Photodegradation of Water-Based Acrylic Coatings Containing Silica

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The durability of acrylic copolymer systems containing silica as a matting agent is investigated, with particular emphasis on the photodegradation process. The effects of the photodegradation process on the films are monitored chemically via reflectance FTIR spectroscopy and UV spectrophotometry and monitored physically via gloss levels, optical properties, film thickness, and film smoothness measurements of the cured film. The findings of this study show that as a result of photooxidation high levels of hydroperoxides are observed. In addition the FTIR results, which are discussed from a mechanistic point of view, indicate that functional group formations and crosslinking reactions which occur as a consequence of photodegradation, play a primary role. Therefore, this study suggests that silica can reduce the durability of acrylic based formulations and that the extent of this photodegradation appears to be dependent on silica type.

INTRODUCTION

Worldwide restrictions on the emission of volatile organic compounds (VOCs) into the atmosphere have forced the surface coatings industry to find more environmentally acceptable replacements to the traditional solvent-based systems currently in use. A number of alternatives have been developed including waterborne technologies. The replacement of organic solvents by water poses a number of challenges to both resin and additive manufacturers, particularly in the areas of film durability and the mechanical properties of cured coatings. The major component of any coating, whether it be solvent- or water-based, is the polymer resin. The photochemical instability of many polymers limits their use in coatings, especially those designed for exterior applications, such as exposure to sunlight for prolonged periods results in photodegradation. Despite extensive literature on photo breakdown mechanisms in polymers, confusion still exists with respect to the definition of photodegradation.

Photodegradation is defined as the chain scission and/or photocrosslinking of the polymer, initiated by the absorption of a photon of light. When this occurs in the presence of air, the process is known as photooxidation. Polymer degradation has been most actively studied in the class of polymers known as the polyolefins. It is generally assumed that the fundamental process underlying the photooxidation of polyolefins is a free radical chain mechanism resulting in the production of polymer hydroperoxides, which are critical intermediates in the photooxidation of many polymers.[1-3] The stability of these hydroperoxides is highly structure dependent and they are known to undergo secondary reactions giving rise to compounds containing hydroxyl, carbonyl, and vinyl groups.

One of the most important film-forming latexes used in waterborne coatings is acrylic resins. These are, for the most part, the acrylate and the methacrylate esters of lower alcohols, of which methanol and butanol have the widest application. Photodegradation studies of polymethyl methacrylate (PMMA) show extensive chain scission and the evolution of methyl formate, methanol, methane, carbon monoxide, carbon dioxide, and hydrogen.[4-7] Despite the close similarity in structure, the degradation behavior of polybutyl acrylate (PBA) differs greatly from that of PMMA. Crosslinking and formation of a high proportion of short chain fragments are characteristic of PBA breakdown, with only extremely small monomer yields.[8-10] Latexes based on copolymers of methyl methacrylate (MMA) and butyl acrylate (BA) are currently being used in waterborne formulations. The differing glass transition temperatures (T_g) of these monomers yield copolymers with good film properties. Limited research into the degradation of MMA and BA copolymers has been carried out, however, Allen et al.[11] suggested possible mechanisms by which photooxidation can take place.

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Table 1—Typical Physical Properties of Silica A and Silica B

Property	Silica A	Silica B
Particle size (Malvern)/μm	9.5	8.0
Surface area (BET)/m^2g^{-1}	240	190
Pore volume (BJH)/ccg^{-1}	1.35	1.15
Surface treatment	None	None

This paper documents part of an ongoing study into the durability of acrylic copolymer systems containing silica with particular emphasis on the photodegradation process. The role of silica within these systems is to produce a matt film. The photooxidation mechanism was evaluated by FTIR spectroscopy to show functional group changes and by colorimetric UV analysis to follow the photochemical generation of hydroperoxides. The effect of photooxidation on the gloss levels, the optical properties, film smoothness, and film thickness was also evaluated.

EXPERIMENTAL

Materials

Two copolymer systems were used in this study. The first (resin 1) was based on a methyl methacrylate, butyl acrylate system, and the second (resin 2) on a methyl methacrylate, butyl acrylate system containing styrene. It is believed that the sequences of MMA and BA are variable within the chain.

Two commercially available silicas used as matting agents in clear acrylic-based waterborne systems were selected: silica A and silica B. Typical physical properties of these silicas are summarized in *Table* 1.

These resins and silicas were incorporated into commercially available lacquer formulations (*Table* 2). In both cases the ingredients were added together in the order listed, one minute apart, and mixed at 2,000 rpm using a Heidolph high-speed stirrer fitted with a Cowles type stirrer head. The mixing speed was increased to 3,000 rmp after the silica was added. A formulation in which water replaced the silica was prepared for each system, and these were used as the controls. Once all the components had been added, the formulation was mixed for an additional 15 min at 3,000 rpm. The lacquers were left to deaerate before films were drawn down with a 100 μm (wet film thickness) K bar, which gave a dry film thickness of 30 μm. The films were left to dry at ambient temperature for 24 hr.

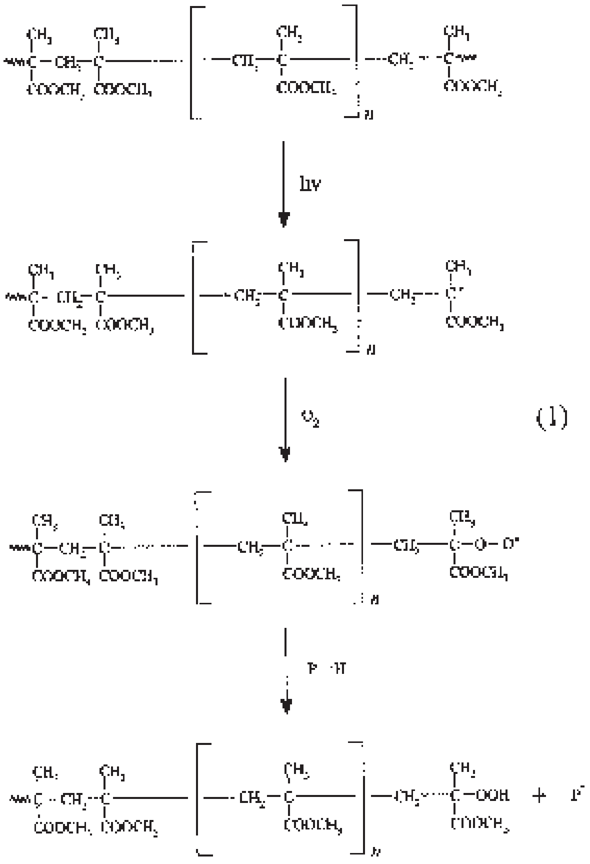
UV Irradiation

Accelerated photodegradation was carried out by irradiating the films in commonly used Microscal units (Microscal Ltd., London), fitted with a 500W high pressure mercury/tungsten lamp (wavelength > 300 nm). An operating temperature of 50°C was used with 50% relative humidity. Samples tested for hydroperoxide analysis, FTIR analysis, and film thickness were coated onto melinex whereas samples tested for matting, optical properties, and film smoothness were coated onto glass microscope slides.

Table 2—Commercially Available Formulations Utilized in this Study

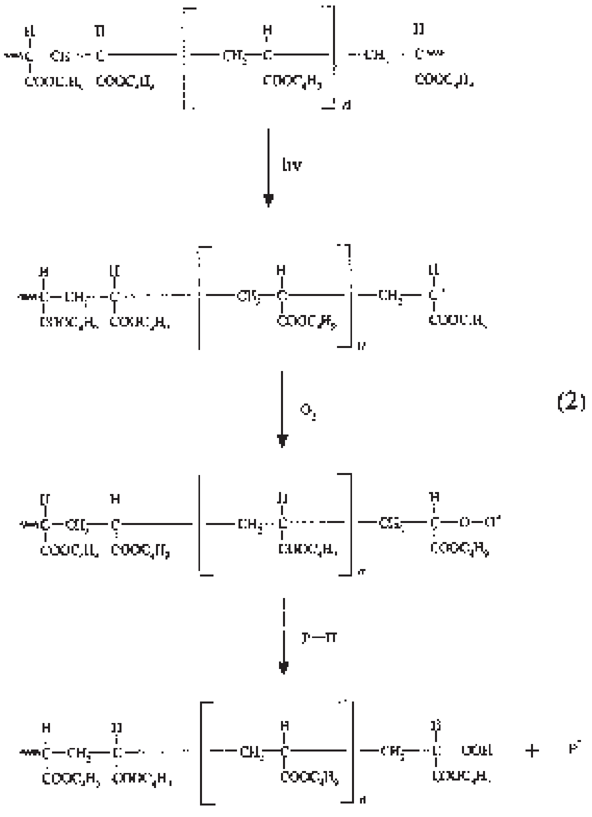
Formulation 1 (F1)		Formulation 2 (F2)	
Resin 1	74.70 g	Resin 2	71.4 g
Estasol (coalescent) (Chemoxy International, Cleveland)	2.99 g	Water	16.80 g
Water	13.91 g	Tegofoamex 1488 (defoamer) (Tego Chemie Service GmbH, Essen)	0.20 g
BYK 024 (defoamer) (BYK Chemie GmbH, Wesel)	0.15 g	Silica (matting agent)	2.50 g
Silica (matting agent)	3.50 g	Dowanol[a] PnB (coalescent) (K&K-Greeff Ltd., Croydon)	3.81 g
Glaswax E1 (wax) (Allied Colloids, Bradford)	4.00 g	Dowanol[a] DPnB (coalescent) (K&K-Greeff Ltd., Croydon)	1.90g
BYK 024 (defoamer) (BYK Chemie GmbH, Wesel)	0.05 g	Tegofoamex 1488 (defoamer) (Tego Chemie Service GmbH, Essen)	0.05 g
Troysol Lac (wetting agent) (Troy Chemical Company, Netherlands)	0.20 g	Troysol Lac (wetting agent) (Troy Chemical Company, Netherlands)	0.50 g
Nopco DSX 1550 (rheology modifier) (Henkel Performance Chemicals, Leeds)	0.50 g	Glaswax E1 (wax) (Allied Colloids, Bradford)	2.14 g
		Nopco DSX1514 (rheology modifier) (Henkel Performance Chemicals, Leeds)	0.80 g

(a) These components were premixed.



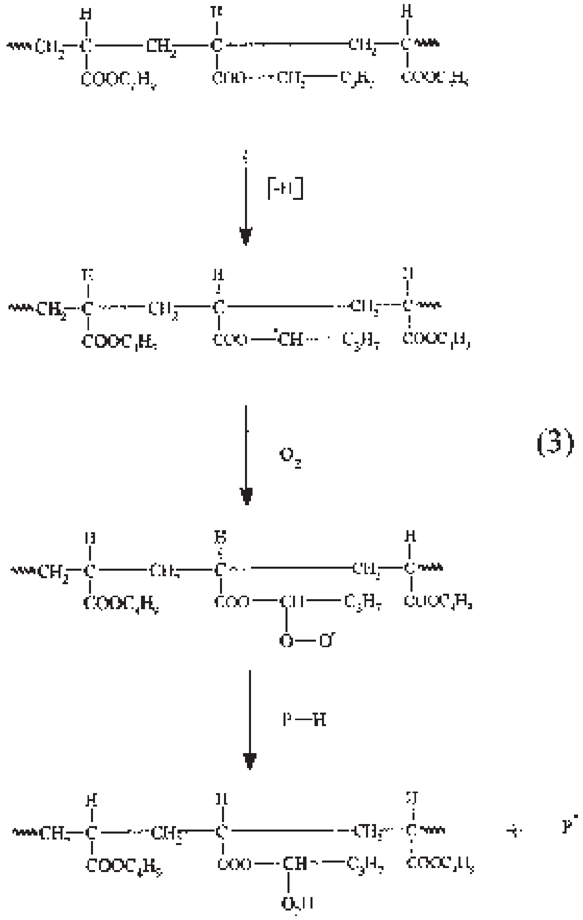
(1)

FORMATION OF TERTIARY HYDROPEROXIDES
Where P-H is the polymer chain



(2)

FORMATION OF SECONDARY HYDROPEROXIDES



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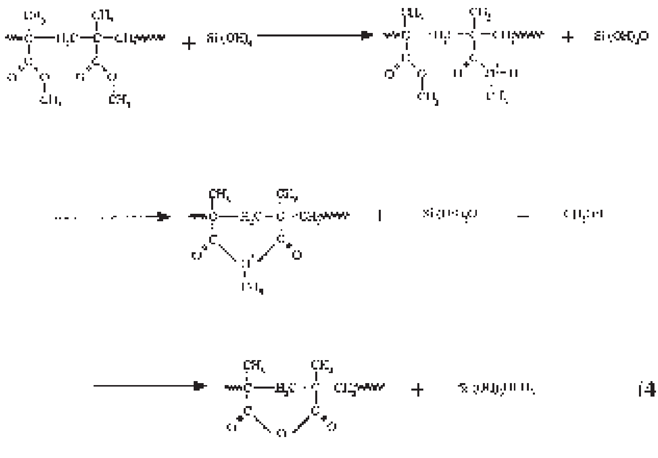
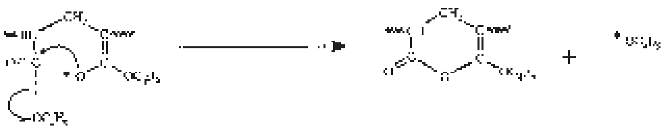
FORMATION OF PRIMARY HYDROPEROXIDES

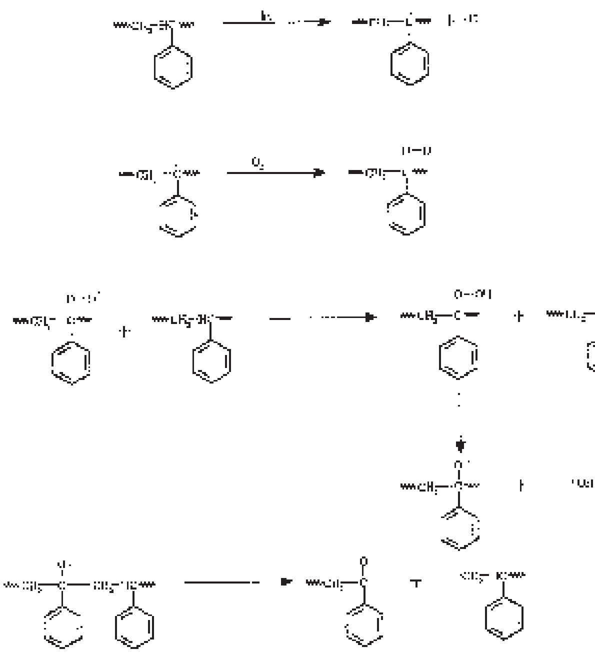


(4)

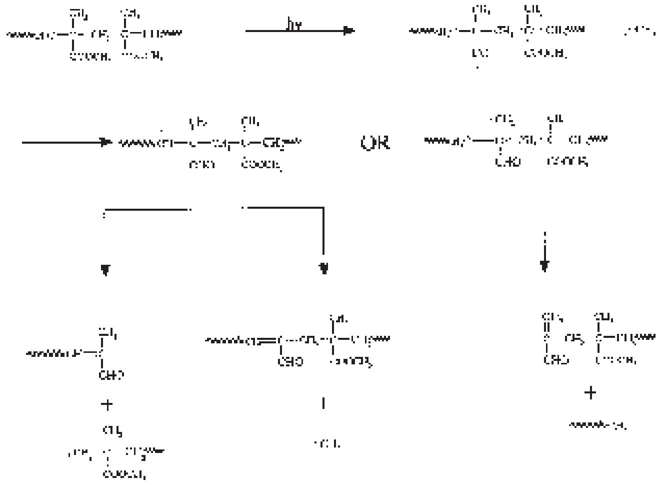
ANHYDRIDE FORMATION



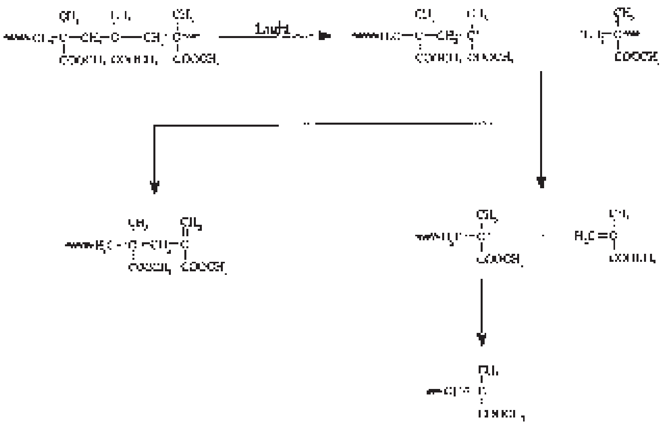
LACTONE FORMATION (5)



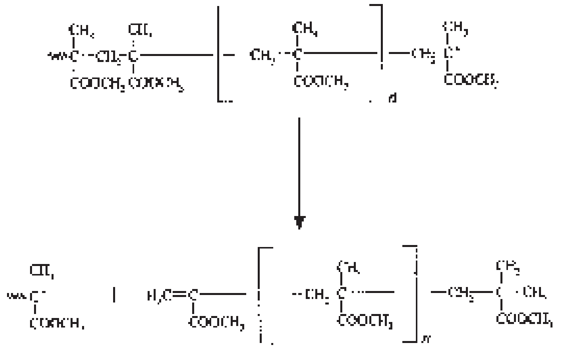
ACETOPHENONE END GROUP FORMATION



VINYL KETONE FORMATION (7)

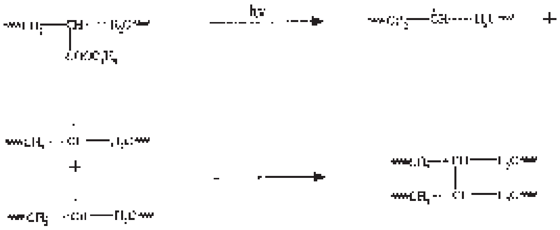


VINYL FORMATION VIA UNZIPPING OF PMMA (8)



(9)

VINYL FORMATION VIA INTRAMOLECULAR TRANSFER PROCESS



(10)

CROSSLINKING OF BA

Hydroperoxide Analysis

Hydroperoxide groups that are stable enough to accumulate to high concentrations may be detected by various methods.[12-14] The method utilized here was the standard iodometric procedure outlined by Carlsson and Wiles.[15]

FTIR Analysis

Functional group changes were monitored by the use of reflectance FTIR spectroscopy. A Bio-rad SPC 3200 FTIR spectrophotometer was used. Difference FTIR spectra were considered as some of the FTIR changes are small but these changes could be marked significantly by small variations in the thickness of the film over the area of analysis.

Cured Film Properties

The effect of photodegradation on the cured film properties was monitored by measuring the following properties of the drawn films: gloss levels (using a Tri-microgloss 20-60-85, 160, glossmeter), optical properties (using a BYK-Gardner haze-gard plus haze meter), film thickness (using a Mitutayo precision digital micrometer) and film smoothness (using a Taylor-Hobson, surtronic 3P smoothness tester).

RESULTS AND DISCUSSION

Hydroperoxide Analysis

Figures 1 and 2 show the formation of hydroperoxides during the photooxidation process as a function of time. The changes in hydroperoxide levels appear to be dependent on the formulation used. For formulation 1 (F1), higher levels of hydroperoxides are observed for the matted system, while for formulation 2 (F2) the matted and the unmatted systems produce similar levels of hydroperoxides. At this stage the results are independent of the silica matting agent utilized. The formulations used differ both in terms of the resin and other additives employed. For example, F1 uses BYK 024 as the defoamer compared to Tegofoamex 1488 in F2. It is possible that one or more of these reagents in F1 as well as the polymer is undergoing photooxidation, thereby increasing the level of hydroperoxides, or it could be that a component of F2 is acting as a radical scavenger such as an amine-based reagent. Another possible explanation is that the inclusion of styrene in resin 2 is adding stability to this system by acting as a blocking agent in the unzipping mechanism of photodegradation of PMMA.

The hydroperoxide curves (*Figures* 1 and 2) fluctuate considerably because the rates of decomposition and formation of hydroperoxide depend on the type of hydroperoxide group. The measured levels of hydroperoxide in these systems are high, approximately 800-1000 μg ml^{-1}; typical values for other systems (e.g., polypropylene) are around 300 μg ml^{-1}.[16] It is possible that the observed hydroperoxide levels are due to tertiary hydroperoxides as these are known to be relatively stable.[1] The tertiary hydroperoxides could form on the PMMA chain as a result of oxidation occurring at the tertiary carbon before chain branching oxidation reactions form other products such as ketones and carboxylic acids[17] [see equation (1)]. In the case of PBA, two types of hydroperoxide are likely to be produced. The first is associated with main chain oxidation and will give rise to less stable secondary hydroperoxides [equation (2)], while the second, which gives rise to unstable primary hydroperoxides, is linked to side-chain oxidation of the methylene adjacent to the ester function [equation (3)].

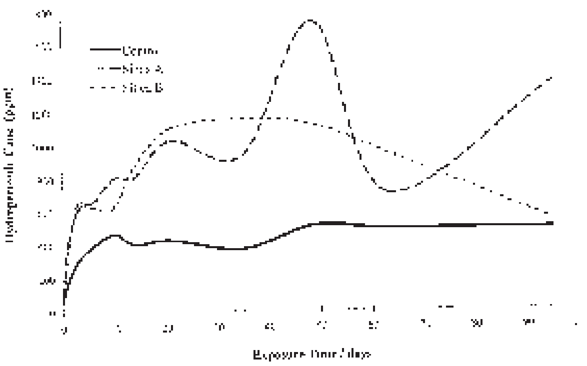


Figure 1—Hydroperoxide formation during the photooxidation process for formulation 1.

FTIR Analysis

Chemical changes in the structure of the lacquers were measured by FTIR spectroscopy as shown in *Figures* 3-8. This technique has been widely used to follow the photooxidative behavior of many polymers.[17] To simplify the complex changes occurring in functionality as the films age, the study concentrates on the following formations: acid anhydride, lactone, acetophenone, vinyl ketone, and vinyl. In addition to these formation reactions, crosslinking mechanisms may occur and these are also discussed.

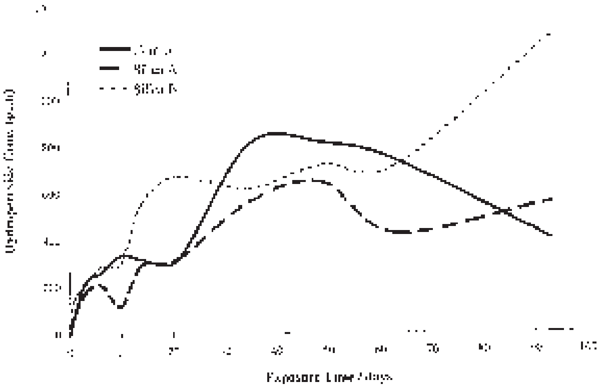


Figure 2—Hydroperoxide formation during the photooxidation process for formulation 2.

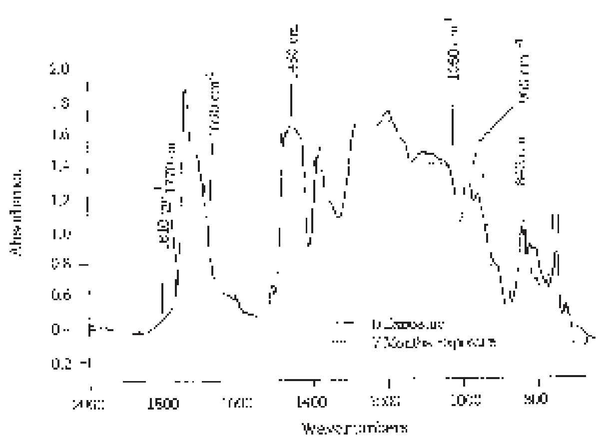


Figure 3—Formulation 1/silica A.

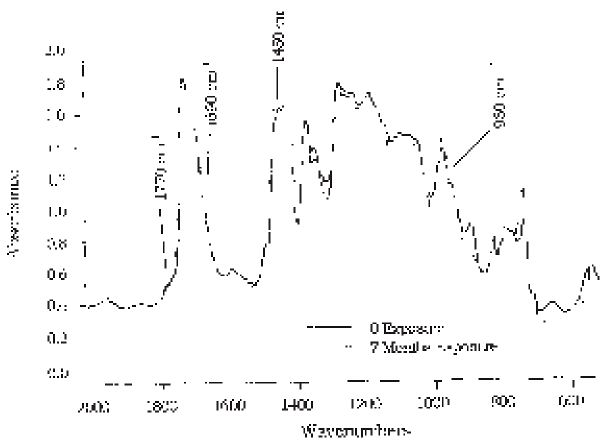


Figure 4—Formulation 1/silica B.

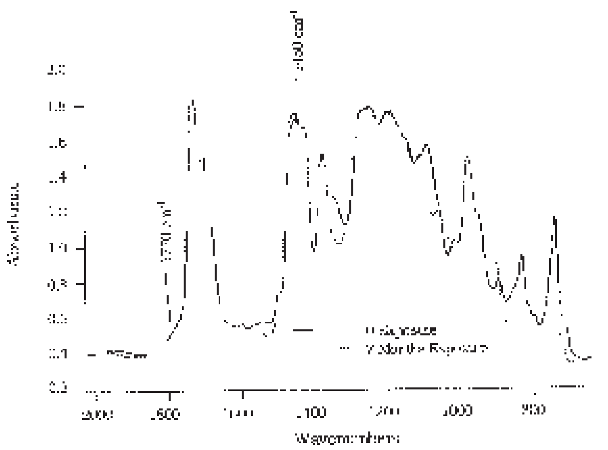


Figure 5—Formulation 1/control.

Anhydride Formation

In both F1 and F2, where silica A was employed as the matting agent, a new absorption band at 1810 cm^{-1} was formed (*Figures* 3 and 6). This possibly may be attributed to anhydride formation which would occur as a result of a cyclization reaction involving PMMA and free silanol groups which would be present within the pores of silica A [equation (4)].[18] No such absorption appears in the control samples or for the silica B samples (*Figures* 4, 5, 7, and 8) suggesting that for this photodegradation pathway, silica A is aiding photooxidation while silica B is having little or no effect.

Lactone Formation

In all samples studied (*Figures* 3-8), the formation of a shoulder on the carbonyl absorption at 1770 cm^{-1} is observed, a possible indication of lactone formation. Equation (5) proposes a possible route for the generation of such a lactone group.[19] This process has previously been reported in conjunction with thermal degradation, however, the mechanism also appears to occur under prolonged irradiation.

Acetophenone Formation

In *Figures* 6-8 a new absorption is observed at 1703 cm^{-1}. This only occurs with F2 films. The absorption for the control (*Figure* 8) and the silica B sample (*Figure* 7) is smaller than that for the silica A sample (*Figure* 6). It is possible that the absorption at 1703 cm^{-1} is associated with the styrene present only in resin 2, since UV irradiation of polystyrene is known to result in acetophenone end group formation[2] [equation (6)]. The formation occurs as a result of the photodecomposition of hydroperoxide groups on the polystryrene. As the observed adsorption is higher for the silica A sample than for the silica B sample, it would appear that silica B causes less photodegradation than silica A.

Vinyl Ketone Formation

When comparing the control with the samples containing silica, it can be seen that a shoulder is forming at 1690 cm^{-1} (*Figures* 3, 4, 6, and 7). This can be attributed to vinyl ketones, which may be produced by a number of different light induced reactions on PMMA [equation (7)]. Since no vinyl ketone formation is observed in the control samples, it is possible that the matting agents are promoting photooxidation in this case.

Vinyl Formation

It can be seen from *Figures* 3 and 6 that there is an increase in the absorption bands occurring at 960 and 842 cm^{-1}. These may be attributed to vinyl group formation: trans vinyl at 960 cm^{-1} and vinylidene at 842 cm^{-1}. It is possible that the photodegradation mechanism of PMMA after long periods of irradiation is similar to its thermal degradation mechanism, which is simply a reverse of polymerization (unzipping)[16] thus leading to very high monomer yields [equation (8)]. It has also been reported[20] that on photodegradation of copolymers of MMA and BA, short chain fragments are produced. These chain fragments are believed to be formed in an intramolecular transfer process that introduces terminal carbon-carbon unsaturation [equation (9)].

It can be seen from *Figure* 8 that only the trans vinyl absorption increases for the control in F2, and that in F1 (*Figure* 5) vinyl formation does not occur. Furthermore, in the samples containing silica B (*Figures* 4 and 7), trans vinyl formation has only been observed in F1 films. It is therefore possible that silica, in particular silica A, is enhancing degradation in terms of photodecomposition to form vinyl groups.

Crosslinking Reactions

The presence of one or more of the following absorption bands suggests that crosslinking is occurring as a result of the light induced reactions on PMMA and PBA; 1600, 1450, 1352, and 1210 cm^{-1}. The effects of UV irradiation on PMMA and PBA differ considerably. PBA simultaneously undergoes chain scission and crosslinking [equation (10)], whereas PMMA has no tendency to crosslink when irradiated. For the films produced from F1, the 1450 cm^{-1} absorption is present in all samples (*Figures* 3-5). Considering films drawn from F2, samples containing silica A have all of these absorptions (*Figure* 6) whereas silica B has only the 1600 cm^{-1} band (*Figure* 7). The control shows all the absorptions except the one at 1210 cm^{-1} (*Figure* 8). Furthermore the absorption at 1050 cm^{-1} in F2 films (*Figure* 6) and 1040 cm^{-1} in F1 films (*Figure* 3) shows a large increase when silica A is present. The observed absorption is due to the ether vibration of the ester group, formed by a crosslinking reaction[21] [equation (11)]. The absorption at 1600 cm^{-1} (a conjugation absorption) present in all of the F2 samples, can possibly be assigned to the formation of dienes, a reaction which is known to occur on UV irradiation of polystyrene. It would therefore seem that the type of crosslinking occurring is dependent on the resin composition. The absorptions relating to these crosslinking reactions are more prevalent in silica A than in silica B, suggesting that silica B causes less photooxidation than silica B, in terms of crosslinking.

Cured Film Properties

Over an irradiation period of about three months, no significant change was observed in either the optical properties or the gloss levels of the matted systems based on F1 and F2. Film smoothness and film thickness also showed little variation.

CONCLUSION

The findings of this paper suggest that the formulations containing silica show more signs of degradation than the formulations without silica. Although the hydroperoxide levels of the matted and unmatted systems in F2 are similar, in F1 the hydroperoxide levels are much higher in the matted system. This suggests that the matting agent reduces the stability of the F1 system, how-

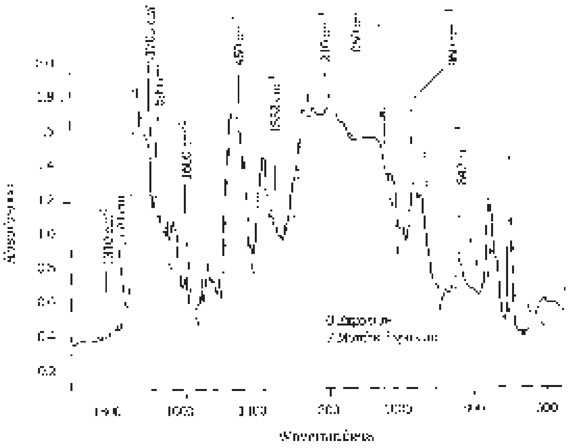


Figure 6—Formulation 2/silica A.

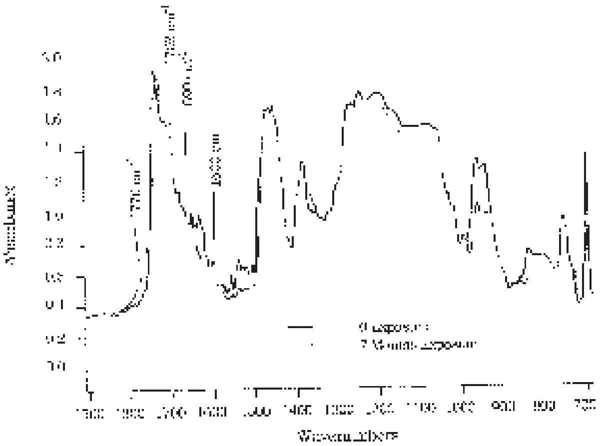


Figure 7—Formulation 2/silica B.

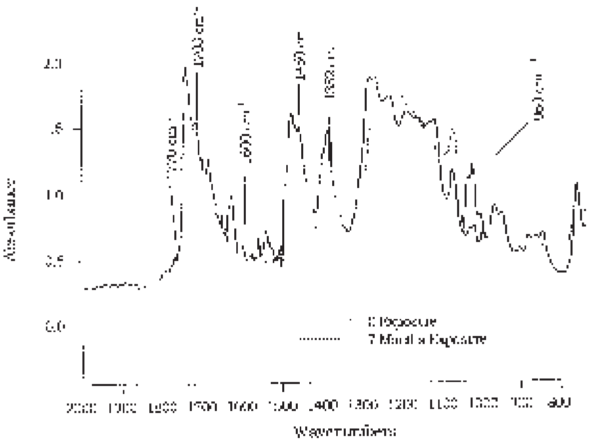


Figure 8—Formulation 2/control.

ever, longer periods of irradiation are required before definite conclusions can be drawn.

From the FTIR results, a number of functional group changes and crosslinking reactions have been identified from new or increased absorptions observed over the seven month exposure period. Since there are differences in the spectra of F1 films compared with F2 films, the type of crosslinking reactions occurring would appear to be dependent on resin composition. Spectral changes can be associated with the products from photooxidation and as there are many more changes for the samples containing silica compared with the control samples, it is likely that the silica is also playing a role in film degradation. An explanation as to why silica plays a role in the film degradation is that the metal ions, present in the silicas as impurities from processing, could be catalyzing the photooxidation degradation of the films. The level of metal ions present in the two silicas differ but as it is thought that a certain level of metal ions will enhance degradation, any further increase will have no effect as a plateau will have been reached. This work also suggests that the silica type (e.g., pore volume and surface area) can affect the mechanism by which photodegradation occurs, as well as its extent; silica A forming more photodegradation products than silica B. A reason for this difference in extent of photooxidation could be related to the adsorbed and associated water contents of the silicas. Silica A has a low adsorbed and associated water content, and it also contains free silanol groups within the silica pores whereas silica B does not.

From studies on the cured films, no conclusions on the effects of photodegradation on the physical properties of the cured films can be drawn.

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