

Surface Modification of Polymer Structures by an Imido-Alkylene Substitution Reaction. I. Polycarbonate

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Synopsis

The surface characteristics of molded polycarbonate sheet was altered via an imido-alkylene substitution reaction. The reaction was effected by contacting the surface with N-hydroxymethylmaleimide and a Friedel-Crafts alkylation catalyst in the presence of a mixture of solvents having limited solubility for polycarbonate. The substitution reaction suggested an aromatic electrophilic substitution mechanism. When N-hydroxymethylmaleimide was used in the surface treatment of polycarbonate sheet, imido-alkylene substitution not only took place but pendent C=C bonds were also incorporated along the polymer chain. When these C=C bonds were photochemically reacted with each other, the surface of the polycarbonate sheet became crosslinked and solvent resistant.

INTRODUCTION

Certain polymers which contain substituted benzene rings in the polymer backbone or as pendent groups along the polymer chain, e.g., polycarbonate, polystyrene, etc., have poor solvent resistance which limits their use in various applications. In general, if the bulk polymer is modified to improve the surface properties of a molded part, other properties of the bulk polymer may be altered.

Tawney et al.¹ reported that N-hydroxymethylmaleimide (N-methylolmaleimide) can react with benzene in concentrated sulfuric acid via imido alkylene substitution. Klebe² reported a Friedel-Crafts alkylation method for introducing imido-alkylene substitution into a variety of aromatic polymers. Reaction was effected by contacting a solution of a polymer, e.g., polycarbonate, and an imidomethylene compound with a Friedel-Crafts catalyst.

This paper describes a surface treatment or modification for certain polymers which results in the enhancement of the properties of molded parts. In essence, the surface characteristics of a molded part composed of a polymer containing substituted benzene rings is altered by contacting the surface with an imido-alkylene compound and a Friedel-Crafts alkylation catalyst in the presence of a solvent or a selected mixture of solvents having a limited solubility for the polymer. When N-hydroxymethyl-

maleimide was used in the surface treatment of polycarbonate sheet, imido-alkylene substitution not only took place but pendent C=C bonds were also incorporated along the polymer chain. When these C=C bonds were photochemically reacted with each other, the surface of the polycarbonate sheet became crosslinked and solvent resistant.

EXPERIMENTAL

Materials

All chemicals used were reagent grade. Polycarbonate sheet, General Electric Lexan Grade 9034, and unstabilized polycarbonate powder, $\bar{M}_w = 32, 170$, were used in the various experiments. N-Hydroxymethylmaleimide was synthesized by the method of Tawney et al.¹

Reaction Conditions

Bulk polycarbonate-N-hydroxymethylmaleimide products, which contained various degrees of imido-alkylene substitution, were prepared by the method of Klebe.² For instance, 1.00 g polycarbonate powder and 0.25 g N-hydroxymethylmaleimide (2/1 mole ratio) were dissolved in 250 ml methylene chloride. BF_3 (gas) was then bubbled into the solution for 30 min while it was stirred and maintained at 25°C. The bulk reaction products were recovered by precipitation in methyl alcohol and dried at room temperature.

Polycarbonate sheet specimens with dimensions of 3 cm \times 1 cm \times 0.3 cm and weighing 1.11 g were used for surface studies. Surface reactions were effected by immersing the specimens in various BF_3 -etherate-methylene chloride solutions (100 ml total volume) which contained 0.30 g (0.0023 mole) N-hydroxymethylmaleimide. The temperature was maintained at 25°C. After the desired reaction time, the specimens were removed from the reaction mixture, washed with water, and dried. A long-wave ultraviolet lamp (Blak-Ray, manufactured by Ultra-Violet Products, Inc., San Gabriel, California) was used to effect crosslinking of the treated surfaces.

The reaction of N-hydroxymethylmaleimide with BF_3 (gas) was studied by using the following procedure: The nuclear magnetic resonance (NMR) spectrum of a saturated solution (1.9%) of N-hydroxymethylmaleimide in CDCl_3 was recorded. Very small amounts of BF_3 (gas) were then introduced consecutively into the sample tube and spectra were recorded again. The total time for the experiment after the first addition of BF_3 was approximately 10 min.

Analyses

NMR spectra were recorded with a JOEL MH 100-MHz spectrometer. Solutions of bulk reaction product in deuterated chloroform were used. Chemical shifts are relative to tetramethylsilane.

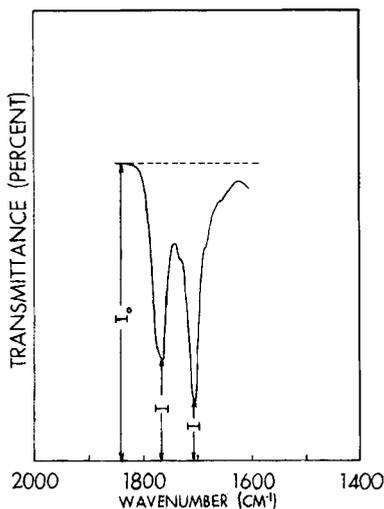


Fig. 1. Internal reflection spectrum of treated polycarbonate sheet showing baseline for absorbance calculation.

Internal reflectance spectra of surfaces were obtained with a Perkin-Elmer Model 621 grating infrared spectrophotometer using the attenuated total reflectance technique. The Wilks Scientific Corp. Model 9 accessory, a KRS-5 plate, and 45° angle of incidence were used to obtain the spectra. A minimal amount of pressure was applied in mounting the specimen in the solid sample holder. The spectrophotometer was calibrated by using a polystyrene standard. The various compartments of the spectrophotometer were continually purged with a dry, CO_2 -free air to minimize atmospheric absorptions. The specimens were placed in the same effective KRS-5 plate area for determining relative intensities of absorption bands. The thickness of the reaction product layer on treated specimens were measured microscopically with a calibrated eyepiece scale.

Quantitative removal of the reaction product layers from the surfaces of treated specimens proved to be difficult. Therefore, the determination of the degree of imido-alkylene substitution by using a method of this kind was abandoned. Instead, an alternate method, which consisted of correlating data obtained from bulk reaction products with those obtained from surface studies, was used. For this purpose, bulk polycarbonate-N-hydroxymethylmaleimide reaction products were prepared at various polymer-imide mole ratios. The per cent substitutions of the bulk samples were determined by integrating the NMR spectra. The ratios of the absorbancies of the 1762 cm^{-1} and 1706 cm^{-1} absorptions, which are characteristic of the carbonyl groups in polycarbonate and N-hydroxymethylmaleimide, respectively, were determined from the internal reflection spectra. The absorbancies were obtained by drawing a parallel baseline from 1860 cm^{-1} (Fig. 1). Data are given in Table I. These data were

TABLE I
Analysis of Bulk Polycarbonate-N-Hydroxymethylmaleimide
Reaction Products

Polymer-imide mole ratio	% Substitution	A1706 cm ⁻¹ /A1762 cm ⁻¹
2/0.5	11	1.11
2/1.0	21	1.50
2/1.5	33	1.97

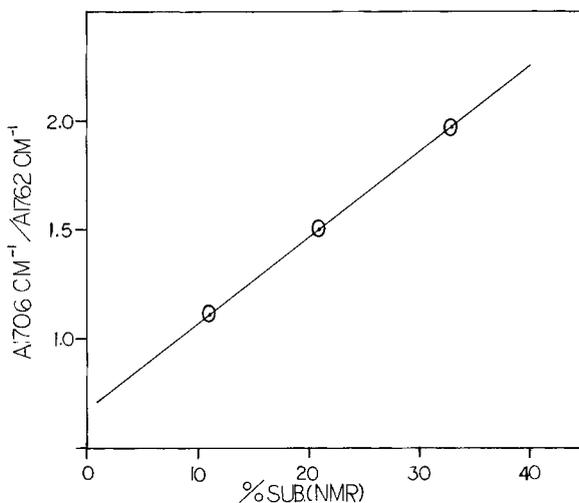


Fig. 2. Graph for determining per cent substitution of polycarbonate-N-hydroxymethylmaleimide surface reaction product.

then used to construct the graph in Figure 2, which was in turn used to determine the per cent substitution in the surface reaction products.

RESULTS AND DISCUSSION

Surface Treatment

The surfaces of polycarbonate sheet specimens which were reacted with N-hydroxymethylmaleimide in solutions of 95%-5%, 85%-15%, and 80%-20% BF₃·etherate-methylene chloride at 25°C for 16 hr were examined by internal reflection spectroscopy. Spectra in the C=O stretching region are shown in Figure 3. A comparison of the relative intensities of the 1762 and 1706 cm⁻¹ absorptions, which are characteristic of the carbonyl groups in polycarbonate and N-hydroxymethylmaleimide, respectively, indicated that the extent of the reaction increased as the concentration of methylene chloride was increased. A visual examination of the specimens showed that the surfaces were opaque and had a high gloss. Very little pitting was noted. Also the thickness of reaction product layers on the specimens prepared in the 95%-5%, 85%-15%, and 80%-20% BF₃·etherate-methy-

lene chloride mixtures were 0.005, 0.07, and 0.31 mm, respectively. A photomicrograph comparing the cross sections of the 80%-20% and untreated specimens is shown in Figure 4. The reaction product appears to be evenly distributed on the surface of the treated specimen.

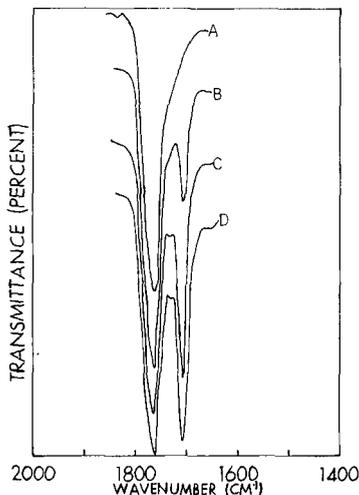


Fig. 3. Internal reflection spectra of polycarbonate sheet: (A) control; (B, C, and D) treated in 95%-5%, 85%-15%, 80%-20% BF_3 etherate-methylene chloride, respectively.

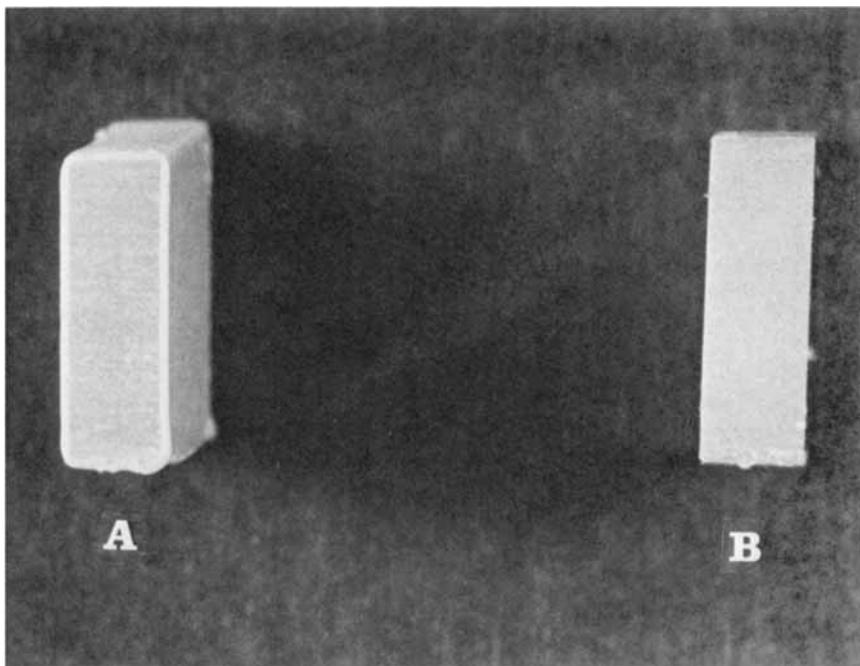


Fig. 4. Cross section photograph of polycarbonate sheet specimens: (A) treated; (B) untreated.

Kinetics

A complete kinetic analysis of the surface reaction is not without difficulty. As was shown in Figure 3, the degree of substitution as well as the thickness of the reaction product layer are dependent on the BF_3 ·etherate-methylene chloride ratio. This indicates that the surface of the polycarbonate sheet has to be swelled to some degree in order for the reaction to be effected. Obviously, this degree of swelling would be difficult to control. Also the entire amount of surface reaction product was difficult to remove from the treated sheet specimen. Therefore, a kinetic treatment with respect to polycarbonate would have little merit. In view of these difficulties, it was decided to study the reaction by using conditions pertinent to a practical process.

Consequently, experiments were carried out with sheet specimens at 25°C in various solvent mixtures containing 0.0023 mole N-hydroxymethylmaleimide. This amount of imide is approximately two times that of the surface reaction product produced in the 80-20 BF_3 ·etherate-methylene chloride experiment that was discussed previously. (The amount of surface reaction product, based on polycarbonate, was calculated from the dimensions and weight of the sheet specimen and the thickness of the reaction product layer.) Internal reflectance spectra of the surfaces were recorded at various reaction times and the $\text{A}1706\text{ cm}^{-1}/\text{A}1762\text{ cm}^{-1}$ ratios were converted to per cent substitution by using the graph in Figure 2. Plots of the data indicated that all reactions were first order with respect to N-hydroxymethylmaleimide, an example shown in Figure 5, and a least-squares treatment of the data using GE Time Sharing COLNR program gave the reaction rate constant listed in Table II. The data in Table II indicate that the rate constant increases as the concentration of methylene chloride increases. This evidently reflects the degree of interaction of the

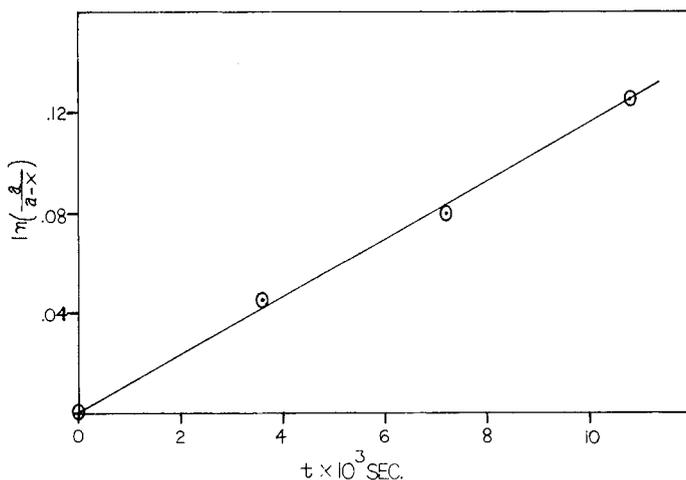


Fig. 5. First-order plot of surface reaction with respect to N-hydroxymethylmaleimide.

TABLE II
Rate Constants of Polycarbonate-N-Hydroxymethylmaleimide
Surface Reactions at 25°C

Expt. no.	% BF ₃ · etherate/% MeCl	Catalyst	$k \times 10^{-6}, \text{sec}^{-1}$
1	70/30	BF ₃ ° etherate	11.2
2	75/25	BF ₃ ° etherate	9.7
3	80/20	BF ₃ ° etherate	8.4
4	80/20	BF ₃ ° etherate + BF ₃ ^a	440

^a Solvent mixture was saturated with BF₃ during reaction.

polycarbonate surface with the various solvent mixtures. A comparison of rate constants for experiments no. 3 and 4 shows that the reaction is approximately 50 times faster when the solvent mixture is saturated with BF₃.

Position of Substitution

The integrated NMR spectrum of the bulk polycarbonate-N-hydroxymethylmaleimide reaction product, which was prepared by Klebe's method using a 2/1 polymer/imide role ratio (Fig. 6), shows the following absorptions: 1.70 ppm, CH₃ protons of polycarbonate; 4.75 and 4.80 ppm, CH₂ protons of N-hydroxymethylmaleimide; 6.67 ppm, HC=CH protons of N-hydroxymethylmaleimide; and 7.27 ppm, aromatic protons of polycarbonate. These assignments were made from the spectra of polycarbonate and N-hydroxymethylmaleimide (Figs. 7 and 8A). The OH proton

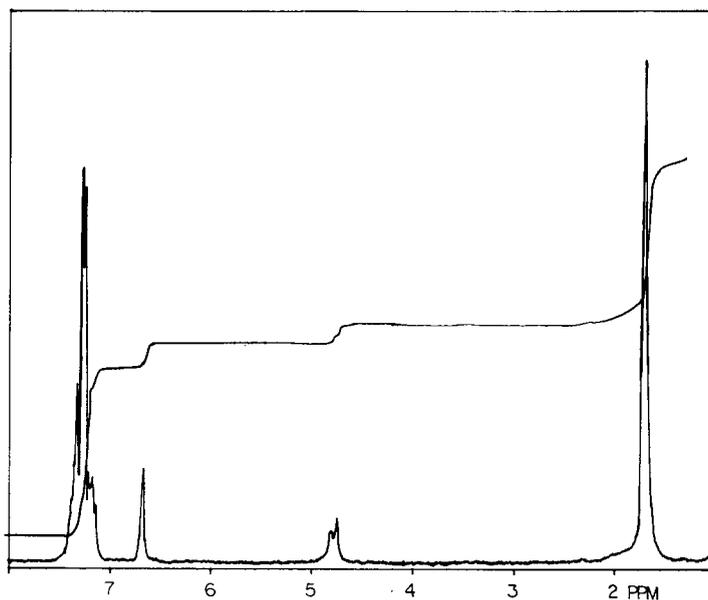


Fig. 6. NMR spectrum of bulk polycarbonate-N-hydroxymethylmaleimide reaction product.

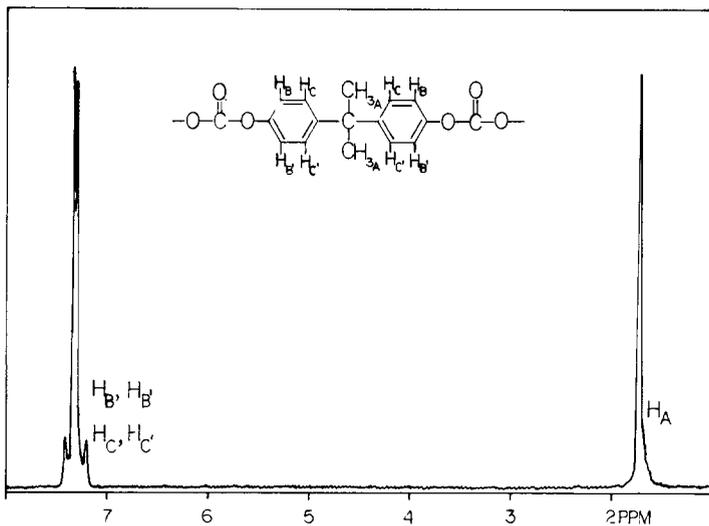
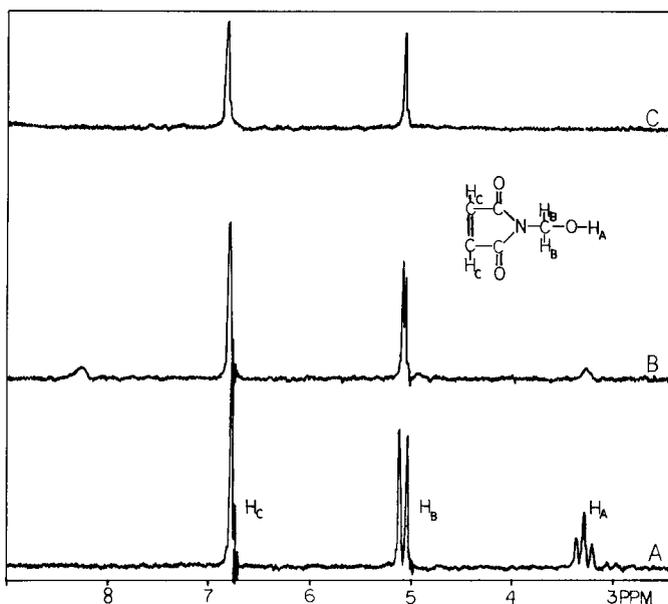


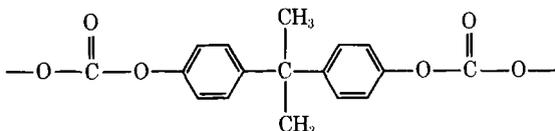
Fig. 7. NMR spectrum of polycarbonate.

Fig. 8. NMR spectra of N-hydroxymethylmaleimide: (A) control; (B and C) after consecutive additions of BF_3 (gas).

absorption of N-hydroxymethylmaleimide is not present in the spectrum of the reaction product (Fig. 6). Therefore, the presence of the doublet assigned to the CH_2 protons in the reaction product (Fig. 6) possibly indicates some form of nonequivalence which cannot be explained at present. Also, a comparison of the absorption patterns of the aromatic protons of

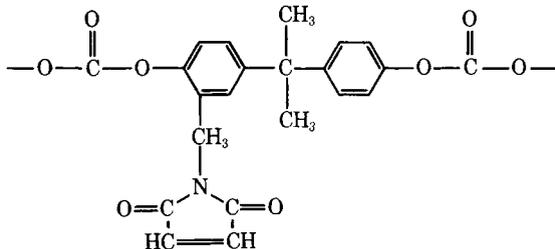
the reaction product and polycarbonate (Figs. 6 and 7) shows a loss of symmetry in the former.

The disubstituted benzene ring of polycarbonate, can be regarded as an



A_2B_2 spin system. In this system, the spectrum due to the A nuclei is the mirror image of the spectrum due to the B nuclei.³ As a result, the absorptions are symmetrical about the midpoint of the spectrum, as shown for the aromatic protons of polycarbonate in Figure 7. However, the absorption pattern of the aromatic protons in the reaction product (Fig. 6) is unsymmetrical, which indicates a substitution reaction at the aromatic ring. The position of substitution cannot be ascertained from the spectrum in Figure 6, but ^{13}C NMR analysis indicated that the hydrogen ortho to the carbonate group was substituted.⁴

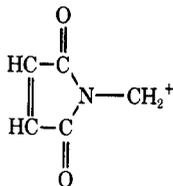
These analyses therefore indicate that the imide groups are pendent along the polycarbonate backbone, e.g.,



In this regard, integration of the areas of the aromatic, $HC=CH$, and CH_2 absorptions (Fig. 6) indicated that, on the average, one out of every five benzene rings of polycarbonate was substituted.

Reaction Mechanism

The absence of a hydroxyl proton absorption in the NMR spectrum of the bulk product prompted a study of the reaction between N-hydroxymethylmaleimide and BF_3 (gas). This study is discussed in the following: The spectrum of unreacted N-hydroxymethylmaleimide (Fig. 8A) shows absorptions at 3.30, 5.05, and 6.77 ppm, which can be assigned to the OH, CH_2 , and $HC=CH$ protons, respectively. Coupling of the OH and CH_2 protons is also shown. As BF_3 (gas) was consecutively introduced into the sample tube, a precipitate was formed, the OH absorption disappeared, the CH_2 doublet collapsed to a singlet and decreased in intensity, and an absorption appeared for a time at 8.27 ppm (Figs. 8B and 8C). The decrease in intensity of the OH absorption, as well as the collapse of the CH_2 doublet, indicate an initial reaction of the OH groups with BF_3 . Such a reaction could generate a carbonium ion, e.g., that would be too unstable to be de-



tected on the NMR time scale.⁵ Reaction of this carbonium ion to form a precipitate would decrease the concentration of N-hydroxymethylmaleimide in the sample tube, and therefore the intensities of the CH₂ and HC=CH absorptions would be decreased (Figs. 8B and 8C).

The exact reaction mechanism of the substitution reaction cannot be determined from the data presented in this report. However, the possible initial generation of a carbonium ion, the absence of the OH proton absorption in the NMR spectrum of the reaction product, and a first-order reaction with respect to N-hydroxymethylmaleimide suggest an aromatic electrophilic substitution mechanism.

Posttreatment of Surface

In the surface reaction of polycarbonate with N-hydroxymethylmaleimide, imido-alkylene substitution not only took place but highly reactive C=C bonds are also incorporated pendent along the chain backbone. The double bonds may be reacted by the application of heat, ultraviolet light, and with various functional groups.² As a result, the surface properties of

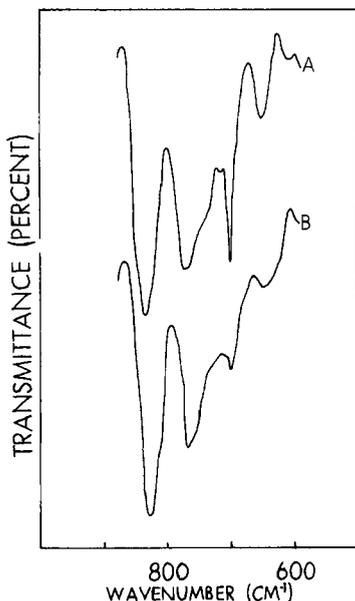


Fig. 9. Internal reflection spectra of treated polycarbonate sheet: (A) control; (B) after exposure to ultraviolet light.

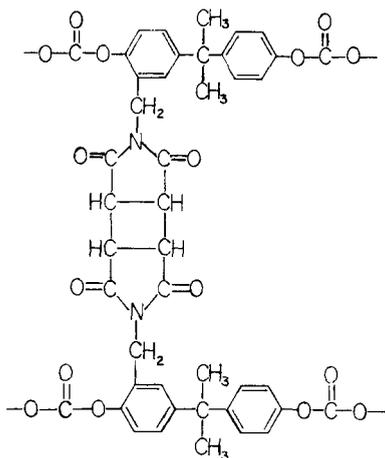


Fig. 10. Proposed structure of crosslinked polycarbonate-N-hydroxymethylmaleimide surface reaction product.

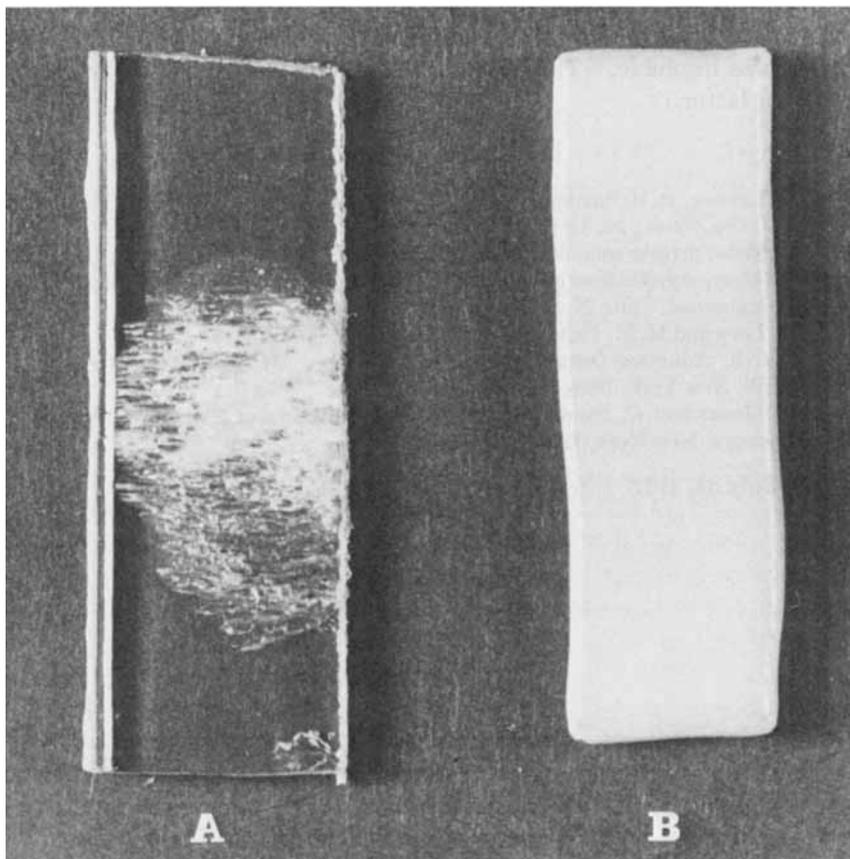


Fig. 11. Photograph of stressed polycarbonate sheet specimens: (A) control; (B) treated and crosslinked.

a polycarbonate sheet can be altered significantly via the imido-alkylene substitution reaction and a postcrosslinking of the C=C bonds. As an example, a polycarbonate sheet specimen which was prepared with a 0.31-mm-thick, 20% substituted reaction product layer was exposed to ultraviolet light for 45 min. The internal reflectance spectrum of the surface after exposure (Fig. 9) shows a decrease in the intensity of the 700 cm^{-1} absorption, which can be assigned to a monocyclic imide ring vibration.⁶ This suggests a reaction of the pendent C=C bonds, thereby forming a cross-linked reaction product layer.

A proposed structure at the point of crosslinking is shown in Figure 10. After the posttreatment with ultraviolet light, the sheet specimen and a control specimen were subjected to a high bending stress. Acetone was applied to the surfaces of both specimens at the points of stress. The untreated control specimen failed immediately. However, the treated specimen remained unchanged, indicating solvent resistance which was due to the crosslinked reaction product surface layer (Fig. 11). The posttreated specimen was then cut into sections which now had untreated surfaces. These sections were placed in chloroform. It was noted that the polycarbonate interior of the sections dissolved, whereas the surface reaction product was insoluble. This gave further evidence of the crosslinked nature of the latter.

References

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