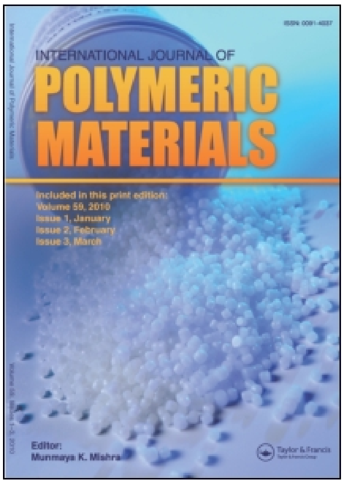

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Effect of the Quenching Temperature on the Fields of Thermal Stresses and on the Mechanical and Thermal Properties of PMMA

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This study explores the photoelasticimetry as a means to investigate factors affecting the residual stresses, particularly the thermal stresses, in polymethyl methacrylate (PMMA). The aim was to study the effect of quenching temperature in three different media: air, water, and ethylene glycol, on the impact strength and thermal properties of PMMA. These temperatures varied from a fixed value of 120°C to various values below Tg and the fields of distribution of cooling stresses have been obtained using a charge-coupled device (CCD) camera. It was observed that the quenching in water at 20°C gives rise to an important density of tensile stresses. However, in the ethylene glycol at 110°C this density has a tendency to disappear. An approximate evaluation of these stresses in a point near the specimen center has been assessed, and it was found that the distribution profile of the fields of tensile stresses was much closer to a parabolic form. Notched Izod impact strength and heat deflection temperature (HDT) were measured, and were found to be particularly sensitive to thermal stresses.

Keywords: heat treatment, photoelasticimetry, PMMA, thermal stresses

INTRODUCTION

Residual stresses, that is, the stress present in a specimen without any external influence on it, in inorganic and polymeric glasses have received much attention in the past because of their technological

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importance [1–3]. The residual stresses that are produced by transient thermal gradients have been extensively studied by the process of free quenching [4–5]. Different techniques have been used for the experimental measurement of residual stresses in polymeric materials. These include the splitting of a disk-shaped specimen [6], hole drilling [7], the layer removal technique [8], the birefringence [9], and the chemical probe technique [10]. Other methods include surface hardness [11], stress relaxation [12], and photoelasticimetry [13]. There are also other techniques that allow to obtain complementary information. For example, immersion in n-heptane can give information about both the direction of the main stresses and their concentration [14]. The Photoelastic method is still a subject for research. The method relies on the birefringence property exhibited by transparent plastics. In particular, the phenomenon of stress (or load) induced birefringence is used where the materials become birefringent under the influence of external loading. This phenomenon was first observed by David Brewster in the early nineteenth century in glass and he foresaw the potential use of this for stress analysis [15]. The technique is easy to apply, quite accurate, and does not require any additional operations but it is limited to transparent polymers exhibiting photoelastic effects such as poly(methyl methacrylate) (PMMA), polystyrene (PS), and polycarbonate (PC). Compressive residual stresses on the surface are known to improve the impact strength by increasing the transition thickness at which the failure mode changes from plane stress to plane strain [16]. Broutman and Krishnakumar examined the effect of residual stresses on the Izod impact strength of PMMA and they observed that it is not influenced by the quenching [17].

Siegmann et al. [18] investigated the effects of the residual stresses on crazing and softening behaviors of PS and PMMA quenched from various temperatures into ice water. Both PS and PMMA showed decreased heat deflection temperatures as the magnitude of the residual stresses increased.

The purpose of this study is to investigate the effect of the temperature of quenching on the distribution of the fields of the thermal stresses, observed in the isochromatic fringe pattern obtained by CCD camera using the photoelasticimetry method. The effects were studied by measuring the Izod and Charpy impact strength and HDT of quenched and untreated samples as a function of the quenching temperature.

PHOTOELASTIC TECHNIQUE

The photoelastic method requires no machining operation. This method is based on accidental birefringence. The experimental setup

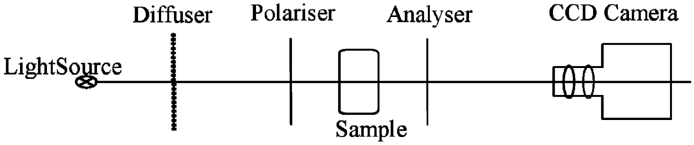


FIGURE 1 Basic arrangement of a polariscope.

is a standard polariscope illustrated in Figure 1. The same traditional transmission-type photoelastic arrangement was employed with a CCD camera to replace the human eyes and record the image. For this study, the isochromatic fringe patterns have been obtained by CCD camera with 512 × 512 pixels (256 levels of gray) coded on 8 bits. Because 256 levels of gray cannot be discerned by the naked eye, it was necessary to decrease these levels to 16, and this by programming in C turbo. Therefore the colors revealed are not real colors. Every level of gray corresponds to a color. By electronic transduction and using a Matrox card, one could store these pictures under the form of a file. Visualization and quantification of the state of stress in some area of a plan of the studied sample is therefore possible.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The material used was a commercial plate of PMMA. Rectangular specimen of dimensions 140 mm long × 9 mm wide × d mm thick, were cut from the plates and polished with iron oxide powder, followed by aluminium oxide powder on a polishing wheel, to remove surface flaws and to provide sufficient clarity for the optical observations. Samples with no detectable residual stresses between the cross polarizer were used. Wider samples were required for this test in order to increase the sensitivity of the CCD camera and improve the observation of the stress fields.

HEAT DEFLECTION TEMPERATURE (HDT) MEASUREMENT

In order to measure the heat deflection temperature (HDT), additional samples were machined from beams (110 × 9.8 × 8 mm). The HDT of the moldings was obtained in accordance with ASTM D648, which defines HDT as the temperature at which the specimen deflects by 0.26 mm under a load of 1.8 MPa while being heated in an oil bath at a rate of $2^{\circ}\mathrm{C\,min^{-1}}$.

MECHANICAL TESTS

Impact Testing

The impact strength of quenched untreated and annealed samples that were heat treated by the process described later as a function of depth of the notch was determined. The commercial sheets were cut into strips. The room temperature (25°C) reverse notched Izod impact test and Charpy impact test were carried out using a 7.5 Joule pendulum following the ASTM256 procedure. The molded test bars were left for 24 h in the testing laboratory prior to notching with a broaching tool. The Izod impact samples (63 × 12.70 × 8 mm) were notched with radii of 0.13 mm, 0.30 mm, and 0.5 mm. They were notched such that the tip of the notch was located in the residual compressive zone, or as near as possible to the boundary between the two zones. These stress zones were determined by photoelastic examination of the sample between cross Polaroids under white light prior to notching. The Charpy impact samples (127 × 12.7 × 8 mm) were notched with radii of 0.5 mm, 1.5 mm, and 2.54 mm. The mean values are shown in Tables 1 and 2.

TABLE 1 Charpy Impact Strength of Untreated Annealed and Quenched PMMA as a Function of Notch Radius

	Charpy impact strength (KJ · m^{-2})				
			Quenching temperature (°C)		
Notch tip radius (mm)	Untreated	Annealed	0	20	40
0.50	19.91	23.33	19.15	24.51	23.75
1.50	24	21.48	20.02	22.32	18.13
2.54	17.84	17.22	16	14.15	31.25

TABLE 2 Izod Impact Strength of Untreated Annealed and Quenched PMMA as a Function of Notch Radius

	Izod impact strength (KJ · m^{-2})				
			Quenching temperature (°C)		
Notch tip radius (mm)	Untreated	Annealed	0	20	40
0.13	3.99	3.23	7.95	9.44	1.09
0.30	3.02	2.77	8.31	5.04	3.27
0.50	2.56	1.79	3.33	4.61	5.12

Hardness Testing

The Shore D hardness and Rockwell R scale were determined on PMMA sheets impact bars (50 × 50 × 3 mm). The Shore D was conducted following ISO/869 test procedure. A 5 Kg load was used on the test stand to apply the durometer indenter onto the flat specimen surface. But the Rockwell R scale hardness was carried out using a 60 Kg major load and steel ball indenter. The mean values are shown in Table 3.

THERMAL TREATMENT OF SAMPLES

Free quenching experiments were carried out using the following procedure. Before quenching, the sample was heated at 120°C in a small hot-oven and held at this temperature for 4 h. At this temperature there was almost no flow of the material, and it can be assumed that the molecular orientations present in the specimen could relax. The aim is to ensure that the sample is in a state so that any stresses (molecular orientation) induced by forming, polishing, and so on are rapidly relaxed, leaving the material in an unstressed state. The sample was then removed from the oven and rapidly dropped into stirred thermostated bath at temperatures equal to 0, 20, 40, 60, and 110°C or in the air at ambient temperature, within a second. In this way, the heat transfer and associated stress development are largely two dimensional and the sample is not allowed to cool at ambient air before the quench and a good reproducibility is achieved. This process placed the outer surface of the sample in a state of residual compressive stress and the inside of the sample in a balancing state of tension. In order to prevent any change in the final stress profile, the samples were allowed to reach slowly ambient temperature. Annealed samples were obtained by slow cooling in the oven to room temperature.

TABLE 3 The Effect of Quenching Temperature on Hardness Shore D, Hardness Rockwell and HDT

Quenching temperature (°C)	Hardness shore D	Hardness Rockwell R	HDT (°C)
0	79.93	28.66	80
20	76.33	24.33	71.50
30	81.26	27	72
40	77.78	27.33	92
60	79.16	27.66	79.5
Untreated	77.86	29.66	85

RESULTS AND DISCUSSION

Cooling Stress

The birefringence of hard polymers like PMMA results from anisotropy of polarizability of atom groups repeating in the backbone chains. This anisotropy is the result of structure deformation, change of valence angles, and changes of distances between atoms [19]. Because the birefringence of PMMA is sensitive to the state of stress in the material, the band separating the compressive strained area, which corresponds to the zero order fringe, appears black when the sample is examined in this manner. The observed molecular anisotropy in a quenched specimen may be explained in terms of "frozen-in entropy stresses" introduced by Struik [20]. These stresses are attributed to the sudden arrest of the micro-brownian motion of molecular chains when the specimen is rapidly cooled to below T_g, the glass transition temperature.

In the case of thermal stress (symmetrical free quenching), due to nonuniformity of cooling of the outer and central layers, compressive and tensile stresses form in the material with two neutral lines, which separate the zones of stresses situated in a symmetrical manner to some percent of the thickness of the sample (Figure 2). With a simple thermo-rheological material like PMMA the stress distribution would be parabolic with the maximum compressive tensile stress at the center of the specimen and the maximum compressive stress at the surface with a magnitude exactly twice that of the maximum tensile stress [21]. These stresses are frozen in, and the material conserves some internal stresses, revealed in polarized light by some colors. Using a standard polariscope, the photoelastic color sequence observed with increasing stress from the neutral line is: black (zero), then yellow, red, blue-green, yellow, red, green, yellow, red, green,

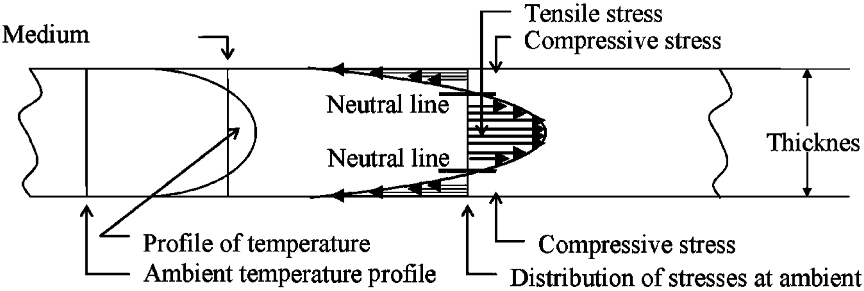
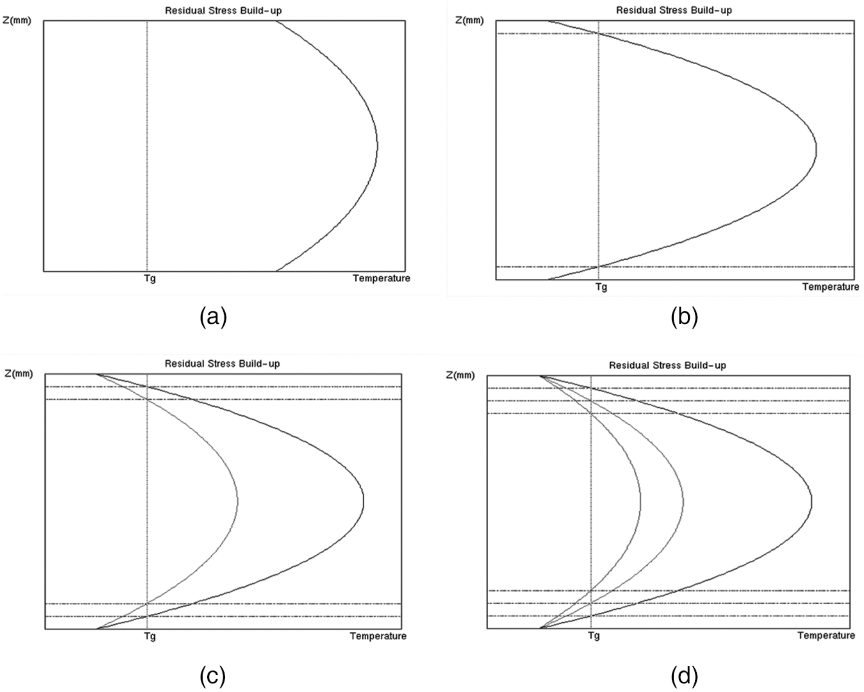


FIGURE 2 Temperature and stress distribution in a plastic resulting from cooling (symmetrical free quenching case).

and so on. The transition line between the red to green colors is defined as a “fringe” (from the phenomenon of birefringence). In this case the appearance of a uniform color represents a uniformly stressed area.

The important advantage of photoelasticity method applied with CCD camera is its ability to quantify the fields of tensile stress. When a photoelastic material is subjected to thermal stress and viewed with polarized light using CCD camera, colorful patterns of area are seen that are directly proportional to the level of stresses and strains in the material. In this case, the appearance of a uniform color represents a certain level of stressed area.

The following figures (Figure 3 (a–d)) [22], despite the fact that the samples in this case were injection molded, based on an assumed parabolic temperature distribution, can be used to illustrate how the residual stress develops in the free quenching specimens during the cooling process. During the cooling stage, the polymer cools at different rates from the surface to the center.



(a) (b)

(c) (d)

FIGURE 3 Profile of temperature through the thickness of the specimen: (a) at time t_o; (b) at time t_1; (c) at time t_2; (d) at time t_3.

At time t_0, cooling starts, the melt temperature is above the glass transition temperature T_g. At time t_1, the outer layer begins to solidify without any resistance from the liquid core when its temperature decreases to the glass transition temperature T_g.

At time t_2, the second layer begins to solidify when its temperature decreases to T_g. Because the outer layer has already solidified, the shrinkage of the inner layer is resisted by the solidified one, thus leading to a tensile stress in the inner layer and compressive stress in the outer layer.

At time t_3, the third layer begins to solidify when its temperature decreases to T_g. Again, the shrinkage of the inner layer is resisted by the solidified outer layers, thus leading to a tensile stress in the core and compressive stress at the surface.

Effect of the Temperature of Quenching and Sample Thickness

The pictures of the isochromatic fringe patterns of tinted and transparent PMMA are represented in Figures 4 and 5. It is observed that for both samples, the area in the central zone of the tensile stresses shows first a small increase with increasing quenching temperature (bath temperature), reaching a maximum and then decreasing. At 20°C, near the ends of the sample the isochromatic fringe are extended and irregular in shape as can be observed in Figure 6 (b). Because fields of thermal stresses are quite large, they are stopped by the fields of thermal stresses of the end effects. This is probably due to the rate of cooling. Of course, the surface layers cool very rapidly, but the interior portions cool at a fairly constant rate as the heat transfer becomes controlled by the thermal diffusivity of the solid. Perhaps this is attributed to the increase of the heat transfer (thermal conductivity). These observations are in disagreement with the works of Mittal and Khan [23], who studied the PMMA and noted that both compressive and tensile stresses increase when temperature of quenching decreases and the temperature of annealing is kept constant.

The formation of stress fields through the thickness of the sample could be explained as follows [4]: Physically one can imagine a situation near the beginning of a quench in which the core is still hot but the surface has already cooled below T_g. The core is largely able to accommodate the contraction of the cool surface because it is still hot and relaxes quickly. In due time, however, the core also drops below T_g and tries to contract, although it is prevented from doing so and is held under tension by the solidified edges. Because the overall sample is exposed to no external stresses, the final situation

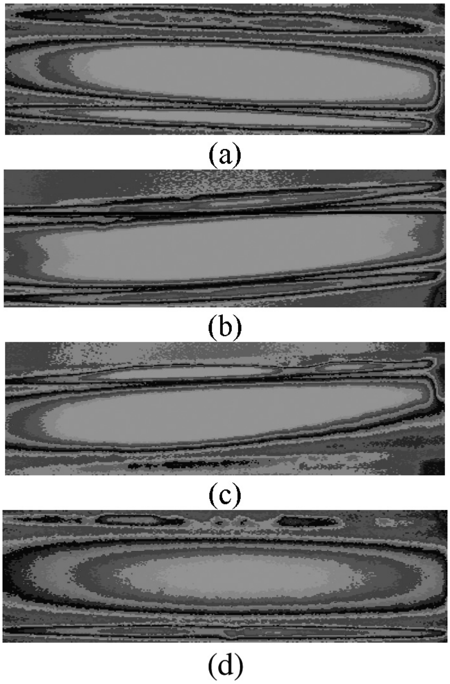


FIGURE 4 Isochromatic fringe patterns obtained by CCD camera (polarizer and analyzer crossed) of samples annealed for 4 h at T = 120°C and quenched at: (a) T = 0°C; (b) T = 20°C; (c) T = 40°C; (d) T = 60°C. Tinted PMMA, d = 10 mm.

is therefore the existence of surface layers being under compression and balanced by central layers under tension. It is clear that the isochromatic fringe patterns in the center that reflect the tensile stresses distribution are very similar to the assumed parabolic temperature distribution.

In tinted PMMA the shape of the isochromatic fringe patterns are regular, due to the presence of the pigment, which increases the thermal conductivity of the material.

From Figure 6, for the sample with a thickness of 15 mm, one notes that at 0°C the concentration of the stress fields is important at the center, because the peripheral layers are cooled rapidly, whereas the center is still hot. In the air (ambient temperature), the stress fields tend to standardize along the thickness. In this case, a gradual cooling takes place between the peripheral and the central layers. The density of the stress fields disappears at 110°C. From Figure 7, starting from the sample with a thickness of 10 mm, one notes the evolution of the

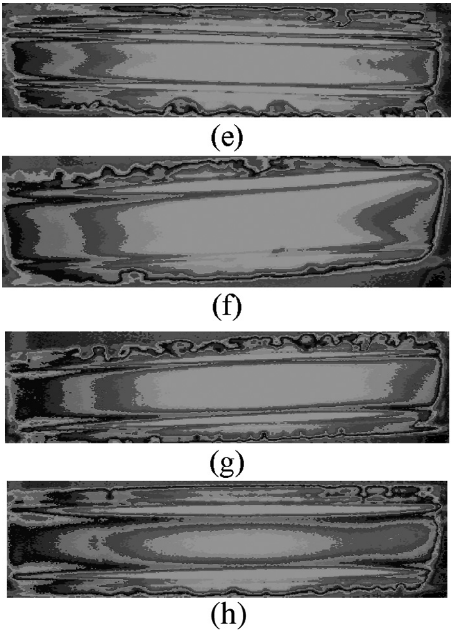


FIGURE 5 Isochromatic fringe patterns obtained by CCD camera (polarizer and analyzer crossed) of samples annealed for 4 h at T = 120°C and quenched at: (e) T = 0°C; (f) T = 20°C; (g) T = 40°C; (h) T = 60°C. Transparent PMMA (d = 10 mm).

fields of tensile stresses toward the layers of surface with the increase of the thickness. It is known that upon increasing the thickness of the polymer sample (above 1/8 inch) a sudden drop in impact strength occurs, resulting from the inefficiency of the cooling system in building up substantial negative stresses (compressive stresses) [24]. This may be explained by the fact that by increasing the thickness, the development of two areas of tensile stresses near the surfaces favored which would decrease the efficiency of cooling.

As can be seen in Tables 1 and 2, heat treatment of PMMA with water quenching improved slightly the reverse Izod impact strength of the specimen quenched at 20°C. The presence of compressive stresses at the surface of the notched specimens enhances the impact strength by promoting the plane stress failure. So if the surface is in compression (i.e., the sheets are rapidly quenched), then crack propagation will be hindered, permitting the increase of the reverse Izod impact strength. However, the Charpy impact strength is not sensitive to quenching temperature.

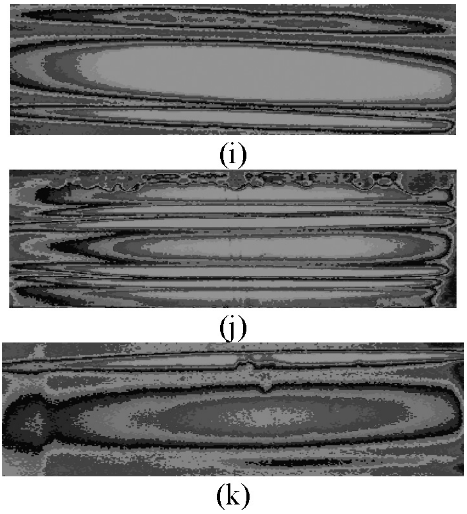


FIGURE 6 Isochromatic fringe patterns obtained by CCD (polarizer and analyzer crossed) of samples (tinted PMMA) annealed for 4 h at T = 120°C and quenched at (i) T = 0°C; (j) Free air; (k) T = 110°C (d = 15 mm).

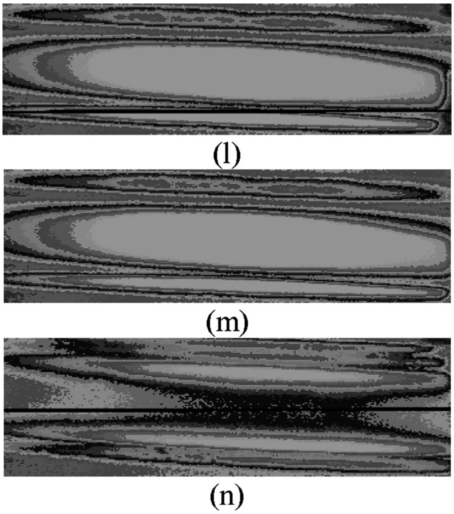


FIGURE 7 Isochromatic fringe patterns obtained by CCD (polarizer and analyzer crossed) of samples (tinted PMMA) annealed for 4 hours at T = 120°C and quenched at T = 0°C; and for different thickness. (l) d = 10 mm; (m) d = 15 mm; (n) d = 19 mm.

The annealing process used in this study appears to have produced a small residual tensile stress at the root of the notch, which resulted in a slight decrease in the apparent strength of the material. This stress may be a result of the incomplete relaxation of machining stresses that occured during the notching process.

The measured values of hardness Shore D, hardness Rockwell R, and HDT are summarized in Table 3. It is interesting to note that a minimum in both types of hardness occurs at the same quenching temperature and correlates with a similar decrease in HDT. At this temperature the chains spread apart, resulting in a loose structure and offering a relatively low resistance to indentation during hardness measurement. This explains the minimum on the hardness values in Table 3. These results point out the peculiarity that on surpassing a 20°C quenching temperature the hardness values reverse and approach the first quench temperature value.

The maximum decrease in HDT, takes place at the same quenching temperature of 20°C. It is important to note that the cooling rate affects the residual surface stresses. These compressive stresses at the surface layers probably relax but the internal layers are not able to relax [18]. Therefore the HDT is controlled by the internal tensile stresses of the material and the external stresses of the load. However, because external stresses are constant during the test of bending, it is therefore the internal stresses that cause the variation of HDT. These tensile stresses are a function of the quenching temperature. The superposition of the external stresses and the internal stresses facilitates the distortion of the material, and consequently lead to the reduction of HDT.

The maximum decrease in HDT, hardness, and the slight increase in Izod impact strength takes place at 20°C, which corresponds to the quenching temperature at which a slight increase of the fields of tensile stresses is observed, as shown in Table 1 and Figure 1. However, HDT values for the quenched samples are also significantly lower than the HDT of the untreated ones.

QUANTITATIVE EVALUATION

Photoelastic Basics

The principles of photoelasticity can be succinctly elucidated by the following two laws: For stress (or strain) induced birefringence, the normally incident polarized light is split into two components along the principal stress directions in a plane perpendicular to the direction of light propagation and are transmitted only along these planes through the specimen.

TABLE 4 Values of the Difference of Principal Stresses for Different Temperatures of Quenching, in PMMA Sample (thickness = 10 mm, fringe order = 1)

Temperature of quenching (°C)	Isochromatic fringe order	Wavelength (nm)	Difference of principal stresses [(σ_1-σ_2)] (MPa)
0	1	590	1,54
20	1	550	1,43
40	1	510	1,33
60	1	510	1,33

Birefringence or optical anisotropy is related to the elastic stresses and orientation release stresses that prevail in oriented polymers, so that:

$$(n_1 - n_2) = C(\sigma_1 - \sigma_2)$$

where $n_1 - n_2$ is in-plane birefringence, C is the relative stress optical coefficient, and $\sigma_1 - \sigma_2$ is the difference of principal stresses.

In particular, by invoking Maxwell's stress optic law wherein the change in load induced refractive index is linearly proportional to the principal stress components, the following relative stress optic law can be deduced [25]. The isochromatic pattern is related to the stress by the fundamental stress–optical law:

$$\sigma_1 - \sigma_2 = \frac{N \cdot \lambda}{C \cdot d}$$

where N is the isochromatic fringe order; $f_\sigma = \lambda/C$ is the material fringe value with λ the wavelength of monochromatic light and C is the relative stress optical coefficient, d is the distance of the light that passes through the sample.

As a result of the relative difference in their velocities, polarized rays vibrating in planes of principal stresses σ_1 and σ_2 will emerge with a relative phase shift and produce color interference fringes or multicolored bands. From isochromatic fringe pattern, in a point near the center (below the neutral line), the values of the difference of the principal stresses were evaluated approximately and are presented in Table 4. One can notice that the difference of the principal stresses decreases with the increase of the temperature of quenching.

CONCLUSION

A novel technique based on photoelasticimetry is developed to investigate the thermal stresses in transparent polymers. The quenching in water at moderate temperature gives an important density of tensile stress, which for PMMA disappears at 110°C. The tensile stresses can be quantified using a CCD camera. The quantitative results obtained by this method are very encouraging; nevertheless some improvements need to be made, especially in the data acquisition and "reading" of colors. A more optically sensitive polymer like polycarbonate would probably give better results. However, this method can be very useful for a first approximation of maximum tensile stresses area. Due to its non-destructive nature, the present method can be effectively used as a quality control method in transparent plastics-processing industries that induce beneficial thermal stresses in order to improve some properties of the material.

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