sign to compensate for the phase difference produced by the stress in the swollen region. The readings of angle of rotation were taken when the equal and opposite optical retardation nullified the retardation in the birefringent zone. The angle of rotation was converted to the corresponding values of optical retardation using the tables supplied by the manufacturer and using stress optical coefficients the residual stress are approximated.

RESULTS AND DISCUSSIONS

Diffusion as a Function of Crosslinking

Penetration front measurement. The diffusion of styrene was observed in polarized light and the thickness of the penetration front was measured as a function of immersion time. The results are shown in Figure 1 for systems A, B, C, and D that represent the samples of increasing degree of crosslinking. Samples of system A have the lowest and of system D have the highest degree of crosslinking. The styrene diffusion follows Fickian behavior in system A due to low degree of crosslinking which allow faster relaxation of the network upon solvent diffusion. The thickness¹ was found to increase as $l = .117t^{.5}$ ($r^2 > .98$). Where, t is time in hours. The term r^2 defines the variability of the data explained by the equation and the value close to 1 represents a good curve fit model.

With an increase in the crosslinking a different diffusion mechanism was observed. For systems B, C and D, faster diffusion and slow relaxation of the network resulted in an anomalous behavior. The observations showed effects such as initial higher front velocity which then significantly reduced and approached a linear behavior and also with the increase in the crosslinking of the samples observable penetration front developed only after a certain time. The significance of these effects is discussed later. In Table I, the initial and final front velocities and the

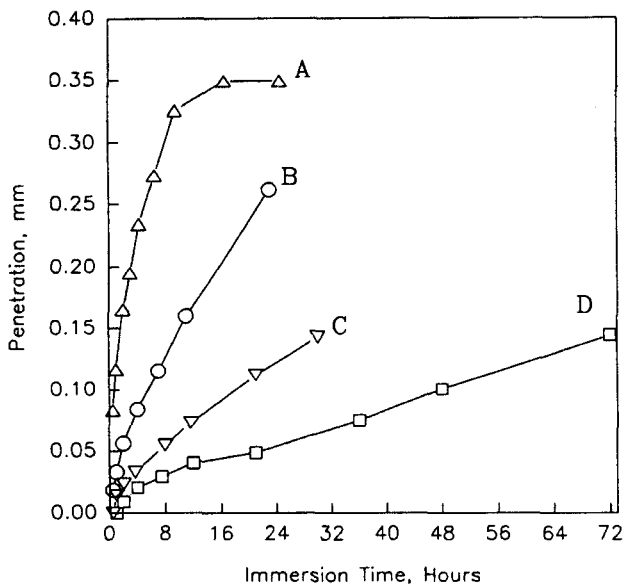


FIGURE 1 Styrene penetration thickness in polyester at various times of immersion for samples prepared under conditions A, B, C and D, as defined in text.

TABLE I
Styrene front velocities in polyester samples

System	Lag Time Hours	Initial velocity [cm/sec]*10 ⁻⁷	Final velocity [cm/sec]*10 ⁻⁷
B	0	6.89	3.22
C	.5	4.08	1.36
D	1	1.50	0.56

lag time for the appearance of the birefringence are reported for systems B, C, and D. Both initial and final velocities decrease with an increase in the crosslinking. The data could be fitted to an equation for all three systems as $l = vt^{.68}$ ($r^2 > .97$), showing the behavior which is neither Fickian ($t^{-.5}$) or linear (t). In this equation, l is the thickness of front, v defines front velocity and t is the immersion time in hours. However, if the initial data points are ignored than the major portion of the diffusion process appear linear with an intercept on Y axis. The addition of the crosslinks in the polymer reduces the segmental mobility and the free volume of the network which reduces the diffusion coefficient for styrene.^{7,13} Hence the network relaxes at different rates depending on the crosslink density. A different diffusion behavior was observed during weight gain experiments.

Weight gain analysis. In Figure 2, the increase in the weight of the polymer due to styrene diffusion is shown. The system A samples picked up styrene following the Fickian behavior while system B, C and D showed linear kinetics indicating non Fickian diffusion. There was no lag time or no initial higher rate of weight pick up was observed. Thus the penetration front measurement and weight gain curves show the different behavior. However the exponents to time for all three (B, C, and D) systems were found to be the same which suggest similar surface effects. Only system A samples showed an equilibrium saturation weight pick up. The other systems did not reach equilibrium conditions due to significant cracking of the samples. The rate equations for weight pick up are shown in Table II.

Delay in the front appearance and initial higher rate of diffusion. It is proven that only after a critical surface concentration is reached does a diffusion front develop in the polymer.^{18,19} This critical surface concentration may be different for each polyester sample exposed to styrene, depending on the crosslinking. The trend of initial higher rate of diffusion and positive intercept on y axis, is often observed during the release of the drug from the polymer gels.²⁰

If the test sample desorb residual styrene during preparation and curing it will exhibit a tensile layer on the surface. Upon exposure to styrene will be absorbed (showing a weight gain but no stress development). When the weight reaches the point at which the surface styrene concentration is equivalent to the bulk, then after this lag time stress will begin to develop.

Stresses developed during styrene absorption. The diffusion of styrene into a polyester network induced significant swelling stresses which appeared in the polyester samples as birefringence in polarized light. The diffusion builds up a stress profile when the unswollen region exerts a compressive force on the outer

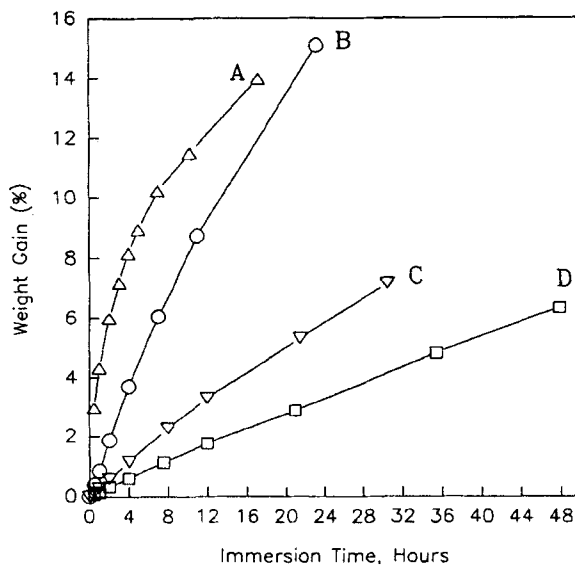


FIGURE 2 % Weight gain of in polyester samples due to styrene absorption after various times of immersion for systems, A, B, C, and D.

TABLE II
Summary of weight gain rates

System	Rate Equation
	$\Delta w\% =$
A	$4.276t^{0.5}$
B	$0.849t$
C	$0.272t$
D	$0.133t$

Here weight gain $\Delta w\%$ is defined as $[(W - W_0)/W_0] * 100$ and time is measured in hours. W = weight of the sample at time t and W_0 is the initial weight.

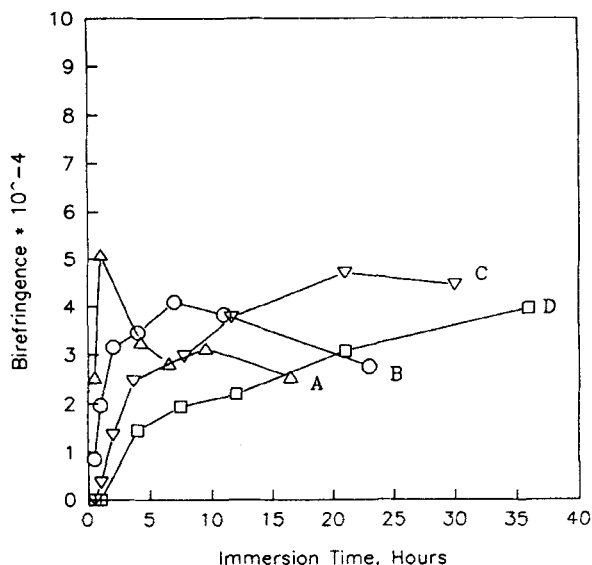


FIGURE 3 Birefringence values at the front due to styrene diffusion for samples of systems A, B, C and D, for various times of immersion in styrene.

swollen layers and the swollen layer exerts a tensile stress on the inner core.^{11,13} The slow vibration direction of birefringence was observed parallel to the compression in the adsorption layer.

In Figures 3 and 4, these results are illustrated for systems A, B, C, and D. The birefringence at the front appears to increase up to a certain magnitude. The time

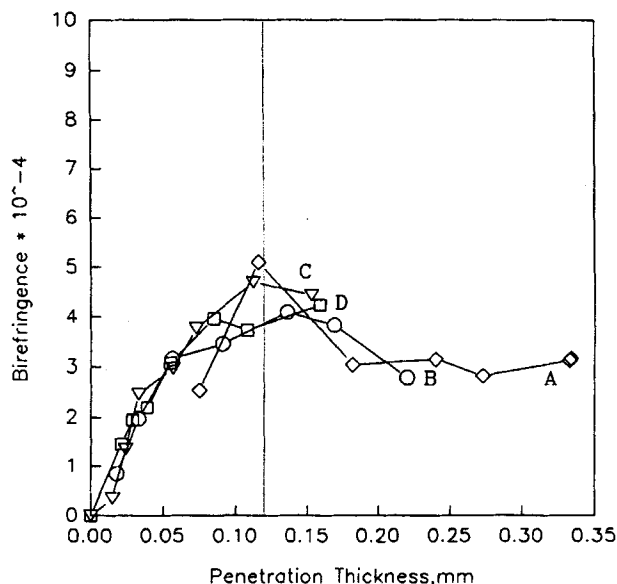


FIGURE 4 Birefringence values at the front and corresponding penetration thickness for samples of systems A, B, C and D.

during which the values increase depends on the degree of crosslinking of the sample. In low crosslinking samples, a rapid increase in the birefringence was observed and subsequent diffusion produced no significant change in the birefringence. With a gradual increase in the crosslinking, the time to reach and highest birefringence values increased. The increased crosslinking offers more resistance to the deformation and hence the birefringence values increase at a slower rate.¹¹ Conversely, with an increase in the crosslinking, the degree of swelling and the penetration are also less. Hence it can be concluded that for a particular crosslinking, the resistance offered will be higher until a certain degree of penetration is reached. These conclusions are supported in Figure 4 where the birefringence values in each system are plotted with the corresponding thickness of penetration. The comparison of the birefringence of systems C and D show that values for system D are lower than the birefringence of system C samples. It has been shown that with an increase in the modulus at higher crosslinking density, the degree of swelling and associated distortions become very small. The phenomenon leads to a drop in the network stresses.¹¹

Our observation of birefringence in the front indicate a decrease behind the front. At the low degree of crosslinking, surface layer appeared black indicating complete relaxation. Robinson²¹ showed that the birefringence values near the front were nearly constant for prolonged exposure to solvent. Thomas and Windle⁸ have illustrated the birefringence during the absorption of methanol in PMMA. The birefringence profile across the swollen layer showed a decrease behind the front. With more diffusion a slight increase in the birefringence at the front was observed. The theoretical treatment by Gurnee¹⁶ also predicted the birefringence profile curves similar to that observed by Thomas and Windle and by us. However,

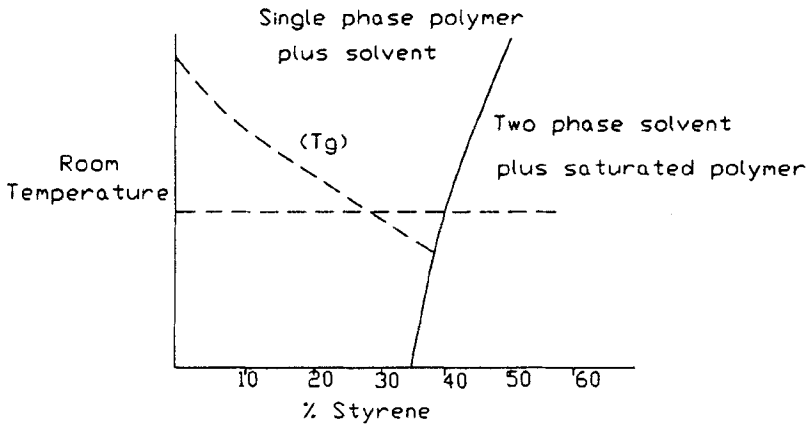


FIGURE 5 Hypothetical phase diagram for the system: polyester-styrene showing the relationship between the glass transition temperature (T_g) and temperature.

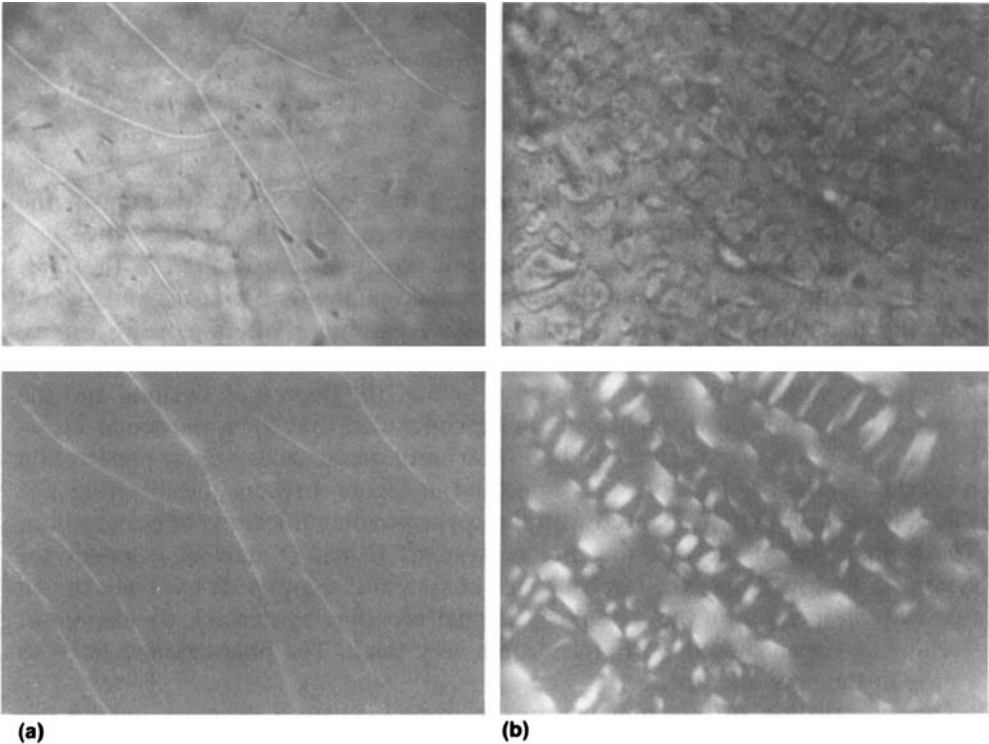


FIGURE 6 Crack (craze) growth in a polyester sample (system A); a) after 12 hours of immersion, b) after 24 hours of immersion in styrene.

it has been shown this situation is dependent on the polymer-penetrant system and different birefringence profile can be observed for different systems.²²

The drop of the birefringence indicating relaxation of stresses behind the front, can be explained by the effect of diffusion on the glass transition temperature. The solvent absorption decreases the glass transition temperature for the polymer al-

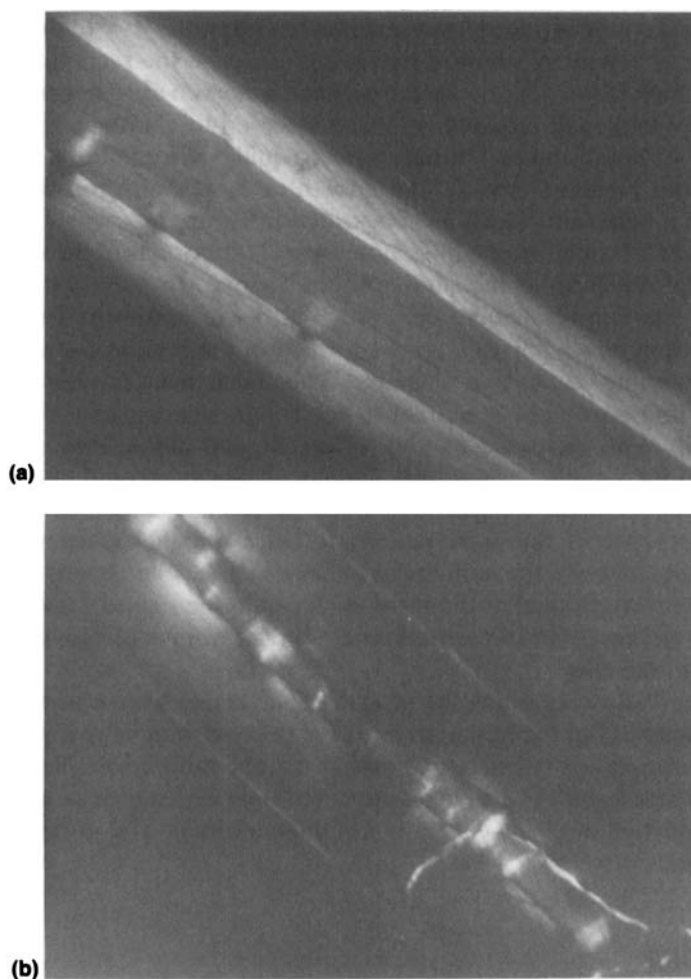


FIGURE 7 Appearance of the cracks at the front. (a) shows crack distribution when the middle region was thick and (b) shows the crack pattern as the two fronts approach each other.

lowing the molecules to become mobile to relieve the stress. With an increase in styrene concentration in the network at a certain time, the values of T_g could drop below room temperature. The change in shape as the front takes place on a time scale within which the swollen material behaves more as a glass than as a rubber and birefringence therefore has characteristics of a deformed glass. In Figure 5, a hypothetical diagram indicates the relationship between the glass transition, the styrene concentration and the temperature.

Crazing of the samples. The diffusion of styrene in the polyester samples induced significant stresses in the samples. With prolonged exposure to styrene, cracks were formed at the diffusion front and the time of appearance of the cracks was dependent on the crosslinking of the sample. It has been shown that the crazing of the sample due to diffusion of solvent into the polymer, is affected by sample thickness, degree of crosslinking and temperature. Other parameters are penetrant

content, critical strain and the glass transition temperature.¹²⁻¹⁴ Lightly crosslinked samples such as system A, showed significant crazes in the section after 17 hours of exposure. First indications of the crazes were observed at 10 hours. The samples with the lower degree of crosslinking were observed to approach equilibrium saturation after 10 hours and at 17 hours a near equilibrium condition was achieved, as evident from Figures 2 and 3. The growth of crazes both in size and number showed certain behaviors which are illustrated in Figure 6.

The cracks first formed as thin lines appearing at the corners of the square sample. The cracks did not form at the surface of the sample. In polarized light, a stress field around this thin lines could be seen. With more diffusion of styrene, initial thin lines thicken and a few thin cracks formed in the regions between two thick cracks thus forming connective channels. The thin cracks formed in the earlier stages of the transport allow penetrant to enter into these regions, thereby causing them to swell. With increased number of cracks, the dimensions of the samples increased and the sample became soft. Finally all cracks merged into a few bigger cracks and the rest of the sample away from the crack was relaxed. This could be due to the presence of the more penetrant, since a higher concentration of the penetrant would increase the mobility of the macromolecular chains. There is proof that the crazes were formed at the front as shown in the Figure 7 and the enlarged crack system grows within the central core as crack from each moving front propagates through the core.

Similar observation regarding the growth of the crazes were observed for highly crosslinked samples but the initiation time was delayed with increasing crosslinking density. The samples of system B, C, and D did not show crazing until 15, 22 and 36 hours. In these samples, the crazes appeared only with a little penetration while a significant portion of glassy core was still unpenetrated. The growth of crazes in the number was also slow.

CONCLUSIONS

The crosslinked network of unsaturated polyester absorbs significant amounts of styrene depending on the degree of crosslinking. The diffusion mechanism is essentially non-Fickian for highly crosslinked samples. The highly crosslinked samples pick up styrene immediately upon absorption but the penetration front does not appear for some time depending on the degree of crosslinking. The prolonged exposure of polyester to styrene causes degradation by cracks formation. These observations suggest that it is necessary to determine the penetrant activity and the interaction of the polyester network to various solvents before the material is used as storage tanks or under conditions of the exposure to those solvents.

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