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31. ESCA Spectroscopy of Polyesters Stabilized with Polymer Bound Ultraviolet Stabilizers

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ABSTRACT

Unsaturated polyester resins were prepared which have the polymerizable ultraviolet stabilizers 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole or 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole permanently incorporated in the polymer. The polyester resins were prepared with azobisisobutyronitrile as initiator at 60° C; the polymer composition consisted of 66% unsaturated polyester and 34% styrene with 0.5 mol % of polymerizable ultraviolet stabilizer.

The polymer-bound ultraviolet stabilizer was evenly distributed throughout the polymer matrix. On accelerated aging, the relative amount of the ultraviolet stabilizer increased on the surface which was seen by ESCA spectroscopy as the polymer surrounding the stabilizer portion degraded. This behavior can also be seen, but not as pronounced, by reflection infrared experiments.

INTRODUCTION

Unsaturated polyester resins are usually prepared from maleic anhydride and/or phthalic anhydride with aliphatic glycols such as ethylene glycol, propanediol-1,3, or butanediol-1,4. These esters, which have varied amounts of maleate and fumerate groups in the short polymer chains, are then dissolved in a monomer, usually in styrene but also in methyl methacrylate, and polymerized with radical initiators to a crosslinked network of unsaturated polyester resin where the maleate or fumerate units of the unsaturated polyesters function as comonomers for the styrene polymerization (1-4).

These unsaturated polyester resins, although widely used, suffer from the problem of limited oxidative and particularly photooxidative stability (5-8). With the availability of polymerizable stabilizers to prevent photooxidation, the potential of preparing unsaturated polyester resins with longer use time has become of increasing interest.

Evaporation or leaching of the low molecular weight stabilizer not only changes the physical properties of the resin if the stabilizer is present in relatively large amounts, but it also changes the chemical resistance of the resin toward thermal or photooxidation as the material is lost from the surface of the polymer. Low molecular weight stabilizers are most prominently leached out of the surface layer, consequently making the upper surface layer the easiest target for oxidation. The position of the stabilizer is therefore of great interest. In recent work (9), it has been shown that the first effect of oxidative damage can be noticed in the change of the wetting angle of the polymer, which is due to the formation of hydroxyl groups on the surface. The changes of the wetting angle probably represent degradation not going deeper than 5 or 20 Å. IR reflection measurements also show changes on the surface of the polymers. Penetration of 1 to 5 µm is the region in which ATIR (attenuated total internal reflection) is most useful for the measurement of the composition. ESCA (electron spectroscopy for chemical analysis) gives the elemental composition of very thin surface layers of about 20-50 Å. It requires the presence of a different chemical element in order to identify the element on the surface, especially when present in small amounts, in order to carry out quantitative measurements.

It was of interest to find out exactly where and how close to the surface our copolymerizable ultraviolet stabilizer was located from the type of 2(2-hydroxyphenyl)2H-benzotriazole, specifically 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole and 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole. It was also important to find out in which position the stabilizers remain in the unsaturated polyester resin during the aging or photooxidative degradation. This study was to be carried out by measurements of ESCA and ATIR spectra at the same samples.

EXPERIMENTAL PART

Materials

Maleic anhydride (Aldrich Chemical Co.), phthalic anhydride (Aldrich Chemical Co.), and propanediol-1,3 (Sigma Chemical Co.) were used without special purification.

The polymerizable ultraviolet absorbers of the 2(2-hydroxyphenyl)2H-benzotriazole category: 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole (2H5V) (11) and 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P) (12) were synthesized as described previously. The preparation of the unsaturated polyester is described below.

Styrene (Aldrich Chemical Co.) was washed twice with 5% aqueous sodium hydroxide solutions and twice with water to remove the polymerization inhibitor; after drying over anhydrous sodium sulfate, styrene was distilled under nitrogen.

Azobisisobutyronitrile (Aldrich Chemical Co.) (AIBN) was recrystallized three times from anhydrous methanol and dried for one day at 0.01 mm and room temperature.

Measurement

ESCA spectra of the samples were measured for the C1s and N1s region using a Leybold-Heraeus spectrometer with $ALK\alpha_{1,2}$ as excitation radiation source. Typical operating conditions for the X-ray gun were 13 kV, current 17 mA, and 6.10^{-8} mbar pressure in the sample chamber.

The atomic sensitivity factors for C, O, and N are 0.27, 0.52, and 0.46, respectively, for ESCA analysis using $ALK\alpha_{1,2}$ X-rays as primary irradiation.

Attenuated Total Internal Reflection (ATIR) IR spectra were obtained with a Perkin-Elmer computerized 580-B spectrometer using a Micro MIR accessory at a crystal angle of 45° incidence. The IR band at 1500-1520 cm^{-1} was studied in detail. The data were normalized using the C-H vibration band at 2920 cm^{-1} as the standard in order to overcome variations in optical density; they result from differences in the contact between the sample and the crystal when ATIR measurements are made.

The UV exposure of the samples was made in an Atlas UVCON irradiator with 8 FS-fluorescent sunlight tubes which have a UV emission rich in the range 280-350 nm (Figure 1).

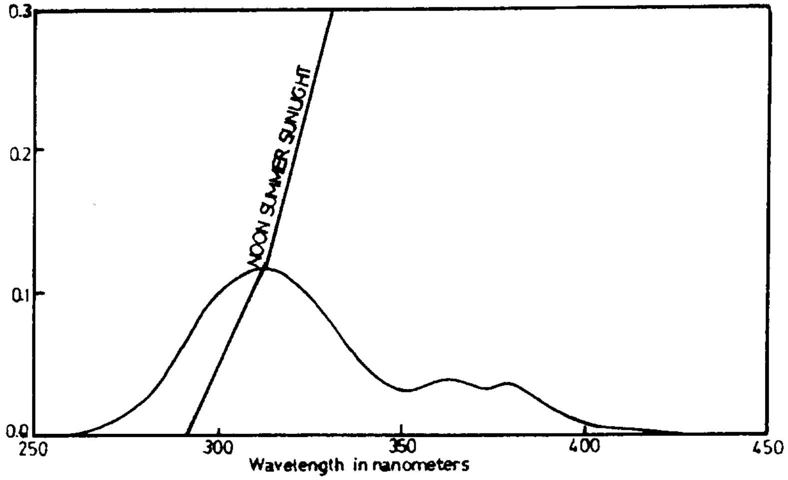


FIGURE 1: Ultraviolet Energy Distribution for FS-40 Fluorescent Sunlamp.

Preparations

Unsaturated Polyester: The unsaturated polyester was prepared as follows: Maleic anhydride (24.5 g, 0.25 mol) and phthalic anhydride (37 g, 0.25 mol) were dissolved in propanediol-1,3 (40 g, 0.5 mol plus 5% excess) and heated to 190° C for 6 hr under nitrogen. The polymer was dissolved in styrene (50 g, 0.48 mol) and a small amount of hydroquinone (18.5 mg, 0.17 mmol) was added as inhibitor.

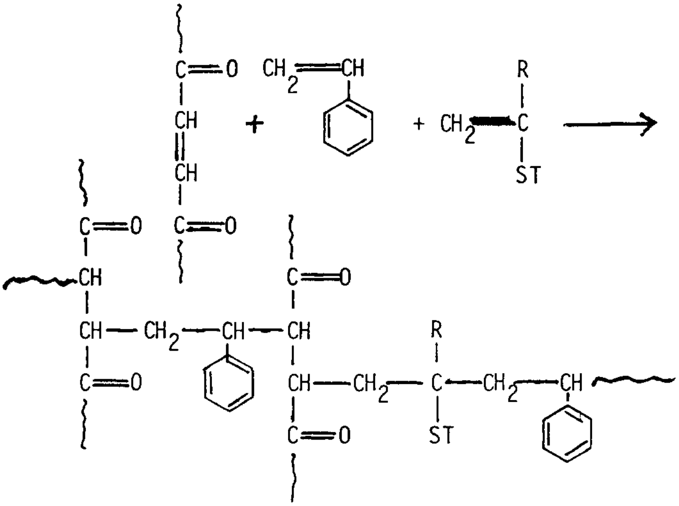
Films of Stabilized Unsaturated Polyester Resin: An assembly was prepared which consisted of two clean Pyrex glass plates approximately 2.5 mm thick separated by an elastomeric spacer which provided a distance between the glass plates of about 1 mm and giving an area of about 50 mm x 100 mm. The glass plates were clamped at the point of the elastomeric spacer with Binder Clip clamps.

To the homogeneous styrene solution of the unsaturated polyester prepared previously was added AIBN as the initiator and the polymerizable ultraviolet stabilizer (2H5V or 2H5P) (Table 1); the solution was placed in a desiccator which was evacuated at 20 mm for 20 min at room temperature to remove dissolved air and the pressure equalized with nitrogen. Approximately 5-6 g of the mixture was poured from the top into the assembly.

The assembly was placed in an oven of 60° C and left there for three days. After the polymerization was complete, the assembly was heated for 20 minutes to 130° C to complete the decomposition of residual AIBN. After cooling to room temperature, the clamps were removed, the glass plates separated, the spacer removed, and the colorless crosslinked polyester films (1 mm thickness) trimmed to the appropriate size. For measurements, only film samples from the center were used (Equation).

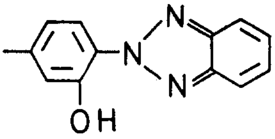
RESULTS AND DISCUSSION

The cured polyester films containing the two kinds of polymerizable ultraviolet stabilizers (2H5V and 2H5P) were examined by ESCA and IR reflection techniques. Sample A contained 5% stabilizer 2H5V and sample B 5% 2H5P. Each sample was irradiated in air at about 40° C for 60, 100, 200, and 300 hr in the Atlas UVCON instrument. The elemental analysis of sample A according to stoichiometric calculation was as follows: Calc. for feed



ST: 2H5= stabilizer

EQUATION



R: H=V

CH_3=P

composition: C, 5.11%; O, 1.83%; N, 0.14%. Found: C, 5.47%; O, 1.68%; N, 0.061% (2.2% 2H5V), which is consistent with the elemental ratio obtained from ESCA analysis of the sample surface: C, 5.47%; O, 1.66%; N, 0.060% (see also Table 2).

Figure 2 shows the ESCA spectra of the C1s, O1s, and N1s bands of sample A before irradiation (0 hr) and after UVCON irradiation in air for 100, 200, and 300 hr; changes in the ESCA spectra are noticed.

The intensity of O1s and N1s signals increased rapidly in relation to the total C1s band, which decreased slowly with irradiation time. The relative composition of the sample surface is gradually changing during irradiation, as shown in Table 1.

The content of N of the sample surface of samples A and B increased by a factor of 3.2 and 3.8, respectively, after irradiation for 300 hr.

Figure 3 shows the intensity ratios of N1s to C1s bands in the ESCA spectra. The strong increase in the N1s/C1s ratio demonstrates that the UV-stabilizer units remained at the sample surface during irradiation, and were destroyed by UV irradiation at a slower rate than the rest of the material. It is known that low molecular weight stabilizers by migration, leaching, and evaporation are gradually lost during irradiation.

Bailey and Vogl (13) summarized briefly the exudation and volatilization for low molecular weight stabilizers. Other workers have investigated the volatilization of low molecular weight stabilizers during high-temperature processing and accelerated end use tests (14,15). Their results show that significant amounts of low molecular weight stabilizers were lost during end use tests.

TABLE 1: Changes of the Relative Composition of the Sample Surface for Samples A and B During UVCON Irradiation as Measured from ESCA Spectra

Number	Relative concentrations from ESCA peak heights			
	C	O	N	Σ, C,O,N
A-0 (0 hr)	500.0	157.8	5.4	663.2
A-60 (60 hr)	481.5	176.9	8.7	667.1
A-100 (100 hr)	463.0	219.2	12.0	694.2
A-200 (200 hr)	422.2	280.8	15.2	718.2
A-300 (300 hr)	370.4	240.4	17.4	628.2
B-0 (0 hr)	507.4	150.0	5.4	662.8
B-60 (60 hr)	459.3	201.9	9.8	671.0
B-100 (100 hr)	414.8	288.5	12.0	715.3
B-200 (200 hr)	422.2	267.3	16.3	705.8
B-300 (300 hr)	411.1	269.2	20.6	700.9

TABLE 2: Unsaturated Polyester Resins with Polymerizable Ultraviolet Stabilizer: 2(2-Hydroxy-5-vinylphenyl)2H-benzotriazole (2H5V) and 2(2-Hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P)

Unsaturated polyester, g	Ultraviolet stabilizer			Actual amount, wt %[a]
		Amount		
	Type	mg	wt %	
5.05	--	--	--	--
4.96	2H5P	50	1	0.99
4.87	2H5P	99	2	1.96
4.78	2H5P	148	3	2.96
4.65	2H5P	245	5	5.16
4.95	2H5V	50	1	1.00
4.88	2H5V	99	2	1.96
4.79	2H5V	148	3	2.91
4.75	2H5V	250	5	4.76

Initiator: AIBN, 40 mg, 0.8 wt %; reaction temperature, 80°C; reaction time, 2 hr. A solution of 66% by weight of unsaturated polyester (17) and 34% by weight of styrene were used.

(a) According to nitrogen analysis, ±0.1% accurate.

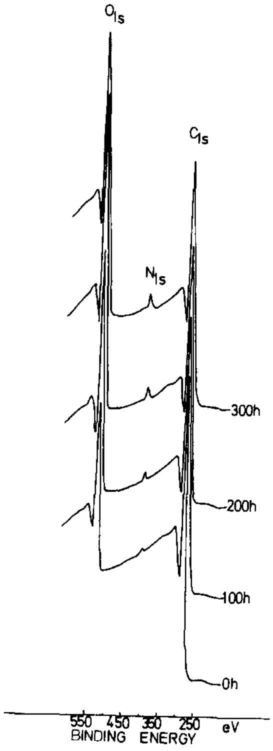


FIGURE 2: ESCA Spectra of the Cls, Ols, and Nls Bands of Sample A Before and After Irradiation in Air for 100, 200, and 300 hr.

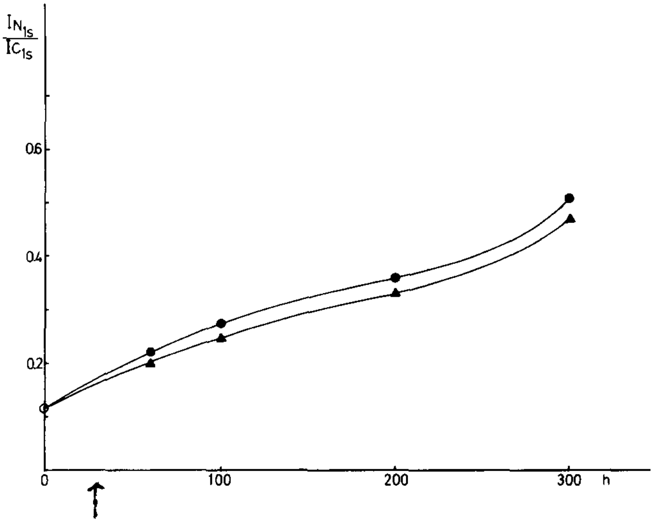


FIGURE 3: Intensity Ratios of Nls to Cls Bands in the ESCA Spectra of Samples B (●) and A (▲) Before and After Irradiation for 100, 200, and 300 hr.

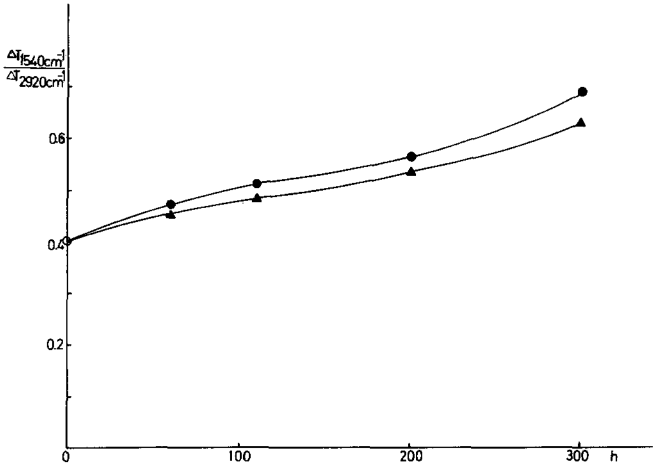


FIGURE 4: Reflection IR Measurements of Samples B (●) and A (▲) Before and After Irradiation for 100, 200, and 300 hr.

Reflection IR experiments (Figure 4) indicate results similar to those of the ESCA measurements, although the observed changes are smaller. This result is expected because the IR reflection measurement penetrates a much thicker surface layer (1-5 μm) than do ESCA measurements. The -C=N- stretching vibration at 1500-1520 cm^{-1} was used for the detection of the 2H5V or 2H5P units (16). More details of the photooxidation of this photostabilized unsaturated polyester resin will be discussed in another paper.

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