

A New Photoelastic Method for Evaluating Durability of Plastics

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Synopsis

This work was undertaken to measure quantitatively the quality change and crack development caused by degradation of plastics with the new photoelastic scale (P scale) using split circular ring-type specimens (C specimen). For an example, a polycarbonate specimen was used under various conditions—photodegradation, thermal degradation, solvent cracking, solvent action, and alkaline degradation. The results indicate that this method is useful for evaluating durability of plastics, and a merit of the method is to provide quick, convenient, nondestructive means of measurement with simple equipment. Besides, this C specimen is easily deflected by a spring plate with two holes. Therefore this method is also applicable to the investigation of effects of deformation on various degradations of plastics.

INTRODUCTION

For evaluating durability of plastics, it is ideal to know the life of a material by using it under actual conditions. Such a method, however, is difficult in practice, as it takes much time and money, so an accelerated test is usually performed with a model specimen under conditions that are more severe than actual.

Accordingly, various testing methods for evaluating durability have been tried,¹ and some of them were adopted² as standard testing methods. These methods, however, are not yet satisfactory, especially in the matter of measurement of quality change and crack development caused by degradation.

The object of this study was to establish a convenient, economical quick testing method for estimating durability of plastic materials. In the beginning, a split circular ring specimen (C specimen) was tried for the purpose of examining effects of deformation of plastics. Then we tried to measure the restoring force of a deflected specimen with a photoelastic technique by putting wire strain gauges on the spring plate which gave deflection of the specimen. Though the strain gauge method was possible in principle, it was not practicable because of the distortion of the spring plate when setting. We tried other methods and finally the photoelastic scale (P scale) made of epoxide plastic plate was adopted for measuring restoring force and photoelastic sensitivity.

By this method, a quality change of material and crack development caused by degradation became measurable. Besides, this method is applicable for obtaining chemorheological information^{3,4} by stress relaxation and birefringence.

In addition to this photoelastic method, we used the weight loading method, that is, the method of measuring the slit width of specimens caused by loading weight. By this loading method, we can get rigidity of samples as well as permanent deformation from the slit width in case of no loading.

PHYSICAL CONSIDERATION

Principal Stress Difference

The physical considerations of this method are shown in Figure 1. In the natural position (1), the slit width L_n is changed from $L_{n,0}$ (at time 0) to $L_{n,t}$ (at time t) under degradation; the difference between $L_{n,0}$ and $L_{n,t}$ shows the degree of permanent deformation. With the P scale attachment (2), the following relations can be derived from the theory of elasticity for this setting:

$$\sigma_r = -A \cos \theta \frac{(r^2 - a^2)(r^2 - b^2)}{(a^2 + b^2)r^3} - \frac{4M}{N} \times \left[a^2 \log(a/r) + b^2 \log(r/b) - \frac{1}{r^2} a^2 b^2 \log(a/b) \right] \quad (1)$$

$$\sigma_\theta = -A \cos \theta \frac{3r^4 - a^2 b^2 - (a^2 + b^2)r^2}{(a^2 + b^2)r^3} - \frac{4M}{N} \times \left[a^2 \log(a/r) + b^2 \log(r/b) + \frac{a^2 b^2}{r^2} \log(a/b) + b^2 - a^2 \right] \quad (2)$$

$$\tau_{r,\theta} = -A \sin \theta \frac{(r^2 - a^2)(r^2 - b^2)}{(a^2 + b^2)r^3} \quad (3)$$

Here,

$$A = P(a^2 + b^2)/[(a^2 + b^2)\log(a/b) - (a^2 - b^2)] \quad (4)$$

$$M = \frac{\sqrt{3}}{4} P(a + b) \quad (5)$$

$$N = (a^2 - b^2)^2 - 4a^2 b^2 [\log(a/b)]^2 \quad (6)$$

where σ_r , σ_θ are radial and tangential normal stresses in polar coordinates (kg/mm²); $\tau_{r,\theta}$ is shearing stress (kg/mm²); and P is the restoring force of C specimen per unit thickness (kg/mm).

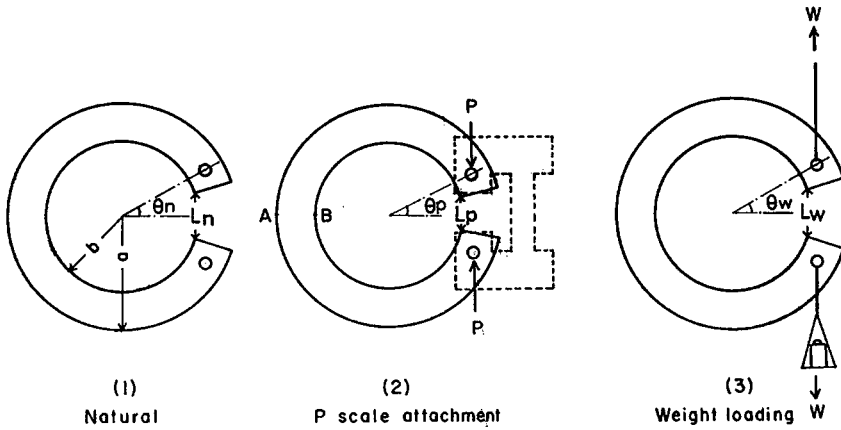


Fig. 1 Schematic diagram of the method.

At the center of the C specimen (on line AB), θ is π , thus $\cos \theta = -1$ and $\sin \theta = 0$.

Accordingly, the principal stress difference at the center $\Delta\sigma$ is given by

$$\Delta\sigma = \sigma_\theta - \sigma_r = 2A \frac{r^4 - a^2b^2}{(a^2 + b^2)r^3} - \frac{4M}{N} \left[2 \frac{a^2b^2}{r^2} \log(a/b) + b^2 - a^2 \right]. \tag{7}$$

At inside point B , where $r = b$, one obtains

$$\Delta\sigma_B = \frac{2(b^2 - a^2)A}{b(a^2 + b^2)} - \frac{4M}{N} [2a^2 \log(a/b) + b^2 - a^2]. \tag{8}$$

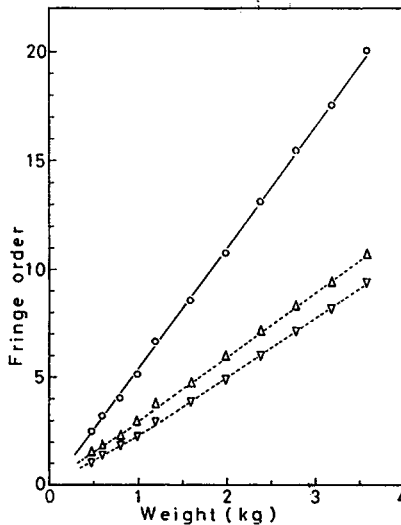


Fig. 2. Calibration curve of P scale: (O) total; (Δ) inside; (∇) outside.

At outside point A , where $r = a$, one obtains

$$\Delta\sigma_A = \frac{2(a^2 - b^2)A}{a(a^2 + b^2)} - \frac{4M}{N} [2b^2 \log(a/b) + b^2 - a^2]. \quad (9)$$

Thus,

$$\Delta\sigma = K_1 P \quad (10)$$

where K_1 is the specimen size constant.

Deformation

The relative displacement in the part of the slit ($L_n - L_p$) in Figure 1 is given by the following relation from the theory of elasticity:

$$\begin{aligned} L_n - L_p = & -\frac{2A \sin 2\theta}{E(a^2 + b^2)} \left[\frac{(a + b)^2}{8} (3 - \nu) + \frac{a^2 + b^2}{2} (1 + \nu) \right. \\ & \left. - \frac{2a^2 b^2}{(a + b)^2} (1 + \nu) \right] - \frac{4A}{E} (\pi - \theta) - \frac{2M \sin \theta}{NE} \\ & \times \left\{ \frac{a + b}{2} (a^2 \log a - b^2 \log b)(1 - \nu) + (b^2 - a^2) \frac{(a + b)}{2} \right. \\ & \times \left(\log \frac{a + b}{2} \right) (1 - \nu) - \frac{(b^2 - a^2)}{2} (a + b) + \frac{2a^2 b^2}{a + b} \\ & \left. \times \log(a/b)(1 + \nu) \right\} - \frac{8M}{NE} (b^2 - a^2)(a + b)(\theta \cos \theta - \pi \cos \theta) \quad (11) \end{aligned}$$

where ν is Poisson's ratio and E is the modulus of elasticity.

Therefore,

$$E = \frac{K_2 P}{(L_n - L_p)} \quad (12)$$

where K_2 is the specimen size constant. Hence, the ratio of the modulus of elasticity at time t and time 0 can be written as follows:

$$\frac{E_t}{E_0} = \frac{P_t(L_{n,0} - L_{p,0})}{P_0(L_{n,t} - L_{p,t})}. \quad (13)$$

These expressions are applicable also to the weight-loading method, excluding the case of large deformation such as heat distortion. In the case of the weight loading method, we must take $L_w - L_n$ and $-W$, in Figure 1, for $L_n - L_p$ and P .

Practical Applications

At first, the calibration curve which shows the relation between the fringe order N_s in the P scale and the restoring force P is obtained by loading weight to P scale. There are two fringe bands on both sides of the zero fringe order line.

The total fringe order N_s is defined as the sum of

$$N_s = N_{s,in} + N_{s,out} \quad (14)$$

where N_s is the total fringe order of the P scale, $N_{s,in}$ is the inside fringe order of the P scale, and $N_{s,out}$ is the outside fringe order of the P scale.

Since N_s is proportional to P from the calibration curve (Figure 2), the change ratio of restoring force is determined by the relation

$$\frac{P_t}{P_0} = \frac{N_{s,t}}{N_{s,0}} \quad (15)$$

Similarly,

$$N_b = N_{b,in} + N_{b,out} \quad (16)$$

Besides, from the relations about stress birefringence,

$$\frac{N_{b,t}}{N_{b,0}} = \frac{C_t \Delta \sigma_t}{C_0 \Delta \sigma_0} \quad (17)$$

where C_t , C_0 are the photoelastic coefficients of degraded and original samples, respectively.

Thus, from eqs. (10), (15), and (17),

$$\frac{N_{b,t}/N_{b,0}}{N_{s,t}/N_{s,0}} = \frac{C_t \Delta \sigma_t / C_0 \Delta \sigma_0}{P_t / P_0} = \frac{C_t K_1 P_t / C_0 K_1 P_0}{P_t / P_0} = \frac{C_t}{C_0} \quad (18)$$

In conclusion, by measuring the changes in N_b and N_s , the changes of P and C can be determined. The quality changes of materials and crack development caused by degradation can be estimated conclusively by changes of N_s and N_b .

EXPERIMENTAL

Photoelastic Method

As shown in Figure 3, when the P scale is attached to the C specimen, N_s and N_b are counted with a low-magnification microscope (Nikon S.M.) equipped with polarizer and analyzer plate, using a mercury lamp through a green filter ($\lambda = 5461 \text{ \AA}$). It is not necessary to use a microscope, but with the naked eye the measurement of fringe order is difficult in many cases.

Weight-Loading Method

The C specimen is loaded with the weight, and the slit width L is measured with a vernier calipers both with and without loading. The loading weight decided upon was 1040 g, to keep the specimen in the creepless region.

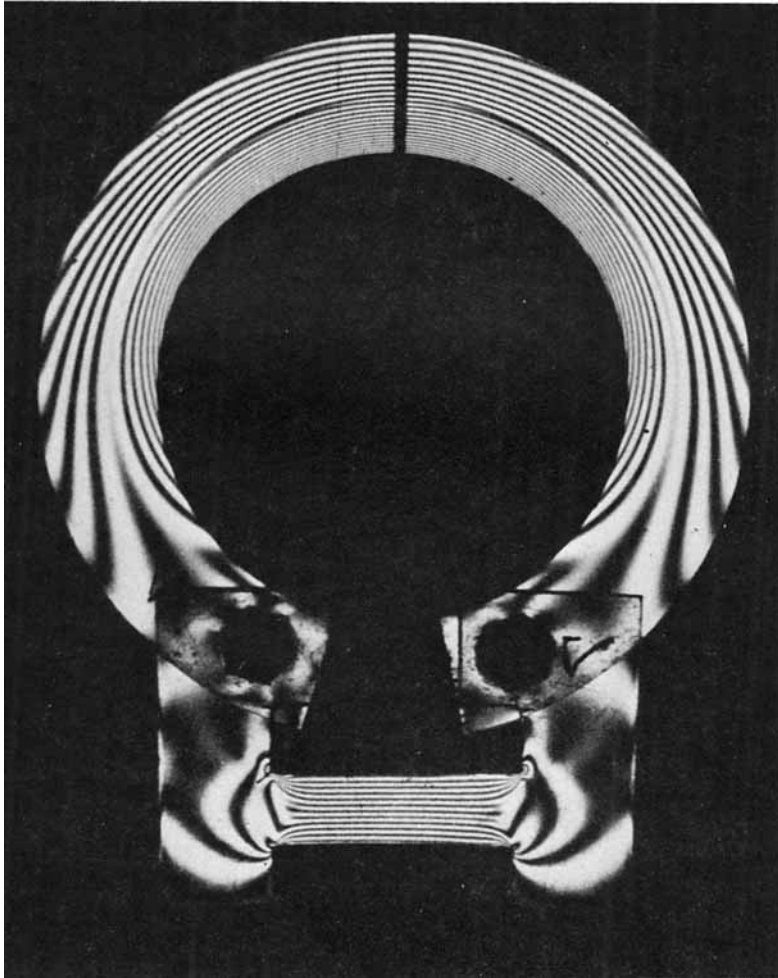


Fig. 3. Photoelastic fringes of C specimen and P scale.

Test Materials

Polycarbonate was used here as model sample to develop a new method, because of its high photoelastic sensibility and clearness.

The sizes of the C specimen and the P scale are shown in Figure 4.

The specimen was machined from a commercial extruded sheet and was used without special conditioning.

Degradation Conditions

In each case, specimens were tested under two conditions: the natural position (N) and the deformed position (D), by attaching a spring plate which was used to study the effect of deformation upon degradation.

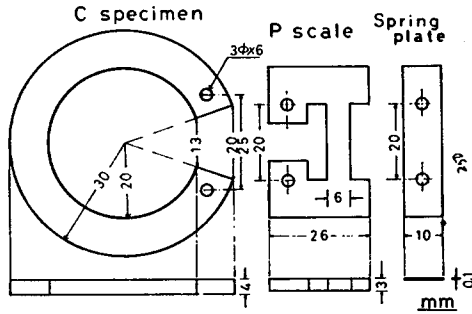


Fig. 4. Dimensions of C specimen, P scale, and spring plate.

Degradation conditions were as follows:

1. Nonactive environment: stored in a glass box with silica gel.
2. Immersed in reagent: (a) solubility in solvent by methylene chloride; (b) solvent cracking by toluene; (c) alkali immersion by 10% and 20% NaOH.
3. Photodegradation: irradiated with two fluorescent sun lamps (20 W, 316 nm), 43 mm apart from both sides of specimen.
4. Thermal degradation: in gear oven tester at 100°C under air circulation.

RESULT AND DISCUSSION

Calibration Curve of P Scale

At first, the calibration curve for measuring the restoring force of the C specimen was obtained by counting the photoelastic fringe order N_s in response to weight load, using standard photoelastic equipment (Riken Keiki PA-300).

This curve is shown in Figure 2. It is clear that this P scale is useful in such linear regions.

Calibration Curve of C Specimen

Figure 5 is the calibration curve of the C specimen by weight loading. This curve is used to investigate the relation between the restoring force P and the stress birefringence of the sample. Figure 5 shows that N_b changes in proportion to P .

Evaluation of Durability

Using the photoelastic method and the weight-loading method, evaluation of durability was tried. It appeared that the weight loading method is not useful, because changes in $(L_w - L_n)$ through degradation are usually not considerable. However, L_n is useful for the measurement of permanent deformation.

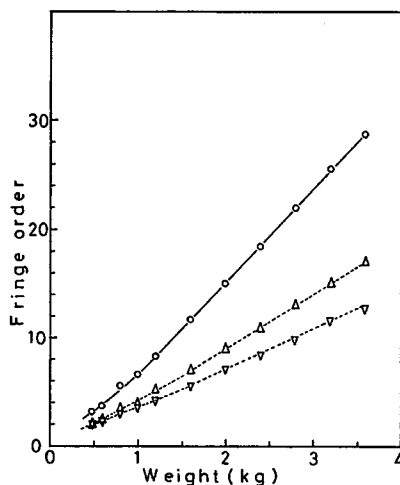


Fig. 5. Calibration curve of C specimen: (○) total; (△) inside; (▽) outside.

Nonactive Environment

Figure 6 shows that N_s and N_b did not change in the natural position (N) but in the deformed position (D); N_s decreased by 5% and N_b decreased somewhat. To conclude, there was no remarkable change caused by storage of 1000 hr in nonactive environment.

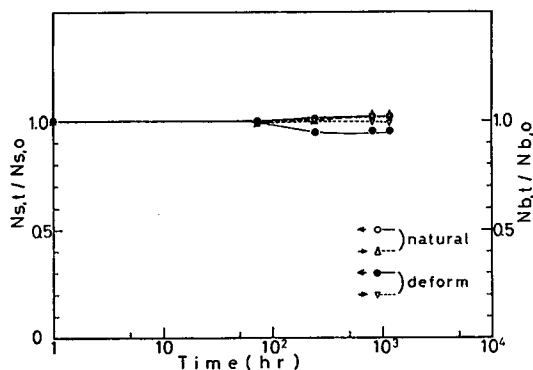


Fig. 6. N_s and N_b changes in nonactive environment.

Immersed in Reagent

Solubility in Solvent. The results are shown in Figure 7. The specimen began to dissolve as soon as it was immersed in methylene chloride. When the specimen was picked up, its surface was covered with white skin, therefore N_b was not measured. In these cases, there was no cracking at all. It is concluded that in solubility without cracking, deformation

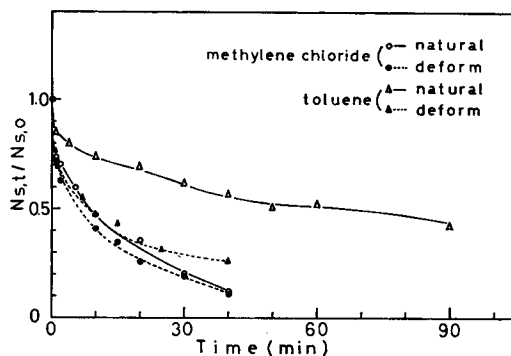


Fig. 7. N_s change by solubility in solvent and solvent cracking.

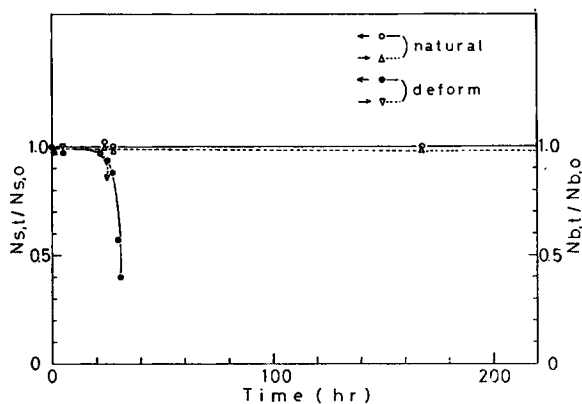


Fig. 8. N_s and N_b changes by alkali immersion.

is not effective, because no difference was seen between positions N and D.

Solvent Cracking. Figure 7 shows that there was a decrease in N_s for both positions N and D during degradation. To conclude, solvent cracking is activated by deformation, because the change in N_s in the deformed position (D) was greater than that in the natural position (N).

Alkali Immersion. Figure 8 shows that in the natural position, neither N_s nor N_b were changed, but in the deformed position, a large amount of change took place. On the other hand, in 10% NaOH, there were no significant changes for both positions N and D after 350 hr of immersion. To conclude, the effects of alkaline degradation are affected by the alkali concentration.

Photodegradation

Figure 9 shows that in the natural position, neither N_s nor N_b were changed, but in the deformed position, N_s was decreased during degradation and N_b was not changed; this indicates an increase in photoelastic

TABLE I
 Examples of Results

	Unit	Position	Photodegradation				Thermal degradation		
			0 hr	93 hr	1900 hr	0 hr	93 hr	1854 hr	
$N_{s,t}/N_{s,0}$	—	N	1.00	1.06	1.00	1.00	0.97	1.00	
		D	1.00	0.89	0.74	1.00	0.36	0.21	
P^a	kg/mm	N	0.41	0.40	0.41	0.45	0.43	0.45	
		D	0.42	0.38	0.33	0.45	0.16	0.09	
$\Delta\sigma_{\text{inside}}^b$	kg/mm ²	N	1.4	1.4	1.4	1.6	1.5	1.6	
		D	1.5	1.3	1.2	1.6	0.56 ^a	0.31 ^b	
$N_{b,t}/N_{b,0}$	—	N	1.00	0.985	0.995	1.00	1.00	1.02	
		D	1.00	0.96	0.97	1.00	0.78	0.61	
$\Delta_{\text{inside}} \times 10^{4c}$	mm	N	62	61	62	63	64	64	
		D	63	60	66	68	53.5	46	
$\Delta n \times 10^{4d}$	—	N	14	14	14	14.5	14.5	14.5	
		D	14.5	13.5	15	15.5	12	10.5	
		N	10	10	10	9.1	9.7	9.1	

$C \times 10^{4e}$	mm ² /kg	D	9.7	10	13	9.7	2.1 ^h	3.4 ^h
		N	12.3	12.4	12.45	12.9	12.9	12.9
L_n	mm	D	12.8	12.4	11.8	12.75	10.45	9.65
		N	1.75	1.7	1.7	1.45	1.55	1.4
$L_w - L_n$	mm	D	1.55	1.45	1.55	1.65	1.5	1.65
	—	N	1.00	1.00	1.00	1.00	0.89	1.00
E_t/E_0^f	—	D	1.00	0.89	0.78	1.00	0.88 ^h	0.20 ^h
	—	N	1.00	0.93	1.00	1.00	1.05	1.00
C_t/C_0^g	—	D	1.00	1.08	1.31	1.00	2.15 ^h	2.91 ^h

^a From the calibration curve of Figure 4.

^b From the relation $\Delta\sigma = K_1 P$ where $K_1 = 3.5$.

^c From the relation $\Delta = \lambda N_b$ where $\lambda = 5.5 \times 10^{-4}$ mm.

^d From the relation $\Delta n = \Delta/t$ where thickness of specimen $t = 4.4$ mm.

^e Photoelastic coefficient from the relation $C = \Delta n/\Delta\sigma$.

^f From the relation $\frac{E_t}{E_0} = \frac{P_t(L_w - L_n)_t}{P_0(L_w - L_n)_0}$.

^g From the relation $\frac{C_t}{C_0} = \frac{N_{b,t}/N_{b,0}}{N_{s,t}/N_{s,0}}$.

^h These values cannot be comparable to original values because specimen size constant changed with cracking.

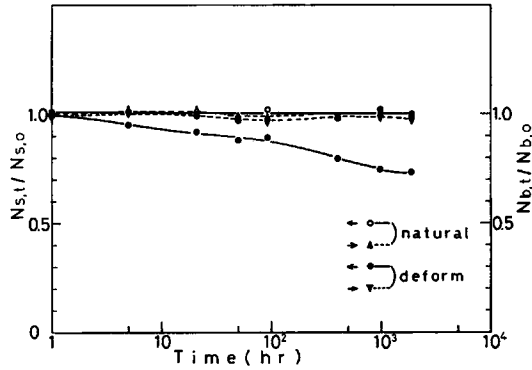


Fig. 9. N_s and N_b changes by photodegradation.

sensitivity. Yellowing took place without cracking for both N and D. To conclude, deformation accelerates photodegradation.

Thermal Degradation

Figure 10 shows that in the natural position, changes in N_s and N_b were not remarkable, but in the deformed position, N_s and N_b were decreased considerably during degradation. The change in N_s in the deformed position for early stages is considered to be caused not by thermal degradation but by thermal deformation.

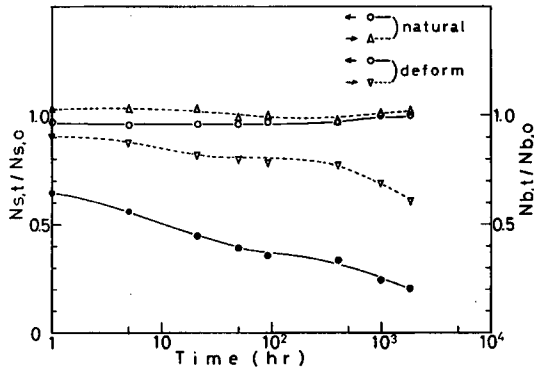


Fig. 10. N_s and N_b changes by thermal degradation.

In the natural position there was no cracking, but in the deformed position crack initiation and development were observed.

To conclude, deformation affects thermal degradation.

Examples of Results

Typical examples of the results obtained by measurement and calculation are shown in Table I.

CONCLUSIONS

The following conclusions were obtained: This photoelastic method is useful for measuring quantitatively resistance for reagents of plastic materials and applicable in evaluating durability for thermal and photo-degradation, by measuring crack development and quality change of material.

By using split circular ring specimens, the effect of deformation upon degradation is easily studied.

A merit of this method is that it provides quick, convenient, nondestructive means of measurement with simple equipment; besides, preparation of the specimen is comparatively easy. On the other hand, there are some limitations, namely, birefringence of the specimen itself cannot be measured when samples have no photoelastic sensibility and transparency.

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