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The Effects of Silica Nanoparticles on the Photocuring Behaviors of UV-Curable Polyester Acrylate-Based Coating Systems

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Introduction

Recent years have seen considerable interest in hybrid organic-inorganic nanocomposites in the materials market, and they are now considered the next-generation composite materials due to their effectiveness in significantly improving the properties of materials used in many engineering applications involving plastics, coatings, rubber, electronics, varnishes, and adhesives. The most commonly used inorganic nanoparticles are SiO_2, TiO_2, ZnO, and $CaCO_3$, of which silica nanospheres were the first nanoparticles produced and have now been studied in diverse polymer systems.[1-4]

Applications of hybrid organic–inorganic UV-curable coatings in the rapid and solvent-free curing of coating films has received particular attention, and these can be made with ready-to-use acrylic monomers or oligomers containing a high content of predispersed silica nanoparticles. Their attractiveness is attributable to the marked improvements in several mechanical and electrical properties, including resistance to scratching and abrasion, thermal stability, and chemical resistance, while maintaining both transparency and gloss.[1-8] In addition, UV-curable coatings using colloidal nanosilica acrylates copolymerized with polyurethane or polyester acrylate (PEA) show remarkable barrier characteristics to gases and moisture as well as very good resistance to staining, which is due to the excellent surface covering by silica nanospheres and their homogeneous distribution in the bulk of the coatings, which usually form through the synergistic effect of the organic and inorganic components.[6-8]

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Whilst many studies have investigated hybrid organic-inorganic nanocomposite systems, there are no detailed reports on the photocuring behaviors of such systems containing silica nanoparticles. In order to understand the aforementioned expected improvements obtained by adding silica nanoparticles, it is important to investigate how these nanoparticles influence the photocuring behaviors within the organic matrix, which would not only allow a quantitative comparison of the photocuring behaviors of different systems with and without silica nanoparticles, but also help to predict photocuring behaviors for process design and control.

This study investigated the photocuring behaviors of UV-initiated free-radical photopolymerizations of PEA-based systems with and without silica nanoparticles using photodifferential scanning calorimetry (photo-DSC), UV-visible spectroscopy, and FTIR spectroscopy.

Experimental

Materials. PEA (Ebecryl 830) with hexa functionality from UCB Chemicals was used as the oligomer, 1,6-hexanediol diacrylate (HDDA) from UCB Chemicals was used as the monomer, and 1-hydroxy-cyclohexyl-phenyl ketone (HCPK, Irgacure 184) from Ciba-Geigy was used as a free-radical photoinitiator. Silica nanoparticles (AEROSIL TT600, hydrophilic fumed silica) with a primary size in the range 7-40 nm were provided by Degussa. All the materials were used as received. The structures of the materials are illustrated in Figure 1.

Preparation of Colloidal Nanosilica Acrylates. Colloidal nanosilica acrylates were prepared by directly mixing nanosilica particles with PEA and HDDA at 30 °C for about 1 h under vigorous stirring whilst using a dissolver (DISPER-

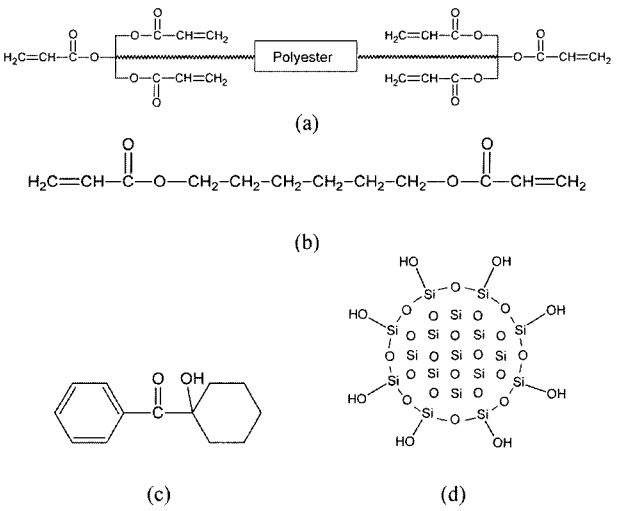

Figure 1. Chemical structures of (a) PEA, (b) HDDA, (c) photoinitiator, and (d) silica nanoparticle.

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Photodifferential Scanning Calorimetry. The photo-DSC experiments were performed using a differential scanning calorimeter equipped with a photocalorimetric accessory (TA 5000/DPC System). The initiation light source was a 200-W high-pressure mercury lamp, which gave a UV light intensity at the sample of 35 mW/cm^2 over a wavelength range of 200-440 nm. Samples weighing 4.0±0.1 (mean± SD) mg were placed in uncovered aluminum pans, and a reference aluminum pan was left empty. TA Instruments software was employed to acquire the data and analyze the results from the photo-DSC experiments.

UV-Visible Spectroscopy. The absorption spectra of acrylate films containing different amounts of silica nanoparticles were recorded on a Cary 3 Bio UV-Visible spectrophotometer in the range 250-425 nm. The films were prepared as follows: the liquid formulations listed in Table I were applied to a glass substrate at a thickness of ~20 μm using a wire-wound rod, and the wet films were exposed to UV radiation at 80 W/cm using a medium-pressure mercury lamp and conventional UV equipment. The UV-curable films were cut into rectangles of size 2×5 cm^2.

FTIR Spectroscopy. Transmission FTIR spectra were collected on a Spectrum GX spectrometer (PerkinElmer). Each set of reference and sample spectra represents the average of 128 scans recorded at a resolution of 8 cm^{-1}. Dry air was continuously purged through the instrument during the measurements. The liquid formulations listed in Table I were sandwiched between KBr windows that were typically ~5 μm thick (using a Teflon spacer), and were exposed to UV radiation from a metal halide lamp (EFOS UV System) via a fiber-optic light pipe. The UV light intensity at the sample was 42 mW/cm^2 over the range 250-410 nm.

Results and Discussion

We used photo-DSC to clarify the effects of silica nanoparticles on the photocuring behaviors of the various UV-curable hybrid organic-inorganic nanocomposite systems listed in Table I. This technique is capable of providing photopolymerization kinetics data in which the measured heat flow can be converted directly to the ultimate percentage conversion and polymerization rate for a given amount of formulation, with the data obtained reflecting the overall curing reaction of the sample.[9-12]

Table I. Formulations of the UV-Curable PEA-Based Systems with Different Amounts of Silica Nanoparticles. Data Values are Weight Percentages

Component	A	B	C	D	E
PEA (acrylate oligomer)[a]	30	30	30	30	30
HDDA (acrylate monomer)[a]	70	70	70	70	70
HCPK (photoinitiator)[b]	3	3	3	3	3
AEROSIL TT600 (silica nanoparticles)[c]	-	2.5	5	10	15

[a]UCB Chemicals, [b]Ciba-Geigy, [c]Degussa.

The photo-DSC exotherms for the photopolymerization of the UV-curable colloidal nanosilica acrylate systems containing various concentrations of silica nanoparticles are illustrated in Figure 2. The amounts of heat released, the induction times, the peak maxima, the ultimate percentage conversions, and the maximum polymerization rate ($R_{p,max}$) derived from Figure 1 are collected in Table II.

Figure 2 and Table II indicate that as the concentration of silica nanoparticles was increased up to 5 wt%, the exotherm and percentage conversion (which are related to the cross-link density) and $R_{p,max}$ all increased, whereas the induction time (which is the time to attain a conversion of 1%, and is related to the efficiency of the photoinitiator) and the peak maximum (which is the time to attain the exotherm maximum) decreased. However, this trend was reversed for silica nanoparticles at above 10 wt%.

The above results suggest that the presence of silica nanoparticles at below 10 wt% accelerated rather than hindered the cure reaction and cure rate of the UV-curable PEA-based systems. At least two factors could be responsible for this behavior. One is that the silica nanoparticles in the formulations behave as an effective flow or diffusion-aid agent for the photopolymerization process, which improves the mobility of propagating chains that gives rise to a noticeable increase in the exotherm and cure rate of the systems containing silica nanoparticles.[13] Another is a lengthening of

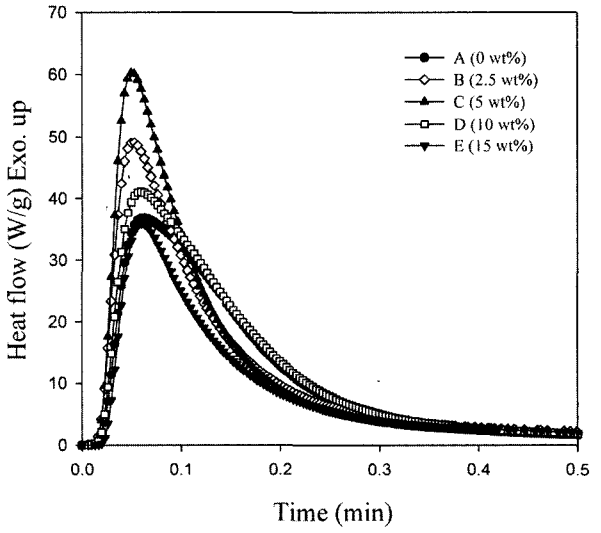

Figure 2. Photo-DSC exotherms for the photopolymerization of formulations A-E listed in Table I. Isothermal curing temperature: 30 °C; sample weight: 4.0 mg; light intensity: 35 mW/cm^2.

Table II. Exothermic Results for the Photopolymerization of Free-Radical Acrylate Formulations under the Conditions Described in the Legend of Figure 2

Formulation	ΔH (J/g)	Induction Time (s)	Peak Maximum (min)	Conversion (%)	$R_{p,max}$[a] (min^{-1})
A (0 wt%)	332	1.58	0.63	73	5.77
B (2.5 wt%)	341	1.34	0.49	75	7.85
C (5 wt%)	368	1.21	0.47	81	9.47
D (10 wt%)	327	1.38	0.58	72	6.63
E (15 wt%)	273	1.53	0.63	60	5.71

[a] $R_{p,max}$: maximum polymerization rate ($R_p = d\alpha/dt$, where α is the fraction of resin converted).

the path of the UV light by partial scattering or reflection. The silica nanoparticles themselves are significantly smaller than the wavelength of UV light, and hence do not scatter or reflect the incident light. However, the silica nanoparticles used here are hydrophilic and possess an excess of -OH groups on their surfaces, and consequently tend to aggregate due to their high surface energy. Therefore, aggregates comprising many nanoparticles could be formed that would cause scattering or reflection of UV light, thereby enhancing the photoinitiation efficiency of UV curing.

In contrast, the addition of silica nanoparticles at above 10 wt% resulted in a decrease in the exotherm, percentage conversion, and $R_{p,max}$, and an increase in the induction time and the peak maximum. This result is probably attributable to the higher concentration of silica nanoparticles increasing the concentration of larger aggregates, which hinders the absorption of the incident radiation by the photoinitiator and thereby reduces the efficiency of the photoinitiation of UV curing.

Figure 3 exhibits the absorption spectra of the PEA-based films with and without silica nanoparticles. The figure indicates that the absorbance in the range 250-450 nm increases as the concentration of silica nanoparticles increases, which infers that the scattering and reflection of UV light by the newly formed silica aggregates increases with an increasing content of silica nanoparticles.

FTIR spectroscopy was used in a separate experiment to obtain mechanistic insight into the effect of silica nanoparticles on the photopolymerization reactivity of the aforementioned formulations.[14] Figure 4 shows the FTIR spectra of the UV-curable PEA-based formulations containing 5 wt% silica nanoparticles obtained before and 15 and 30 s after UV curing. The band at 1455 cm^{-1} (due to $-CH_2$ bending vibration in HDDA) was used as an internal reference peak since its intensity was relatively stable during the photocrosslinking reaction, whereas the band at 812 cm^{-1} (due to $=CH_2$ deformation modes of the acryl group) was also used as a measure of the extent of cure, because this band decreases as the photocuring reaction proceeds.

The FTIR relative intensity ratio (812 cm^{-1}/1455 cm^{-1}) of the UV-curable PEA-based films containing different amounts of silica nanoparticles as a function of the concentration of silica nanoparticles after 30 s of UV curing is presented in Figure 5. This figure indicates that the extent of the cure reaction increased gradually as the concentration of silica nanoparticles was increased up to 5 wt%, whereas it decreased above 10 wt%. This result is consistent with the photo-DSC results, and hence provides a comprehensive

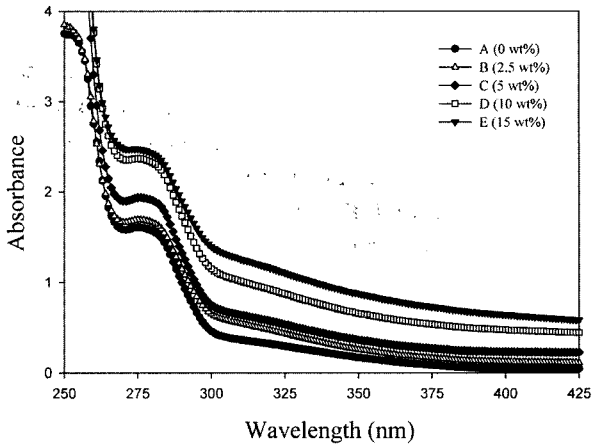

Figure 3. Absorption spectra of PEA-based films containing various concentrations of silica nanoparticles.

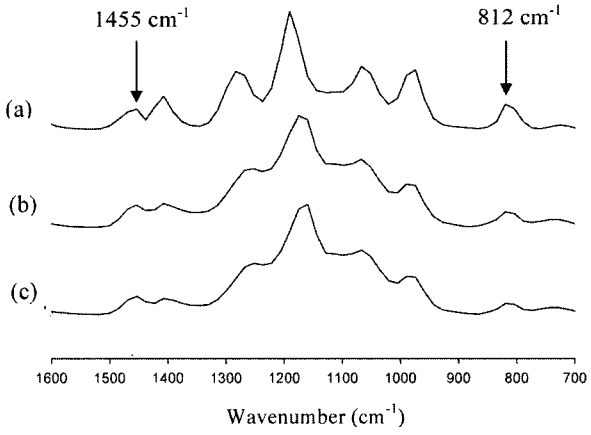

Figure 4. Transmission FTIR spectra of a PEA-based formulation containing 5 wt% silica nanoparticles obtained before (a), 15 s (b), and 30 s (c) after UV curing.

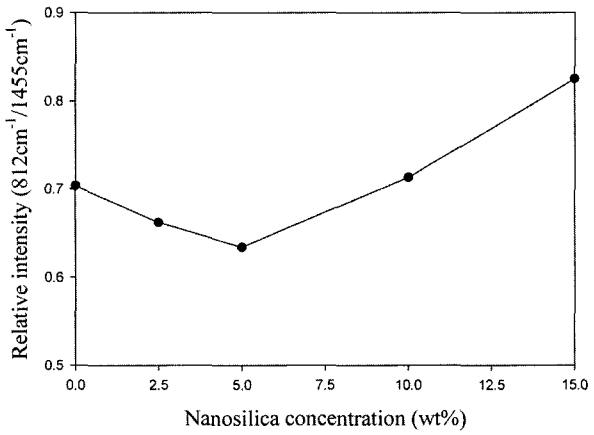

Figure 5. Plot of the FTIR relative intensity ratio (812 cm^{-1}/ 1455 cm^{-1}) of UV-curable PEA-based films versus the concentration of silica nanoparticles after 30 s of curing.

insight into the effect of silica nanoparticles on the photocuring behaviors of UV-curable PEA-based coating systems.

Conclusions

The photocuring behaviors of UV-curable PEA-based coating systems with and without silica nanoparticles have been studied by photo-DSC, UV-visible spectroscopy, and FTIR spectroscopy. Photo-DSC analysis revealed that as the concentration of silica nanoparticles was increased up to 5 wt%, the exotherm, ultimate percentage conversion, and cure rate increased gradually, whereas they decreased above 10 wt%. This result was confirmed by FTIR spectroscopy analysis and indicated that the presence of silica nanoparticles at below 10 wt% accelerated the cure reaction and cure rate of the UV-curable PEA-based systems due to the synergistic effect of silica nanoparticles as an effective flow or diffusion-aid agent during the photopolymerization process and by lengthening the path of the UV light by partial scattering or reflection. However, a decrease in photopolymerization reactivity occurred when the silica content was increased above 10 wt%, which is attributable to aggregation of silica nanoparticles due to their high surface energy.

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