ments, such as counterion activities, light scattering, and electrophoresis, may also be useful for our understanding of the problem. However, the present experiments indicate that viscosity alone is sufficient to yield a direct demonstration of the specificity of the counterion effects of simple monovalent anions on the solution behavior of a protonated base, poly(ethylenimine). This study shows that, in the presence of simple counterions, a physical picture of polyelectrolytes in solution may sometimes be difficult to obtain in terms of electrostatic interactions of structureless charged units only, but often requires a detailed consideration of all specific counterion effects on the charged macromolecules. This includes not only the electrostatic repulsion of the polyion and the decrease of solvent power for the polymer, but also the possibility of induced intramolecular associations of the polyelectrolyte.

Acknowledgment. The author wishes to express his appreciation to Dr. Robert Ullman for valuable discussions and to Mrs. Libby Zirkin for experimental help.

The Role of Organic Agents in the Stress Crazing and Cracking of Poly(2,6-dimethyl-1,4-phenylene oxide)

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Received March 12, 1968

ABSTRACT: The critical flexural strain ϵ_c for crazing or cracking has been determined for compression molded bars of poly(2,6-dimethyl-1,4-phenylene oxide) in air and in 28 different small molecule organic liquids. Measurements have also been made of equilibrium solubility of liquid in the polymer and in some cases the drop in polymer T_g caused thereby. Studies of the degree of solvent-induced crystallinity and Instron stress–strain behavior of sorption-equilibrated films have also been effected. Both surface energy and plasticization effects are thought to be observable in liquid-induced crazing and cracking. Transformation from cold drawing to crazing as the mode of failure is effected even by liquids of negligible solubility in the polymer suggesting that they act by reducing the surface energy of the holes in the craze making their formation easier. However, the difference in crazing and cracking resistance between good and poor swelling agents correlates well with the solubility parameter, with actual solubilities in the polymer, and with consequent differences in polymer T_g. Such a difference is almost wholly a plasticization phenomenon.

There exist in the general literature no systematic and careful studies of the influence of organic agents on the susceptibility of glassy polymers to crazing and cracking under stress. In fact there is known to the authors only one set of systematic data in this regard.[1] In light of the scarcity of data and the multiplicity of processes known or suspected to take place in a stressed glassy polymer in contact with a liquid, it is not surprising that the role of organic agents in the mechanism of so-called environmental stress crazing and cracking has remained obscure.

Two theories that attempt to rationalize "solvent" crazing and cracking have existed primarily in one form or another for more than a decade. By analogy with certain effects in inorganic systems, the first postulated that organic agents, having generally low surface tensions, spread on polymer surfaces and thus reduce the surface energy for crack formation.[1–3] Upon discovery that crazes were not cracks but rather thin platelike regions of porous polymer of very high specific internal surface area (*e.g.*, 100 m^2/g) and upon development of a "domain" theory of the structure of glassy polymers,[4] it became reasonable to suspect that organic agents could serve to reduce the surface energy of craze internal surface area formation. The best evidence in support of the surface energy hypothesis comes from the poly(methyl methacrylate) study[1]—tensile strength falls in proportion to surface tension decrease in a series of alcohols and alcohol–water mixtures used as immersion fluids. Attempts to extend this correlation to PMMA in other liquids are not very successful.

The second theory holds that the organic agent acts as a plasticizer. Originally it was supposed that solvent crazes (then thought to be cracks) occurred when the combination of stress and plasticizer lowered the polymer T_g to ambient temperature. Because of our present knowledge of the structure and mechanical properties of crazes and because of current concepts about flow in the glassy state under stress,[5] a modern casting of this hypothesis would be that limited plasticization lowers T_g to a limited degree and application of sufficient stress promotes a liquidlike flow of the glass in the stress direction. The lower T_g is the smaller will be the strain energy input required to induce flow.

Lowering of T_g depends directly on plasticizer concentration and to a first approximation the latter is expected to increase directly as the difference between the cohesive energy density, CED, of polymer and environmental liquid decreases. Thus a plot of tensile

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(1) E. Wieser, Doctoral Thesis, Aachen, Germany, 1959.
(2) L. E. Nielsen, *J. Appl. Polym. Sci.*, **1**, 24 (1959).
(3) H. A. Stuart, G. Markowski, and D. Jeshke, *Kunststoffe*, **54**, 618 (1964).
(4) R. E. Robertson, *J. Phys. Chem.*, **69**, 1575 (1965).
(5) R. E. Robertson, *J. Chem. Phys.*, **44**, 3950 (1966).

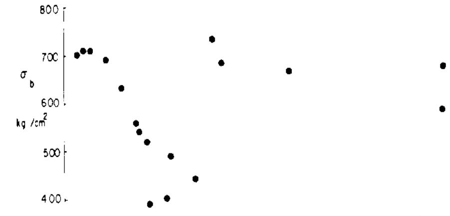

Figure 1. Tensile strength of poly(methyl methacrylate) *vs.* cohesive energy density (CED) of immersion fluid (strength data from ref 1).

strength *vs.* CED should show a minimum at the CED of the polymer; from the PMMA results (Figure 1) it might only be said that the CED criterion appears to be a necessary but not sufficient condition for reduction in polymer strength.

Other factors have been considered to be of importance when a stressed polymer is placed in an organic agent. In particular, stress-accelerated absorption has been postulated to play a controlling role in solvent stress crazing and cracking.[6,7] In short, all polymer surfaces contain stress concentration points; since tensile stress is known to accelerate solvent absorption and attendant stress relaxation, it is postulated that such processes occur preferentially at these points in such a way that craze and/or crack initiation tends to occur at these locations. Since absorption rates of different liquids are accelerated to different degrees by stress,[7] these acceleration factors might strongly influence liquid efficiency in causing environmental failure.

The ability to distinguish between the surface energy and plasticizer theories of strength reduction is made more difficult by the well-known fact that cohesive energy density and surface tension γ_{la} of an organic liquid are usually closely related to each other, both being measures of intermolecular forces existent in the liquid. This is exemplified in Figure 2 in which γ_{la} is plotted for the agents used in this study *vs.* their solubility parameters δ. Most other organic liquids fall along the line designated the main branch. For linear aliphatic monohydric alcohols γ_{la} is essentially independent of δ undoubtedly because the surfaces of these liquids consist of molecules the aliphatic ends of which are oriented outward.[8] Except for peculiarities like those of the alcohol series γ_{la} and δ are directly related so that empirical correlation of a strength property of a polymer with one function automatically implies correlation with the other.

Having in mind the various factors discussed above, all of which could be important, it has been easily conceivable that no simple correlation for environmental crazing exists. However, we have also been aware of the difficulty of obtaining optimum experimental data; solvent crazing and cracking are strongly dependent on time under stress and upon degree and direction of polymer preorientation as well as upon surface flaws. Thus lack of a good correlation to date could have been the result of experimental difficulties. The work reported herein on poly(2,6-dimethyl-1,4-phenylene oxide) has been aimed at clearing up the uncertainties discussed above.

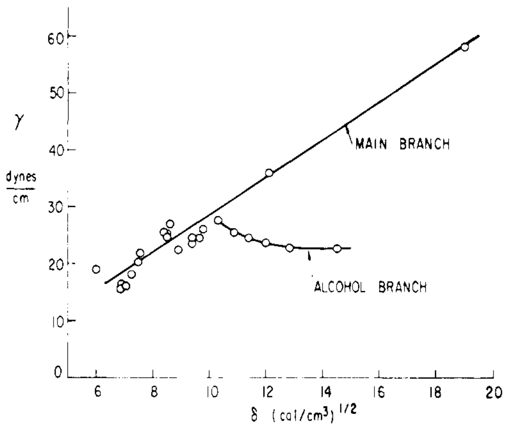

Figure 2. Surface tension γ *vs.* solubility parameter δ for some agents used in this study. Most other agents also fall along the main branch.

Experimental Section

A. Critical Strains for Craze and Crack Formation. Values of the critical strain ϵ_c below which neither crazing nor cracking occurred scattered considerably for annealed injected, molded bars. Consequently, critical strain studies were shifted to bars cut from 0.1-in. thick sheets compression molded from polymer powder of $[\eta] = 0.51$ dl/g which had been dried at 150° under vacuum for 15 hr. In the molding treatment the powder was first cold pressed. The plate was then sandwiched between sheets of aluminum foil which had been coated with a thin layer of polytetrafluoroethylene release agent (S122 Fluorocarbon release agent, Miller-Stephenson Chemical Co.). The sandwich was placed in a mold at 265° for 1 min at zero pressure, pressed for 2 min at about 1200 psi and transferred to a steam-heated press at 180° and 450 psi; in 3.5 min the plate cooled from 265 to 220°. Pressure was then released and the plate cooled to below 100° in 10 min. These sheets exhibited first-order birefringence colors as did the annealed molded bars, but birefringence was generally more uniform over the sheet surface than in molded annealed bars. Critical strains for craze formation were much more reproducible with the sheet material than with the annealed bars.

Bars 0.5 × 5 in. were cut from the sheets and milled to size, the milling direction being parallel to the long dimension of the bar. The resulting edges were not smoothed further. Prior to testing, each bar was washed in soapy water, rinsed, and dried with lens tissue.

Straining was accomplished in a three-point bending jig such that maximum fiber stress was in one of the machined edges (Figure 3). Maximum deflection was measured with calipers. The jig was then placed in a rectangular glass cell that had optically flat faces and contained the test fluid. Liquids of reagent grade quality were used without further purification. Crazes and cracks were easily detected by shining light into the cell at an oblique incident angle, and inspecting the specimen edge at the angle of reflection. In general the critical strain ϵ_c was taken as that strain below which no craze or crack could be observed to form over a period of roughly 3 hr. More exactly, a strain could be found at which only one or two crazes or cracks developed; in another bar a slightly lower strain was set and, if no craze or crack developed, these two values then set limits on the critical strain. Parenthetically, in contrast

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(6) E. W. Russell, *Nature*, **165**, 91 (1950).

(7) R. P. Kambour, unpublished observations.

(8) A. W. Adamson, "Physical Chemistry of Surfaces," 2nd ed, Interscience Publishers, New York, N. Y., 1967.

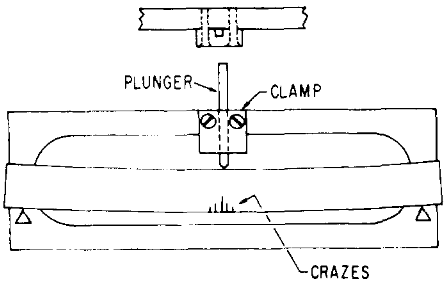

Figure 3. Three-point bending jig for craze formation. Strain level is set by mounting jig in table vise, driving plunger in to proper distance and tightening clamp screws. Friction then holds plunger in position.

to experience with well-prepared films,[9] it was found possible to fix critical strain to a considerably greater degree of precision with these bars, which is surprising bearing in mind the much smoother surface of cast films.

Maximum fiber strains were calculated from the following equation which is easily derived from standard theory of elastically stressed beams[10]

$$\epsilon_{\max} = 6dy_{\max}/l^2$$

where $\epsilon_{\max}$ is the maximum fiber strain, $y_{\max}$ is the deflection of the bar at its center, d is bar width (dimension parallel to the direction of deflection) and l is the span length.

B. Sorption Kinetics and Equilibria. Vapor sorption studies, using most of the same liquids employed in critical strain determination, were made on film specimens of the polymer 0.003 in. thick and of lateral dimensions 1.5 × 0.5 in. These specimens were cut from large sheets of film initially of $[\eta] = 0.46$ dl/g which had been clamped in a restraining frame to prevent distortion and thickening and annealed under vacuum. Oven temperature were kept at 195° for 12 hr for degassing purposes and then at 225° for 4 hr for deorientation.

The specimens were suspended in stoppered test tubes above 1-cc quantities of the organic liquids, and removed periodically for weighing on an analytical balance. Desorption during the 30 sec in which these specimens were out of their enclosures for weighing was not detectable.

C. Solvent-Induced Crystallization. Poly(2,6-dimethyl-1,4-phenylene oxide) is known to behave in analogous fashion to polycarbonate and several other polymers which can crystallize but, in the melt, do so only with difficulty. Quenching then produces a metastable glass. As with polycarbonate,[11] crystallization during slow evaporation of a solvent from the polymer occurs much more easily than in the melt. In certain instances evidence of possible crystallization induced by plasticization was observed during absorption in the films; in particular, several of the films became somewhat translucent.

Some of these films were thus dried carefully under vacuum at temperatures gradually raised to 100° and were then subjected to crystallinity measurement using a Perkin-Elmer DSC scanning calorimeter. By employing the heat of fusion value 13.5 cal/cm³ of crystal[12] and planimetric measurement of the endotherm peak areas, estimates of degrees of crystallinity were made.

D. Glass Transitions in Plasticized Films. In a few cases the glass transition temperature of the film containing the organic agent at its room temperature equilibrium concentration was determined. Several disks of film were cut from the particular equilibrated specimen with a no. 1 cork borer; they were placed in a Perkin-Elmer DSC volatile sample pan and the cover was crimped in place. When properly closed the pan was airtight and withstood internal pressures up to about 2 atm. It was thus possible to prevent escape from the sample of the volatile agents used in this study up to fairly high temperatures; in those cases where solubility in the polymer had lowered its T_g sufficiently and the boiling point of the liquid was sufficiently high, the DSC chart trace exhibited the shift typically associated with a polymeric glass transition before pressure increase inside the sample pan caused it to burst.

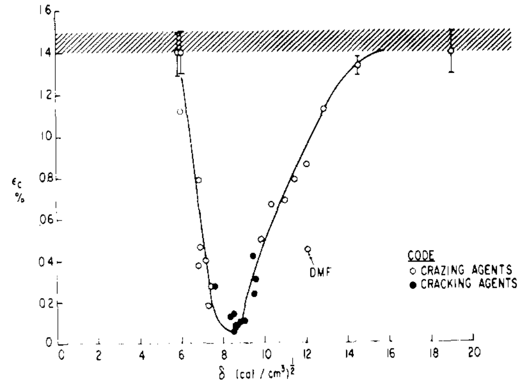

Figure 4. Critical strain ϵ_c for crazing or cracking *vs.* solubility parameter δ of liquid environment. Shaded band indicates ϵ_c value of the resin in air: ●, cracking agents; ○, crazing agents; DMF, dimethylformamide.

E. Tensile Properties of Equilibrated Films. Conventional environmental strength tests all involve stressing or straining of the sample followed or accompanied by application of the test environment and this is of course true of our three-point bending tests. Occasionally experimenters have soaked specimens for varying periods of time prior to load application.[1] However, inspection of the reports of these studies makes evident the fact that the thicknesses of the specimens and soaking times employed rule out the possibility that sorption equilibrium had obtained before loading commenced.

Because of concern about various rate effects on the strength behavior of polymer in contact with liquid with which it is not equilibrated, Instron tensile tests were conducted on equilibrated polymer films at a constant strain rate of 0.5 in/min. The specimens cut from 0.0025 in. thick annealed film of $[\eta] = 0.71$ dl/g had test sections which were 0.125 in. wide and 1.25 in. long. Each specimen was mounted in a special tensile jig which fit into a glass enclosure similar to a test tube in shape. An O ring at the joint between glass and metal made a reasonably tight seal. In the bottom of each enclosure was placed 1–2 cc of the test liquid before sealing up the assembly which was then left with the specimen unstressed for the known equilibration time period (up to several months) before testing in order that sorption equilibrium be assured. The cell was then attached by means of a special fitting to the Instron crosshead, the top tensile chuck being attached *via* a connecting rod to the load cell. In this way tests were performed without removal of the films from their equilibration atmospheres.

Results

All data obtained experimentally in this study as well as relevant physical properties of the agents used are summarized in Table I.

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(9) R. E. Robertson, unpublished results.

(10) R. J. Roark, "Formulas for Stress and Strain," McGraw-Hill Book Co., Inc., New York, N. Y., 1954.

(11) R. P. Kambour, F. E. Karasz, and J. H. Daane, *J. Polym. Sci., Part A-2*, **4**, 327 (1966).

(12) A. R. Shultz, unpublished results.

Table I

No.	Organic liquid (z = crazing agent; k = cracking agent)	δ,[a] (cal/cm^3)$^{1/2}$	ρ,[b] g/cm^3	T_g,[c] °K	γ,[d] dyn/cm	ϵ_c, %	S_w, g/g	γ_{DSC}, %	Equilibrated film S, cc/cc	Equilibrated film T_g, °C	Equilibrated film σ_{cfy} psi
1	Methanol (z)	14.5	0.793	110	22.6	1.29–1.38	0.043		0.058		
2	Ethanol (z)	12.85	0.789	100	22.8	1.06–1.13	0.053		0.071		
3	*n*-Propyl alcohol (z)	12.0	0.804	109	23.8	0.82–0.86	0.124		0.164	107	3520
4	*n*-Butyl alcohol (z)	11.4	0.810	118	24.6	0.75–0.78	0.074		0.097		
5	*n*-Amyl alcohol (z)	10.9	0.814	124	25.6	0.68	0.136		0.177	103	4800
6	*n*-Octyl alcohol (z)	10.3	0.824		27.7	0.67					
7	Dimethylformamide (z)	12.1	0.944		36.0	0.44–0.45	0.256		.288	57	2400
8	Acetone (z)	9.8	0.792		26.0	0.49–0.50	0.160	3.2	0.214		2240
9	Methyl ethyl ketone (k)	9.4	0.805		24.6	0.19–0.22	0.196	15.4	0.256		
10	Methyl propyl ketone (k)	8.9	0.812		22.4	0.079–0.093	0.315	23.8	0.407		
11	Methyl *n*-butyrate (k)	8.9	0.898		24.2	0.068–0.095	0.395	26.8	0.462		
12	Carbon tetrachloride (k)	8.6	1.595		27.0	0.08					
13	*n*-Octane (z)	7.55	0.704	85	21.8	0.238–0.274	0.220		0.331	63	800
14	*n*-Heptane (z)	7.45	0.684	84	20.3	0.264–0.277	0.196		0.300		
15	*n*-Hexane (z)	7.25	0.660	70	18.0	0.185	0.169		0.271		
16	*n*-Pentane (z)	7.05	0.626	64	16.0	0.370–0.396	0.170		0.290		
17	2-Methylbutane (z)	6.9	0.621		15.5	0.37					
18	2,2-Dimethylbutane (z)	6.9	0.649		16.2	0.74–0.79					
19	2,2,3-Trimethylbutane (z)	6.9	0.690		18.9	0.37–0.46					
20	Hexamethyldisiloxane (z)	6.0	0.762		19.0	1.06–1.12	0.011		0.015		
21	Perfluorodimethylcyclohexane (z)	6.0				$-1.2+$	$\sim$0	$\sim$0	$\sim$0		5430
22	Perfluoromethylcyclohexane (z)	5.85				$-1.4+$					
23	Formamide (z)	19.0	1.134		58.2	$-1.4+$	$\sim$0	$\sim$0	$\sim$0		
24	Methyl acetate (k)	9.6	0.927		24.6	0.307–0.316	0.177		0.201		
25	Ethyl formate (k)	9.4	0.924		23.6	0.396–0.436	0.181		0.206		
26	Tetrahydrofuran (k)	9.2	0.888				0.310		0.367		
27	Isoamyl formate (k)	8.5	0.871		24.6	0.053–0.066			0.487		
28	*n*-Butyl acetate (k)	8.5	0.882		25.2	0.120–0.146	0.426		0.506		
29	Methyl butyl ketone (k)	8.4	0.830		25.5	0.107–0.133	0.379	22.0	0.443		
30	Poly(2,6-dimethyl-1,4-phenylene oxide)	8.9	1.06	488	$\sim$33–43						

[a] H. Burrell and B. Immergut, "Polymer Handbook," J. Bandrup and E. H. Immergut, Ed., Interscience Publishers, New York, N. Y., 1966; C. J. Sheehan and A. L. Bisio, *Rubber Chem. Tech.*, **39,** 1 149 (1966); J. L. Gardon, Encyclopedia of Polymer Science and Technology, Vol. 3, Mark Gaylord and Bikales, Ed., Interscience Publishers, New York, N. Y., 1965; G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54,** 1731 (1958); F. R. Blanks and J. M. Prausnitz, *Ind. Eng. Chem., Fundam.*, **3,** 1 (1964); G. Allem, G. Gee, and G. J. Wilson, *Polymer*, **1,** 456 (1960); K. C. Baranwal, *Macromol. Chem.*, **100,** 242 (1967); P. A. Small, *J. Appl. Chem.*, **3,** 71 (1953). [b] G. Allen, G. Gee, and G. J. Wilson, "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1967. ([c]) J. A. Faucher and J. V. Koleske, *Phys. Chem. Glasses*, **7,** 202 (1966); A. A. Miller, *J. Polym. Sci., Part A-2*, in press. [d] O. R. Qauyle, *Chem. Rev.*, **53,** 439 (1953);. F. M. Fowkes, "Chemistry and Physics of Interfaces," American Chemical Society, Washington, D. C., 1965.

A. Critical Strain Correlations. In contrast to previous results, correlation between critical strain and solubility parameter of the test liquid is excellent. This is the case for all liquids including the alcohols but excepting dimethylformamide (Figure 4); values of ϵ_c are seen to range from 1.4 to 1.5%, which is characteristic of the polymer in air and in liquids of δ far removed from that of the polymer down to values at or below 0.1% for liquids of δ near 8.6. For the polymer itself δ is estimated by Small's method to be 8.9 (Table I, footnote a). A necessary *and* sufficient condition for inducing a low value of ϵ_c in this polymer would appear to be in general proximity of δ_{liquid} to δ_{polymer}. Those liquids of δ closest to 8.9 do not allow stable crazes to be produced; that is, for $\epsilon > \epsilon_c$ cracks are produced which proceed more or less rapidly completely through the specimen while for $\epsilon < \epsilon_c$ no light reflections indicative of crazes or cracks are seen at all. These agents are designated cracking agents in contrast to crazing agents in which crazes can exist for some length of time over a finite range of applied strain.

In Figure 5 equilibrium volume solubility S_v of the saturated vapor in the polymer is plotted *vs.* δ ($S_v = S_w\rho_2/\rho_1$ where S_w is solubility in weight absorbed per unit weight of polymer, and ρ_2 and ρ_1 are the densities of polymer and liquid, respecively). As expected solubilities rise from essentially zero on this scale to the maximum observed at δ close to 8.6. With CCl_4 the film actually dissolved completely so that a value of sorbed weight could not be determined. As in Figure 4, dimethylformamide is the discrepant agent which reflects its well-known enhanced solvent behavior. The S_v *vs.* δ curve is skewed as has been observed with other polymers. In this system the "excess" solubility at $\delta > 8.9$ probably arises largely from hydrogen bonding to the polymer's ether oxygen. In this regard it should be noted that we have used no aliphatic hydrohalocarbons, some of which are the best solvents

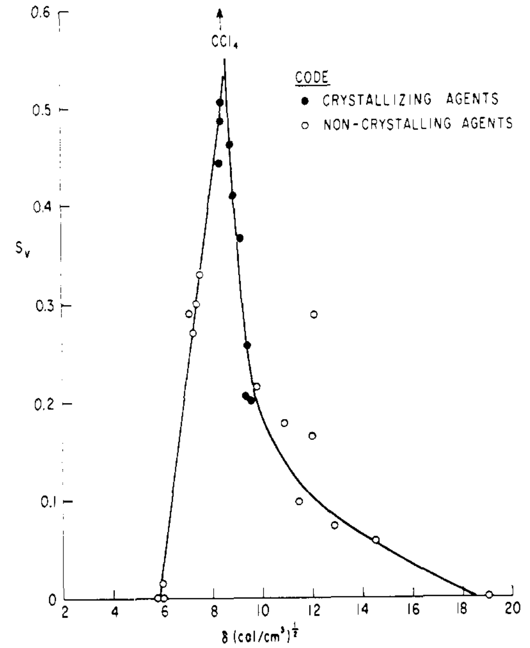

Figure 5. Equilibrium volume solubility S_v of saturated vapor in polymer *vs.* δ.

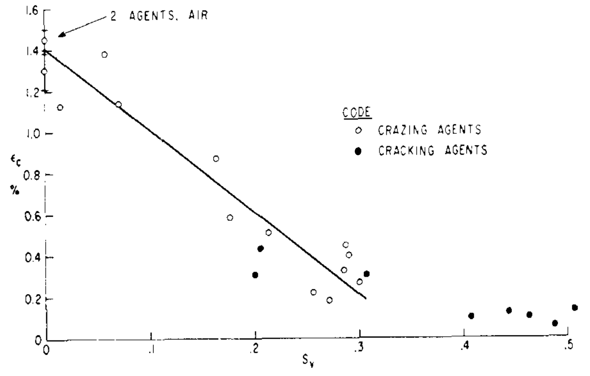

Figure 6. Critical strain for crazing and cracking ϵ_c *vs.* equilibrium volume solubility S_v.

for this polymer. In general their δ's are higher than 8.9, and are thought to interact *via* hydrogen bonding with the ether oxygen.

In Figure 6, ϵ_c is plotted *vs.* S_v for 16 agents; this plot serves to bring data from the two branches of the previous curves together in a single monotonic correlation. Dimethylformamide is seen in this framework to act no differently than do other agents of similar solubility, in contradistinction to appearances in Figure 4. It is to be noted that all agents of $S_v > 0.3$ are in the cracking class.

DSC crystallinity results on some of the solvent-treated, translucent specimens and on the original film are displayed *vs.* equilibrium solubility in Figure 7. It is clear from Figures 6 and 7 that in general those agents of $S_v > 0.3$ constitute both the cracking agents and crystallizing agents. In the polycarbonate–acetone system crystallization occurs only when plasticization has lowered T_g below ambient temperature.[11] By analogy then, we conclude that both solvent cracking and solvent-induced crystallization in poly(2,6-dimethyl-1,4-phenylene oxide) are effects allowed by plasticization of the polymer to the extent that T_g at equilibrium swelling lies below room temperature.

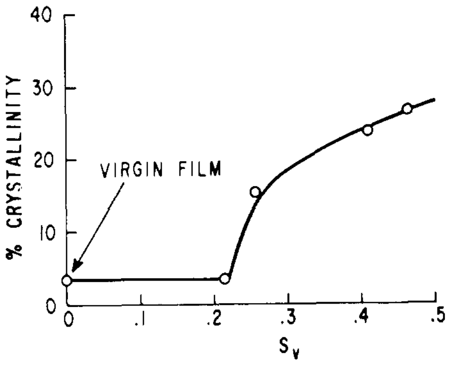

Figure 7. Degree of polymer crystallinity *vs.* equilibrium volume solubility S_v.

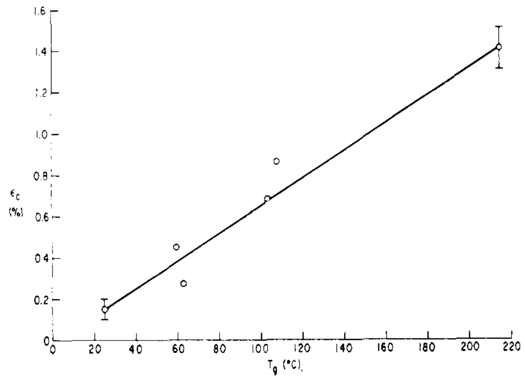

Figure 8. Critical strain for crazing ϵ_c *vs.* T_g of polymer swollen to varying degrees by equilibration with different agents.

Figure 8 shows ϵ_c *vs.* T_g of the plasticized film equilibrated with different agents. The straight line is drawn between the point for dry polymer and that for polymer swollen just enough so that its T_g is at room temperature. That is, in the latter case ϵ_c is the average for $S_v = 0.3$ which is the approximate dividing solubility between crazing and cracking agents as indicated above. For the four swollen films in which T_g's could be found, DSC results lie close to the established line in spite of the experimental difficulties involved in both ϵ_c and T_g determinations. On this plot again the point for dimethylformamide lies as close to the line as the points for two of the other three agents.

B. Tensile Behavior of Equilibrated Films. Curve 3 of Figure 9 is a stress–strain curve 0.05 in./min extension rate of the polymer film equilibrated with saturated acetone vapor.[13] Crazing was observed to initiate at very low stresses, each craze tending to develop rapidly and often to run through the whole cross section of the film in a time of the order of 10–20 sec. Craze initiation and growth accelerated with stress until near the yield stress (2200 psi) the whole test section was opaque with crazes. The yield stress may be taken as the stress at which plastic deformation due to craze formation equals the rate of machine extension. Extension was continued until the upper tensile chuck

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(13) R. P. Kambour and G. A. Bernier, *Macromolecules*, **1**, 190 (1968).

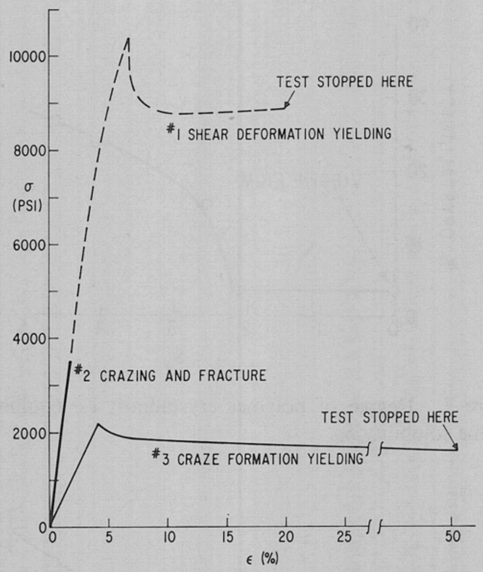

Figure 9. Stress-strain curves at 0.05 in./min elongation for (I) dry film, (II) film exposed to acetone at initiation of tensile testing, and (III) acetone-equilibrated film. In I drawing is by shear deformation; in III it is by craze formation.

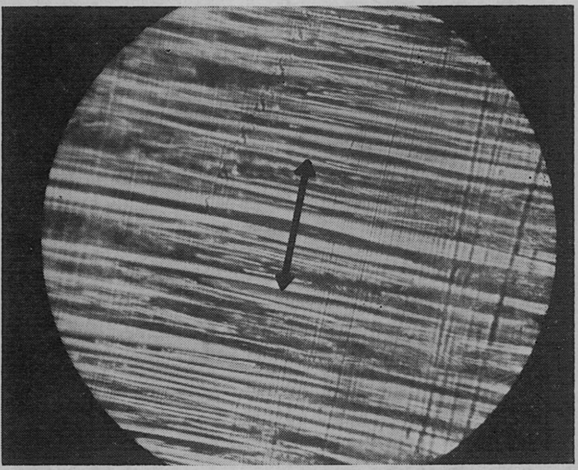

Figure 10. Photomicrograph of surface of film subsequent to test III in Figure 9 showing extensive craze formation; field diameter = 0.05 cm.

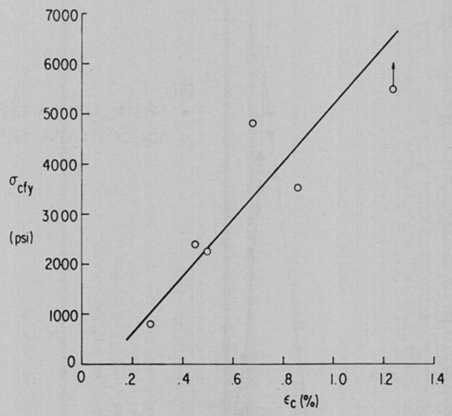

Figure 11. Craze formation yield stress σ_{cfy} in equilibrated films *vs.* critical strain for craze formation ϵ_c in compression molded bars.

reached the limit of its travel in the jig. A total extension of roughly 50% remained in the film after removal from the jig. For comparison, tensile curves for the dry film (curve 1) and for film immersed in acetone at the start of the test (curve 2) are shown. In curve 1 a conventional shear deformation yield stress σ_{sdy} of 10,500 psi is exhibited. Figure 10 is a photomicrograph of the surface of the equilibrated film subsequent to testing showing that the sum of the thicknesses of the crazes developed accounts for roughly half its total length.

Figure 11 shows the craze formation yield stress σ_{cfy} (determined for equilibrated films by this test) *vs.* ϵ_c, the critical strain for craze formation in the compression molded bars. One exception is to be noted. In the case of perfluorodimethylcyclohexane, crazing began at low stress but did not accelerate rapidly at higher stresses as with the other agents. Rather the film fractured at one of the crazes and this value of stress is denoted as the lower limit above which the craze formation yield stress must lie. In spite of the extreme differences in agent exposure times and testing rates (remembering that ϵ_c is determined in a time length of the order of several minutes to several hours) for the two kinds of measurement of the ease of craze formation, there appears to be a rough correlation between the two.

Discussion

A. Plasticization Effects. The correlations presented in Figures 3–9 indicate that most small organic molecules act as plasticizers in reducing resistance to craze formation in poly(2,6-dimethyl-1,4-phenylene oxide). The ϵ_c *vs.* T_g correlation of Figure 8 provides the most fundamental support for this hypothesis in spite of the paucity of data here. The degree of success of the correlations of Figures 4 and 6 depends in part on the T_g's of the agents used in this study, of which all T_g's are probably extremely low. It will be noted from Table I that these lie between 60 and 120°K roughly (by comparison with $T_g = 480$°K for the dry polymer). When additivity relationships are used with these liquids (*e.g.*, $T_{g1,2}^{-1} = W_1T_{g1}^{-1} + W_2T_{g2}^{-1}$ where W_i and T_{gi} are the weight fraction and T_g of the *i*th component) to estimate $T_{g1,2}$ of the swollen film, it becomes clear that T_{g2} of the agent is so low that W_2T_{g2} contributes in a minor way to $T_{g1,2}$. In effect T_g lowering depends primarily on $W_1 = 1 - W_2$. This will not be true for agents of substantially higher T_g.

It should also be remembered that the S_v *vs.* δ correlation in Figure 5 is also successful because the uniformly small size of these agents implies a roughly constant value for the configurational entropy of mixing. A second effect influencing the S *vs.* δ curve probably occurs with liquids which induce crystallization. Sorbents are considered to be insoluble in polymer crystals; by analogy with other systems (*e.g.*, polycarbonate and acetone[11]) we expect that partial crystallization of the film produces a lower equilibrium weight uptake than would otherwise occur.

We have recognized several other processes operating which could have obscured or distorted correlations of the types shown in Figures 4, 6, and 8. The first, and perhaps the most serious, of these is the differential expansion in specimen volume due to swelling. In the transient state of the swelling of a polymer by an agent there is, of course, a concentration gradient set up. The increase in surface layer volume in specimens not under external stress occurs primarily by polymer movement normal to the face of the polymer slab resulting in polymer orientation in that direction; that strong compressive forces were also set up in the swollen skin, balanced by tensile stresses in the dry core of the specimen, is most strikingly demonstrated by observations of core fracture.[14] If the specimen being swollen is under an external stress, then swelling tends to reduce the surface layer tensile stress simply by the volume increase. Unless crazing or homogeneous creep occurs rapidly enough, the surface layer tensile stress can easily be negated entirely in this manner. Furthermore, the greater is the equilibrium solubility of the agent in the polymer, the greater will be the stress reduction produced by swelling.

Often a plot of applied stress or strain *vs.* log time to craze initiation in a glassy polymer is a curve which asymptotically approaches a finite stress or strain level at infinite time. By contrast, in most of the crazing and cracking media used with poly(2,6-dimethyl-1,4-phenylene oxide) craze or crack initiation cannot commence after a certain maximum time $t_{\max}$. Different liquids produce different values of $t_{\max}$: in acetone $t_{\max} \simeq 3$ min, in hexamethyldisiloxane $t_{\max} \simeq 4$ hr, and in air $t_{\max} > 24$ hr. Thus the values of ϵ_c correspond unavoidably to different times under strain and thus to different rates of craze initiation.

Clearly $t_{\max}$ depends on the magnitude of S and to this degree is correlated by δ. However, it also must depend on the diffusion coefficient, D, of the agent in the polymer. Not only is D well known to exhibit concentration and time dependence but also a marked dependence on diffusant molecular size. These variations of D and S might be expected to combine to produce rather complex changes in $t_{\max}$ from one liquid to the next.

Craze initiation and growth are, of course, rate processes involving viscous movements in the glassy polymer, so that ϵ_c is time dependent for that reason alone. Tests designed to elucidate critically the most fundamental aspects of solvent crazing would ideally determine the strains at which, in a given environment, craze initiation occurred at the same time. For the foregoing reasons these cannot be determined while the agent is being adsorbed by the stressed polymer. The rough proportionality between ϵ_c and σ_{cfy} exhibited in Figure 11 provides an indication that the ranking of ϵ_c values is not grossly distorted by kinetic aspects of swelling, however.

A second source of potential distortion in ϵ_c arises from the competition of homogeneous creep with craze formation as a means of reducing elastic strain energy. Creep of this kind has been shown here to begin in the strain range 1–2% and since orientation is known to make craze formation more difficult, the values of ϵ_c are somewhat altered when high applied strain levels are necessary (*i.e.*, in air, formamide, and the perfluorocarbons).

In general tests in which the concentration of the agent under study is made uniform throughout the polymer before application of external stress are potentially capable of elucidating in a more ideal fashion the fundamental role of the crazing agent. The tensile tests on the equilibrated thin films reported here may be regarded as first approximations to what is needed. However, this procedure cannot be used to examine the reduction in craze resistance of the polymer from the dry state since a craze formation yield stress is not observable in the dry polymer. It might ultimately prove more satisfactory therefore to compression mold sheets from previously equilibrated polymer powder and to perform static fatigue tests on bar specimens cut from such sheets.

B. Surface Energy Effects. There still remains the question of why craze formation exists as a competitive mode of plastic deformation. More specifically, why does not the incorporation of plasticizer in the polymer simply lower the shear yield stress? Increasing the test temperature is well known to cause a roughly linear decrease in σ_{sdy} to approximately zero at T_g.[15-17] The same appears to be true of the critical stress or strain for crazing although available data are more scarce.[18,19] We might expect then that if temperature increase and plasticizer incorporation were interchangeable in their effects that such incorporation into a shear-deformable polymer like poly(2,6-dimethyl-1,4-phenylene oxide) or polycarbonate would simply cause a reduction in σ_{sdy}. We believe that part of the answer involves the ability of the agent to stabilize energetically the surfaces of the holes in the craze and thus make easier its formation.

We wish to set down here three sets of observations and arguments which are consistent with the hypothesis that environmental stress crazing agents act as surface stabilizers (an equilibrium function) independently of their plasticizing action (a kinetic function). First, it is suggested that certain liquids of δ so far removed from that of the polymer that they are insoluble in it still reduce polymer surface free energy to zero, or nearly so. Second, these same liquids produce a noticeable enhancement in the ease of craze formation.

The difference between the free energy of the internal surface of the craze when air filled and when liquid filled is given by $\gamma_{\mathrm{sa}} - \gamma_{\mathrm{sl}}$, where γ_{sa} is the solid–air surface tension and γ_{sl} is the solid–liquid interfacial tension.[8] When a drop of liquid exhibits a finite equilibrium contact angle θ on the solid, then of course the Young equation is applicable

$$\gamma_{\mathrm{sa}} - \gamma_{\mathrm{sl}} = \gamma_{\mathrm{la}} \cos \theta$$

where γ_{la} is the liquid–air surface tension. Unfortunately, all of the agents used here except formamide

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[14] P. H. Hermans, "A Contribution to the Physics of Cellulose Fibers," Elsevier Publishing Co., New York, N. Y., 1946, p 23.

[15] R. A. Ekvall and J. R. Low, Jr., *J. Appl. Polym. Sci.*, **8**, 1677 (1964).

[16] R. E. Robertson, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; *Polym. Preprints*, 1501 (1967).

[17] R. D. Andrews and W. Whitney, Textile Division Report No. TD-123-64, submitted to U. S. Army Natick Laboratories, May 1, 1964.

[18] E. E. Ziegler and W. E. Brown, *Plast. Technol.*, **1**, 341, 409 (1955).

[19] M. A. Sherman and B. M. Axilrod, *ASTM Bull.*, **191**, 65 (1953).

spread on the surface of poly(2,6-dimethyl-1,4-phenylene oxide) and therefore with them no equilibrium contact angle exists. With few exceptions therefore $\gamma_{sa} - \gamma_{sl}$ cannot be determined so that it is not possible to determine directly and simply the degree of energetic stabilization by all these liquids at the surfaces of the holes in the craze.

However, on polymer film which has been cleansed by rinsing with hexane, the contact angles of distilled water and of formamide are about 75 and 51°, respectively, as measured here. These values together with the values of γ_{la} for these liquids lead to $\gamma_{sa} - \gamma_{sl}$ equal to 21 and 36.5 dyn/cm, respectively. Polystyrene has a critical surface tension γ_c of 33–43 dyn/cm according to Ellison and Zisman.[20a] If γ_c is equal to γ_{sa} as several workers maintain,[20b] then we expect, on the basis of similar values of δ for poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene, that γ_{sa} for the former will be in the range of 35–40 dyn/cm also.[21] Thus filling the craze holes with pure water reduces their surface energy by about 50%, while use of formamide nearly obliterates their surface free energy if these estimates are approximately correct.

Although ϵ_c in formamide appears to be rather similar to that in air (Figure 4), there are nevertheless striking differences observable in ease of craze growth and in craze strength in these media. In particular, constant strain rate tests (0.05 in./min) carried out on films of the polymer show that (a) when air is the surrounding medium the polymer fails at 10,500 psi in the shear mode of ductility as in Figure 9, no sign of craze formation being observed; (b) when water is brought in contact with the polymer at the time of test initiation, a few crazes are seen to develop sometimes, but gross failure nevertheless always occurs at the same stress by shear ductility; and (c) when formamide is brought in contact with the polymer at the initiation of testing, craze formation is more widespread and fracture of one of the crazes is the mode of failure. (The fact that perfluorodimethylcyclohexane, another insoluble liquid, also causes craze formation and fracture is undoubtedly explicable in the same way.) The implication of these results is that the mode of failure of the polymer under Instron rate conditions is shifted from "ductile" to "brittle" simply by the presence of insoluble, but surface-stabilizing liquids.

Third, it is also likely that surface energy effects are largely responsible for the marked difference in the sizes of crazes in air and in a liquid. Grown in air they never attain a size of more than a fraction of a square millimeter in the plane of the craze. Grown, for example, in methanol, an agent of low solubility, they can cover the entire cross section of a linearly stressed specimen in 15 min or less. Since methanol solubility is small, it seems likely that this difference in ease of initiation and growth arises largely from craze internal surface stabilization by the liquid.

The foregoing analysis suggests that surface stabilization can be effected almost completely by liquids as dissimilar in δ from the resin under study as is formamide, while the observations of the effects of these liquids on mode of failure suggest that surface stabilization is sufficient to cause a transition to the crazing mode of failure. It then follows that all further reduction in craze resistance observed with liquids of δ more similar to that of the polymer is due almost exclusively to the plasticization effects detailed above.

Conclusions

Both plasticization and internal surface stabilization have been shown to influence craze formation and related phenomena. Evidence for the two effects has been obtained by way of a number of different experiments utilizing a large number of small-molecule liquids.

Surface stabilization by liquids appears tentatively to be responsible for switching the mode of failure from conventional cold drawing to crazing and fracture. This effect appears to approach saturation at values of δ of the crazing agent far removed from that of the polymer.

Plasticization, on the other hand, appears responsible for the marked reduction in critical strain at which crazes form. By contrast with surface stabilization, plasticization and its effect on crazing are sharply peaked near $\delta_{\text{liquid}} = \delta_{\text{polymer}}$. It is this difference in the regions of δ at which the two effects appear that makes possible a quantitative assessment of each effect.

Finally, stable crazes can no longer be formed when swelling occurs to the extent that T_g is reduced below room temperature. Crack formation occurs without intermediate craze formation.

Acknowledgments. We wish to thank Dr. S. W. Kantor for suggesting this problem and Drs. G. L. Gaines and R. E. Robertson for helpful discussions.

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[20] (a) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **58**, 503 (1954); (b) *e.g.*, F. M. Fowkes in the Symposium on the Chemistry and Physics of Interfaces, sponsored and published by the Division of Industrial and Engineering Chemistry, American Chemical Society, Washington, D. C., June 1964.

[21] Another method of estimating γ_{sa} utilizes the parachor, $P = \gamma^{1/4}M\rho$ where P is a material constant rather accurately calculable from constituent equivalents for different atoms and bond types, γ is the surface tension of the substance against air, M is molecular weight, and ρ is substance density. From this equation γ_{sa} for polystyrene is calculated to be about 42 dyn/cm and that for poly(2,6-dimethyl-1,4-phenylene oxide), 34.5 dyn/cm.