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Voids as a Source of Haze in Weathered Poly (2,2,4,4-Tetramethyl-1,3-cyclobutylene Carbonate)*

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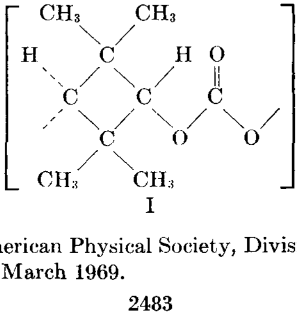
Synopsis

Long-term weathering studies of the subject transparent thermoplastic polymer revealed that sheets extruded from pristine resin gradually became hazy. Electron microscopy of fracture surfaces showed that minute voids were created during outdoor exposure. By the application of the Mie light scattering theory, it was possible to calculate that the average void size was 4×10^3 Å and that the concentration of voids numbered about 10^6/mm^3. Yet the total void volume of the poorest sample, which had a haze value of 26%, was less than 0.05%. The average void size decreased over a three-year period, but the concentration increased with exposure. A mechanism of void formation was formulated based on photo-induced molecular degradation. Chemical evidence suggests that molecular degradation occurs by complete unzippering of a molecule, resulting in the formation of carbon dioxide and 2,2,4-trimethylpentene-3-al. The aldehyde is believed to plasticize the polymer in the vicinity of a growing void and the carbon dioxide acts as a blowing agent, thereby generating a void. Simultaneously, free radicals formed during molecular decomposition initiate further degradation of neighboring molecules. The propensity of this resin to haze can be effectively overcome by suitable cleanup and stabilization procedures.

INTRODUCTION

Although the subject polymer (I) reportedly can be prepared over a wide range of *cis-trans* compositions,[1,2] the present study is restricted to amorphous polymers having a *cis/trans* ratio of 1.3 or more. At ratios near 1.0 the crystallizability increases, leading to possible impairment of optical properties during the molding or extrusion of this polymer.



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Long-term outdoor weathering tests of slot-extruded sheets prepared from pristine resin[3] revealed that haze developed in these sheets even though the mechanical stability was essentially unimpaired. Spontaneous crystallization was ruled out as a primary source of haze, partially on the basis of x-ray evidence, but mostly by observing that the transparency of hazy weathered sheets could be restored by cold pressing. Similarly, healing could be accomplished by briefly heating the sheets below the glass transition temperature (T_g 140–145°C).

Since the largest refractive index gradients arise from air–polymer interfaces, a microscopic examination for crazes, cracks, or other forms of voids was undertaken. Subsequently, spectrophotometric studies were conducted which enabled us to calculate the average size and concentration of voids in weathered sheets by the application of light scattering theory.

EXPERIMENTAL

Optical Microscopy

Some of the first experimental batches of slot-extruded sheet contained occasional cloudy regions which scattered light intensely. They were visible before weathering, even though the great majority of the extrusion had a transmittance of 91% in 0.45 mm sheets, which approaches the theoretical limit[4] of 93.3% for this thermoplastic polymer. The cloudiness is due to clumps of polymer which had an abnormally long residence time in the extruder. Microscopic examination reveals that these cloudy areas are made up of tiny individual bubbles which are either transparent gels or hollow spheres, mostly organized in the form of swirls or conic-like patterns

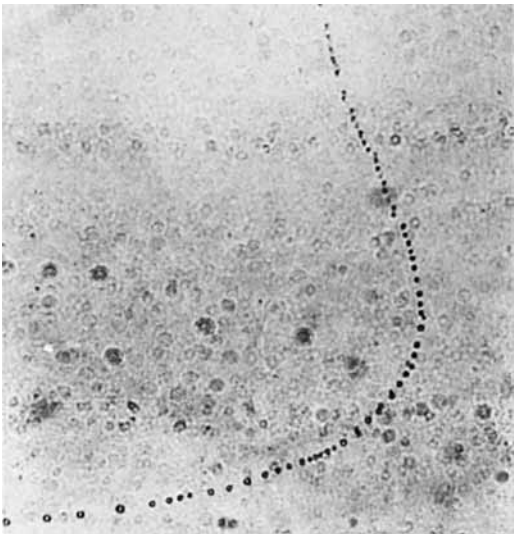


Fig. 1. A string of voids in thermally abused extruded first-generation polymer. Transmission optical micrograph ×325.

(Fig. 1). Contrariwise, the faint haze scattering sites in 0.25 to 0.50 mm weathered slot-extruded sheets cannot be resolved with the optical microscope.

Electron Microscopy

The cloudy region which afforded Figure 1 was fractured under liquid nitrogen. A two-stage poly(vinyl alcohol) and carbon replica was prepared of the fracture surface, which had been shadowed at an angle of 30° with uranium. Figure 2 is a fortuitous observation of a fracture through a conic-like section shown in Figure 1. Since Figure 2 is an electron micrograph of a negative replica, the hemispherical centers which appear to be raised are actually cavities in the original fracture surface. These depressed regions, which measure about 1.6 to 2 μ in diameter, are believed to be voids. The areas immediately surrounding the void cavities have a smoother fracture morphology than the major portion of the matrix. The reason for this smoother texture will be discussed later.

Fig. 2. Replica of a fracture surface of I generated under liquid nitrogen, corresponding to a string of voids such as was shown in Fig. 1. The round centers (voids) are surrounded by polymer which exhibits a smoother fracture morphology than the majority of the matrix. See text for explanation. Electron micrograph ×8,640.

Similar but smaller occlusions were found in fracture surfaces of extruded sheets that were originally highly transparent but developed visible haze after six months of exposure in Arizona (Fig. 3). The distribution of these scattering sites, which resemble fried eggs, was fairly random throughout the polymer. A rough calculation based on the population of scattering sites shown in Figure 3 reveals that there are about 10^6 scattering sites in each cubic millimeter of this particular weathered sheet.

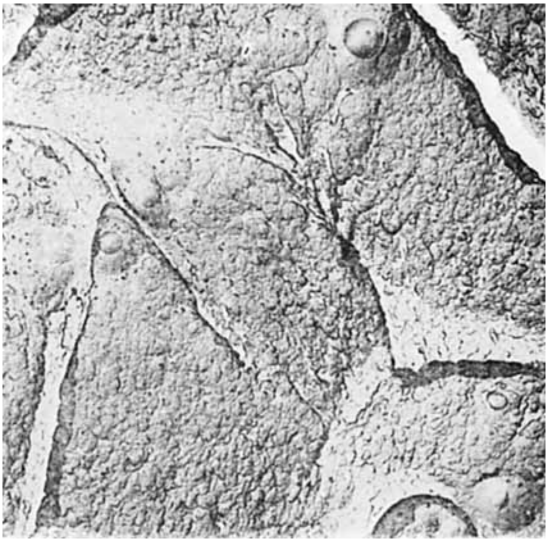


Fig. 3. Replica of a typical fracture surface of a hazy weathered polymer I. Fried egg-like inclusions similar to those shown in Fig. 2 are found scattered throughout the polymer. Electron micrograph ×6,210.

Healing of Voids

The foregoing microscopic evidence indicates not only that myriad small voids are formed during outdoor weathering tests, but also that the mechanism of formation may be very similar to the process which resulted in void formation owing to thermal abuse during extrusion. The conclusion that the optical scattering sites are voids is qualitatively supported by simple thermal and mechanical healing experiments.

It is a well-known fact that crazed glassy polymers can be healed by heating in the region of the glass transition temperature.[5,6] Therefore, we heated an extruded sheet that had developed a haze value of 26% during a two-year exposure in Arizona (ASTM test D1003, procedure A, using the Gardner pivotable sphere haze meter). The annealing was conducted in vacuo for 2 hr at 126°C, after which the sample had regained its original transparency.

The same weathered film that could be healed thermally was cold-pressed briefly at room temperature (24°C) at a pressure of 44,000 kg/cm^2. The film was clear after this treatment.

Density Measurements

It seemed reasonable to expect that an observable density change should accompany the formation of numerous voids in weathered sheets. Yet measurements conducted in a density gradient column did not reveal any difference between weathered and control films. The slight variations (± 0.0003 g/cm^3) were random and fell within the experimental errors of the measurement. The light scattering experiments in the next section will show clearly why a reduction in density could not be measured in weathered films.

Light Scattering Theory

According to light scattering theory, the size and concentration of a particle in a material of different refractive index can be calculated. The theory imposes several restrictions[7] which must be considered: (1) The shape of the particle must be known (sphere, plate, or rod). In the light of the electron microscope study, it seems quite valid to consider the voids as spherical. (2) The refractive index of the particle and medium must be known. In the present case, the refractive index of voids is taken as 1.00, and the polymer index as 1.457 at 5893 Å. (3) The particles must be independent, i.e., not aggregated or organized, so that scattering by all particles can be considered without regard to phase. The scattering is then incoherent. (4) The particles must be separated by at least three times the radius of the particle. If this criterion is not met, the effect of multiple scattering should be considered.

Criteria 3 and 4 can be tested experimentally. Although the electron micrograph (Fig. 3) indicates that the distribution of voids is not uniform, a test of the data was made which established that multiple scattering is negligible for most weathered sheets.[7] This subject is discussed in greater detail in the appendix.

There are basically two methods which afford a means of characterizing the inhomogeneities responsible for scattering light in a transparent medium. One is to direct a narrow beam of radiation upon a sample and study the angular distribution of scattered radiation. This radiation may be small-angle or wide-angle x-rays or visible light, depending on the average size of the inhomogeneity to be characterized.[8,9]

Although these experiments are simple to perform in principle, they are encumbered with practical difficulties.[10] Furthermore, the necessary equipment was not available in the writer's laboratory, nor were samples of the desired rod shape available.

Therefore, a simple transmittance method based on the exact Mie theory[7,11] was selected for this study. The method requires only that measurements be made in highly monochromatic light and that rays scattered by the sample be excluded from the detector. We employed a Cary Model 14 spectrophotometer (Applied Physics Corp., Pasadena, Calif.) which reportedly has a resolving power of 1 Å in the visible spectrum. Scattering is minimized by the sample chamber design and by maintaining the adjustable slit opening below 0.1 mm in the wavelength region of interest (near the sodium D line where the polymer refractive index is measured). The Cary Model 14 is a double-beam instrument that conveniently plots differential absorbance as a function of wavelength. Furthermore, a high-sensitivity scale is available for this instrument so that small absorbances can be measured with adequate accuracy.

The Modified Mie Theory

One simply measures the amount of light incident upon a polymer film, I_0, and the transmitted light, I, as a function of wavelength, λ_0. These experimentally derived values are related by

$$\eta = \frac{d(\ln|A|)}{d(\ln \lambda_0)} \tag{1}$$

where the absorbance A is equal to $\ln(I/I_0)$. The slope, η, is obtained from a plot of $\ln|A|$ versus $\ln \lambda_0$. We have adopted the symbols used by Zhurkov, Marikhin, and Slutsker[12] and Slutsker and Marikhin,[13] who first applied this theory to voids in crazed polymers.

Slope η is also a theoretically derived function of the average particle radius R, particle refractive index m_i, and the polymer index m_0. From the experimental η and the theoretical relation between R and η (at constant m_i and m_0) one obtains a measure of R. Then, the concentration of scatterers N can be determined for a sheet of thickness h. A more detailed discussion of the derivation of these parameters and a description of the experimental procedure is found in the appendix.

TABLE I
Calculated Diameter, Concentration, and Volume of Voids for Slot-Extruded Sheets Weathered in Florida and Arizona

Sample	Location	Exposure, months	Haze, %	Absorbance (@ 5893 Å)	Average void diam., Å	Void concentration, voids/mm^3 $\times 10^{-6}$	Void volume, %
1	Arizona	0	3.1	—	—	—	—
		6	6.5	0.017	4,900	0.17	0.0011
		12	9.0	0.025	3,300	1.1	0.0021
		24	10.0	0.032	2,900	2.5	0.0030
1	Florida	6	6.5	0.015	5,500	0.14	0.0012
		12	7.5	0.021	5,300	0.19	0.0014
		24	11.5	0.031	4,400	0.64	0.0028
		36	16.5	0.043	3,800	1.4	0.0040
2	Arizona	0	1.9	—	—	—	—
		6	3.0	—	—	—	—
		12	4.5	—	—	—	—
		24	9.0	0.036	2,700	5.5	0.0055
		36	18.7	0.085	2,600	12.6	0.013
2	Florida	6	3.0	—	—	—	—
		12	4.5	—	—	—	—
		24	5.0	0.015	2,000	5.8	0.0023
		36	12.1	0.038	2,100	15.9	0.0075
3	Arizona	0	1.8	—	—	—	—
		6	8.5	0.121	1,600	110	0.020[a]
		12	19.5	0.156	2,100	34	0.017[a]
		24	26.5	0.187	1,400	320	0.045[a]

[a] Values may be too large due to double scattering. See Appendix for discussion.

The size and concentration of voids calculated by application of the Mie theory is listed in Table I for several polymers weathered in a semitropical (Florida) and an arid (Arizona) climate. The corresponding void volume is also presented in Table I. The extremely small amount of void volume (0.001 to 0.045%) explains why density measurements could not detect the voids.

There is an apparently linear relationship between void volume and haze for samples 1 and 2 (Fig. 4) which is independent of the test location but dependent on the sample under investigation. The deviation between sample 1 weathered in Arizona or Florida may be real (Fig. 4) or due in part to the fact that haze measurements and light scattering measurements were not conducted on identical portions of film. The absorbance for samples having haze values below about 5% could not be determined with sufficient accuracy. This is the reason why suitably stabilized resins which have haze values of less than 5% after three years of weathering are excluded from this study. Such stabilized resins have initial light transmission values averaging 92.4%.

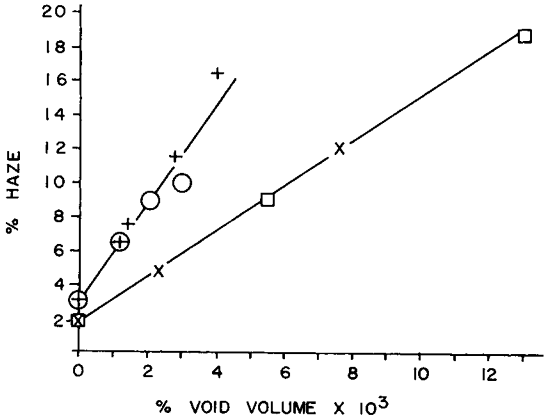


Fig. 4. Measured haze vs. calculated void volume determined for unstabilized sheets weathered in Arizona and Florida (Table I). (○) sample 1, Arizona; (+) sample 1, Florida; (□) sample 2, Arizona; (×) sample 2, Florida.

The data in Table I also reveal that the average void diameter decreases with the duration of outdoor exposure. Apparently, some sites are more photosensitive than others. These sites propagate the decomposition of a greater number of molecules and consequently form larger voids than sites which are not activated until prolonged exposure has taken place.

Sample 3 is an example of a sheet which exhibits double scattering as defined in the appendix. This effect was neglected in the calculation of the average void diameter. Consequently, the calculated void volume of 0.045% for a sample weathered two years in Arizona is greater than the true void volume.

Mechanism of Void Formation

It was recently disclosed that poly(2,2,4,4-tetramethyl-1,3-cyclobutylene carbonate) (I) thermally degrades in a unique nonuniform manner,[3] namely, that once a molecule begins to degrade, it degrades completely. The net effect is that the molecular weight of the remaining polymer is not substantially reduced by heating to pyrolysis temperatures, despite the fact that large volumes of gaseous decomposition products are generated.

The foregoing enables us to formulate the following simple hypothesis: Voids are formed in polymer I by a photoinitiated process which results in the probable total decomposition of any molecule once degradation is initiated in that molecule. The voids are larger than the volume occupied by any single molecule, but are not expected to be larger than about 0.5 μ since they generally cannot be seen by optical microscopy. Contrariwise, they must be greater than half a wavelength of light because they scatter light so intensely. The voids are spherical in shape, as contrasted to planar crazes, which are formed by an entirely different mechanism.

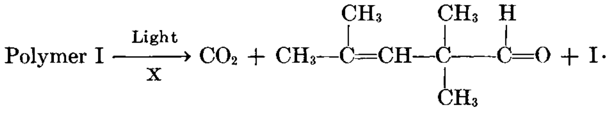
The photoinitiated process culminating in the development of haze is believed to follow the usual activated reaction sequence of induction, initiation, propagation, and termination.

Induction and Initiation

Haze formation is not spontaneous in polymer I when exposed to light. Even exposure to a highly intense source of light rich in the ultraviolet spectrum does not develop measurable haze within a 2 to 4 hr period. (A GE AH 6 lamp was located at one focus of an elliptical mirror, affording an intensity of 44 W/cm^2 at the second focus where the sample was mounted.)[14] This leads one to suspect that an additional catalytic agent such as oxygen must diffuse to a potential haze-forming site. The addition of weak acid salts or strongly basic metallic hydroxides is known to catalyze the controlled thermal degradation of I.[3] Since lithium hydroxide is reported to be a polymerization catalyst,[3] it is conceivable that trace quantities of residual catalyst may also act as a photoinitiated depolymerization catalyst. (Recall that this paper is concerned with the formation of haze in extruded sheets prepared from neat resins which had not been cleaned up or stabilized in any way. However, the resin can be prepared so as to afford products of exceptional ultraviolet stability.[3,15])

Visual and microscopic examination of sheets weathered six to 36 months gives one the impression that the scattering sites do not increase significantly in size. Therefore, the concentration and not the size of voids increases with time. This conclusion is corroborated by the results of the light scattering study summarized in Table I. Also, the amount of haze increases linearly with exposure time in two-year weathering studies.[3] Hence we conclude that the initiation of a haze site is a random process.

The evolution of trace quantities of 2,2,4-trimethylpentene-3-al and CO_2 was observed by mass spectroscopy of weathered sheets.[16] These substances were reported to occur by decomposition of I during polymerization by base-catalyzed ester interchange.[2] We do not observe these degradation products during polymerization by the route described by D'Onofrio.[3] The aldehyde is a solvent for I, although under some conditions it can also act as a crystallizing agent. These observations provide the key to at least one possible route to void formation in I. Photoinitiation of molecular degradation in I is feasible by the following route[17]:



$$\text{Polymer I} \xrightarrow[\text{X}]{\text{Light}} \text{CO}_2 + \text{CH}_3\text{—}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{=CH—}\underset{\text{CH}_3}{\underset{|}{\overset{\text{CH}_3}{\overset{|}{\text{C}}}}}\text{——}\overset{\text{H}}{\overset{|}{\text{C}}}\text{=O} + \text{I}\cdot$$

where X may be oxygen, catalyst residue, a radical, a susceptible site on the polymer chain, or any combination of these.

Propagation

Once a radical is generated, the entire molecule unzippers, releasing more CO_2 and aldehyde. It is also possible that photolysis of the aldehyde may occur,[18] releasing more volatiles and radicals which may initiate the decomposition of neighboring molecules. It is inappropriate to further discuss the many possible degradation routes that have been considered, particularly since little corroborative evidence is available.

The main point we wish to make is that both the aldehyde and CO_2 are believed to be essential to void formation. The aldehyde may be regarded as a localized plasticizer in the immediate vicinity of the growing void, which reduces the glass transition temperature to the environmental test temperature or lower, thereby enabling the CO_2 to act as blowing agent which enlarges or otherwise maintains the void while it is being formed.

One molecule of I, having a typical average molecular weight of 40,000, can release enough CO_2 upon degradation to generate a void whose diameter is about 500 Å at 1 atm. This assumes that no diffusion of CO_2 occurs away from the void site. Quite obviously, more than one molecule must degrade to form voids of an order of magnitude greater in size such as were found in this study.

Polymer I is quite permeable to CO_2. For example, 0.64 cc (STP) diffuses through a 0.25-mm sheet per cm^2 per 24 hr when a pressure of 29 kg/cm^2 is maintained on one side of the film.[19] We conclude that degradation at a growing void site must be very rapid once photolysis has been initiated, despite the fact that initiation may not occur for many years of outdoor exposure. The permeability of CO_2 through I plasticized with the aldehyde has not been determined.

Termination

Termination may be due to at least three factors: (1) The photoinitiated decomposition reaction may self-terminate if the cocatalyst X is immobilized or chemically inactivated. (2) The internal stress generated by the growing void is balanced by the polymer matrix surrounding the void. (3) The polymer molecules at the void surface become oriented. Since the aldehyde can induce crystallization of I, it is conceivable that the polymer at the void surface may crystallize. This results in the formation of a higher modulus region which resists further deformation.

There is indirect evidence which supports the third proposal. X-Ray diffractometer traces were recorded for a weathered sheet and the corresponding unweathered control. A slight shoulder appears on the broad amorphous halo of the weathered sample at the expected position of the most prominent reflection (110).[20] The most logical location of this very small amount of crystallinity would be in the plasticized region surrounding a void. However, the observation that voids can be thermally and mechanically healed would seem to contradict the crystallization proposal.

CONCLUSIONS

Void formation is often associated with crystallization of crystallizable polymers.[21] For example, it is well established that cracks form along the edge of polypropylene spherulite fibrils.[22,23] These voids form because of a volume contraction which occurs as most polymers crystallize. A notable exception is poly-4-methylpentene-1, which expands on crystallization at room temperature.[24] However, the evidence we have presented clearly indicates that the voids in I are not due to crystallization of the bulk polymer.

It has also been reported that "frosting" (unresolved crazes) can be caused by the loss of some volatile or leechable component.[4] However, crazes are planar whereas our voids are spherical. The electron micrographs of fracture surfaces inform us that smooth cavities exist in weathered samples of I. (It is quite reasonable to assume that fracture occurred through the voids, thereby exposing the hemispherical cavities.) A more objective argument in support of the void hypothesis is the excellent agreement between the expected and calculated average void size.

The computations based on light scattering theory inform us that the scattering sites (1) have a large refractive index difference from the polymer, (2) are small in size, and (3) are large in number. If the wrong mathematical model had been employed, the results would have been anomalous.

APPENDIX

Following Zhurkov, Marikhin, and Slutsker[12] (ZMS), we note that η can be expressed as a theoretical function of R, as follows:

$$\eta = \frac{\rho}{K(\rho, m_i)} \frac{\partial K(\rho, m_i)}{\partial \rho} \qquad (2)$$

where

$$\rho = 2\pi R\, m_0/\lambda_0. \qquad (3)$$

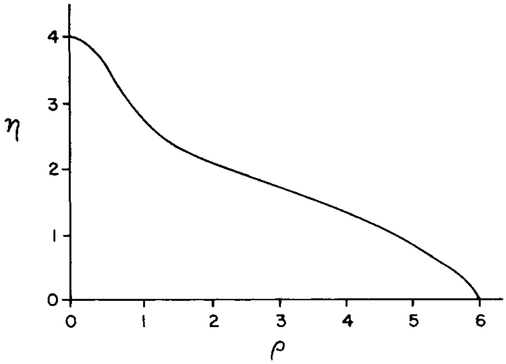


Fig. 5. η derived from the Mie theory vs. ρ, for a void in a medium of refractive index = 1.50. (After Zhurkov, Marikhin, and Slutsker.[12] Reprinted with the permission of the American Physical Society.)

$K(\rho, m_i)$ can be evaluated from the Mie theory if m_0 and m_i are known. ZMS calculated the scattering coefficient $K(\rho, m_i)$ for spherical cavities ($m_i = 1$) dispersed in a medium of refractive index $m_0 = 1.50$. This afforded a plot of η vs. ρ (Fig. 5)[13] from which the average radius of the scatterer R can be calculated by eq. (3). Finally, from the relation between $K(\rho, m_i)$ and ρ (Table II), one obtains the concentration N of scatterers from eq. (4)[13]:

$$A = \pi R^2 N h K(\rho, m_i). \tag{4}$$

It is now possible to reduce the experimental data in the following manner. The absorbance A is measured as a function of λ_0, and then the absorbance is plotted against λ_0 on log-log paper. The slope of the curve obtained at the appropriate λ_0 gives the value of η, which in turn enables one to obtain ρ from Figure 5. The average particle radius is now obtained from eq. (3). Then, the concentration N is obtained from eq. (4), supplying the appropriate value of $K(\rho, m_i)$ from Table II.

TABLE II

The Functions ρ and $k(\rho, m_i)$ for $m_0 = 1.5$ and $m_i = 1.0$[a]

ρ	$k(\rho, m_i)$
0	0
0.5	0.0072
1.0	0.0753
1.2	0.1255
1.4	0.1892
1.6	0.2653
2.0	0.436
2.2	0.539
2.8	0.865
3.0	0.981

[a] From Zhurkov, Marikhin, and Slutsker.[12] With the permission of the American Physical Society.

Errors

The values of η presented in Figure 5 were derived from $m_t = 1.50$. This introduces an error of about 1% in η for I which has a refractive index of 1.46. Similarly, $K(\rho, m_t)$ values in Table II are slightly too high for the same reason. However, the error introduced is negligible, since the absorbance is only reproducible to ± 5% for a given film, primarily because haze varies somewhat over a weathered film and the film thickness is not known to be better than 3%. The films studied in behalf of this paper were slot extruded and contained numerous striations that contribute to the uncertainty in absorbance measurement. The experimental data reported in Table I represent the average of triplicate measurements.

An additional source of error is introduced in the experimental determination of absorbance, due to the relatively large slit size employed in this investigation. Smart and Willis[25] reported that the receiver system of the Cary Model 14 spectrophotometer affords too large an aperture for the accurate measurement of refractive index. (These authors found it necessary to reduce the apertures of the instrument in order to measure the refractive index of polystyrene latices to ± 0.002.)

We estimated the extent of this source of error in the present study by selecting a representative film having a haze value of 11% and then measuring the absorbance as a function of wavelength for slits ranging from 0.007 mm (the smallest practical width) to 0.022 mm (the widest slit encountered in our studies at 5893 Å). We obtained a linear relation between slit size and η (measured) over this range of slit sizes. Extrapolating to zero slit width, for the purpose of estimating the largest error on η, we find that η_0 is 6% less than $\eta_{0.011}$. The latter is the value of η determined for an average slit width of 0.011 mm at 5893 Å. We regard this error as representing the maximum error that is introduced in η for a typical sample, for as the slit size is reduced, η (true) will be somewhere between η (measured) and η_0.

The effect of a 6% error on ρ, $\Delta\rho$, depends on the value of η (Fig. 5). Generally, for the data in the present study, $\Delta\rho$ does not exceed +10%. The average void diameter listed in Table I may, therefore, be as much as 10% too large. A similar consideration of the concentration N for $\Delta\rho = +10\%$ reveals that N could be up to 50% less than presented in Table I. Finally, the void volume could be $^1/_3$ less than shown in Table I. It should be emphasized that these estimates represent maximum errors which could be attributed to slit size. Still, these seemingly large errors should not detract from the primary objective of this paper, which is to establish that voids are the source of light scattering in weathered films of polymer I.

Illustrative Determination of Void Volume

In order to obtain the absorbance in weathered films which is due only to light scattered from voids, it is necessary to subtract the contribution of scattering from the polymer surface and from internal sources such as

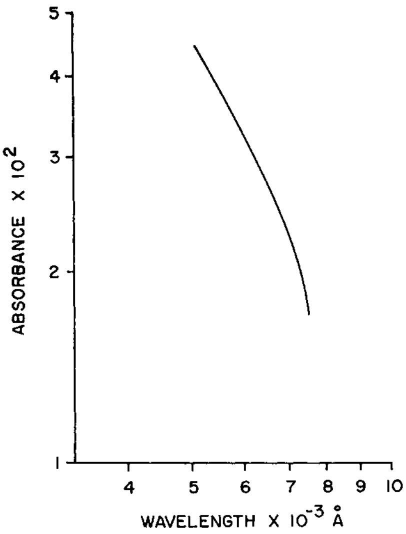


Fig. 6. Absorbance vs. wavelength for sample 1 weathered 24 months in Arizona. Thickness 0.30 mm. Referenced against a neighboring region of weathered film that had been healed at 124°C for 5 hr in vacuo. Note that slope η is a function of λ. From the appropriate value of η one determines ρ from Fig. 5, which then affords R, the average void radius, eq. (3).

opaque foreign bodies. In principle, this can be accomplished in a very simple manner in a double-beam spectrophotometer by placing a suitable unweathered film in the reference beam. Unfortunately, the experimental resins we examined were slightly colored, having a faint absorption band just below 6,000 Å. This yellow color fades upon outdoor exposure, which is very desirable from a practical standpoint but introduces the complication that color variations between the sample and reference material interfere with the absorbance measurements of haze.

For this reason, thermally healed weathered films were used to compensate the weathered films. The variations in sample thickness, color, and inhomogeneity concentration can then be perfectly balanced, since a portion of film immediately adjacent to the test specimen can be healed. The only requirement is that healing must be complete. This can be qualitatively established by visual inspection. Tests were conducted and it was found that healed samples heated for 5 hr do indeed make better reference samples than unweathered films. A suitable healing temperature was found to be 125–130°C, although low-haze films may require a higher temperature and high-haze films[6] a lower temperature. The upper healing temperature is limited by a tendency for the resin to crystallize.

The reference and sample films are measured to the nearest 0.05 mm. The films are inserted in matched 1 mm slotted sample cells containing an immersion fluid of the same refractive index as the polymer. This minimizes the effect of scattering from the rough surface of the slot-extruded sheets.

It was also found helpful to mount the films so that the direction of extrusion is at 90° to the length of the slit in the spectrophotometer in order to average out thickness variations.

Absorbance differences of 0.001 can be detected with the high-sensitivity slide wire of the Cary spectrophotometer. The slit width is adjusted to the lowest level which will still maintain automatic slit compensation in the visible spectrum. This provides sufficient energy to detect meaningful absorbance differences associated with haze values of 5% or more (Table I) and yet the slit width at 5893 Å is less than 0.03 mm. The resulting absorbance–wavelength curve is then read over the spectral range of 5000 to 7500 Å. The data are then plotted on log-log paper as illustrated in Figure 6.

It can be seen that there is a slight curvature to Figure 6, whereas the literature describes these curves as straight lines.[12, 13] Since ρ is a function of λ_0, the slope of Figure 6, η, cannot be a constant. Instead it is expected that the slope should vary as shown in Figure 6. The anomaly in the published data may be due to the fact that the theory was based on the assumption of the existence of spherical voids, whereas the crazes which these authors were studying are generally regarded as planar.

Once the slope of Figure 6 is determined for a sample (we measured the slope at 5893 Å, the value at which the refractive index was measured), the corresponding ρ value is read from Figure 5. This leads to a calculation of R and N as described earlier.

Criterion of Independent Scattering

Light scattering problems are considerably simplified if independent particles exist such as the water droplets in a fog. If the particles are sufficiently far from one another, it is possible to study the scattering by a single particle without reference to the other particles. The assumption of independent scattering implies that there is no systematic relation between the phase of rays scattered from different portions of the sample. For all practical purposes, the intensities scattered by the various particles must be added without regard to phase.

Independent scattering occurs for particles separated by more than three times the average particle radius. To determine if single scattering occurs, the intensity of beam passing through a sample is reduced by extinction to e^{-A} of its original value. If A is less than 0.1, single scattering prevails, and for $0.1 < A < 0.3$ a correction for double scattering may be needed. For $A > 0.3$, multiple scattering theory applies (ASTM test D 1003, procedure A).

Referring to Table I, the absorbance of sample 3 is greater than 0.1. Consequently, the data for this resin is in error, since no allowance for double scattering was made. Failure to apply a correction will make the calculated void volume appear too large. Hence, the true void volume of the sample having a haze value of 26% is less than 0.045%.

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