Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 46 (2005) 6640–6648
polymer
www.elsevier.com/locate/polymer

Synthesis of nanocomposite polymers by UV-radiation curing

Christian Decker*, Laurent Keller, Khalid Zahouily, Said Benfarhi[1]

*Département de Photochimie Générale (CNRS—UMR no 7525), Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute-Alsace,
3 rue Werner, 68200 Mulhouse, France*

Available online 14 June 2005

Abstract

Clay-based nanocomposite polymers have been synthesized by photoinitiated crosslinking polymerization of acrylate and epoxy functionalized oligomers. The solvent-free resin containing a small amount (3 wt%) of organophilic clay was cured within seconds upon UV irradiation at ambient temperature. The polymerization reaction was followed by infrared spectroscopy and shown to proceed at a great extent in thick samples (2 mm), due to the higher exotherm and the resulting rise in temperature. The organoclay was shown to have no slowing down effect on the photopolymerization of both acrylate and epoxy resins. The addition of clay nanoparticles was found to reduce the gloss of UV-cured coatings due to an enhanced surface roughness. The viscoelastic and tensile properties of the nanocomposite photopolymer were comparable to those of the neat UV-cured polymer, while their resistance to moisture was significantly increased.

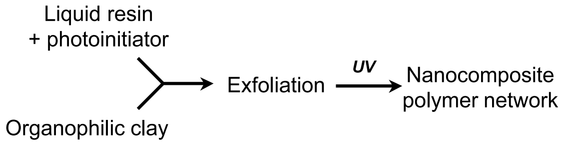
© 2005 Elsevier Ltd. All rights reserved.

Keywords: UV-curing; Nanocomposites; Acrylates

1. Introduction

Nanocomposite polymers have drawn increased attention over the last decade because of their distinct characteristics, in particular superior mechanical and barrier properties, as well as improved thermal stability and fire retardancy [1–3]. Most of such nanocomposites are made of nanosize mineral particles, like colloid silica or clay platelets, which are dispersed in a polymer matrix. In the case of the most widely used clay–polymer nanocomposites, the phillosilicate filler has to be made organophilic by exchange of the alkaline cations through alkylammonium cations in order to improve its compatibility with the host polymer and ensure exfoliation of the one nanometer thick platelets [4]. Complete exfoliation is usually difficult to achieve because of strong ionic bonding between the silicate layers and the intergallery cations. This leads to the additional formation of non-crystalline intercalated structures consisting of disordered stacks of clay platelets embedded into the polymer matrix. With exfoliated nanocomposites, optimum performance can already be achieved at a quite low filler content (3–5 wt%), because of their special morphology and the tendency of such nanoparticles to form skeleton-like superstructures [5]. The clay filler can be incorporated either in the melted polymer or in the monomer which is thermally polymerized subsequently. In both case, thermodegradation (in particular of the alkylammonium salt) may occur during processing, thus affecting both the exfoliation process and the composite thermal resistance.

Clay-based nanocomposites are often made of linear polymers (polyamides [2], polyolefins [6–8], polystyrene [9,10], polyurethanes [11]) which are completely soluble in the organic solvents. They show therefore a limited chemical resistance, which can be substantially improved by using as binder some crosslinked polymer like epoxy-based thermosets [12–14] or acrylate-based photosets [15]. We have recently demonstrated that clay–polymer nanocomposites can be rapidly produced by photoinitiated crosslinking polymerization of multifunctional monomers and oligomers [16–18]. The basic principle of this in situ curing process can be represented schematically as follows:



This well-proven technology, called UV-radiation curing, offers a number of advantages which make it

---

* Corresponding author.

[1] On leave from the University of Batna (Algeria).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.05.018

Table 1
Components of the UV-curable nanocomposite formulations

UV-curable resin	Radical-type	Cationic-type
Photoinitiator	Hydroxyphenylketone (2 wt%) (Darocur 1173 from Ciba) Bisacylphosphine oxide (1 wt%) (Irgacure 819 from Ciba)	Triaylsulfonium salt (3 wt%) (Cyracure UVI-6979 from Dow Chemicals)
Telechelic oligomer	Polyurethane-acrylate (Ebecryl 284 from UCB)	Biscycloaliphatic diepoxide (Araldite CY-179 from Ciba)
	Polyphenoxy-acrylate (Ebecryl 600 from UCB) Polyester-acrylate (Ebecryl 830 from UCB)	
Monomer	Hexanedioldiacrylate (27 wt%) (HDDA from UCB)	
Mineral filler	Interfoliar space (Angströms)	
	Clay	Organoclay
Bentonite T	12.5	17.9
Montmorillonite K10	13.3	17.6
Beidellite LMM	12.5	28.5
Nanomer I-30E (Nanocor)	–	24.5

particularly well suited for the synthesis of nanocomposite polymers [15,19]:

- a solvent-free resin of controlled viscosity through the addition of a monomer acting as reactive diluent;
- a precise control of the swelling time to ensure an optimum exfoliation of the silicate platelets and interpenetration of the resin in the clay galleries;
- an ultrafast polymerization proceeding at the desired rate, by adjustment of the light intensity;
- a processing performed at ambient temperature in the presence of air, thus avoiding any thermal degradation.

Because of its very low consumption of energy and its minor emission of volatile organic compounds, this UV-curing technology has become specially attractive, given today's increasing concern in the industry for the environment. Moreover, UV-cured polymers are known to exhibit superior chemical and heat resistance as a result of their high crosslink density: a typical branch point concentration of 4 mol kg^{-1}, i.e. an average M_c value of 250 g. In addition, their viscoelastic and mechanical properties can be adjusted in a wide range by a proper choice of the telechelic oligomer, from soft and flexible composite materials to hard and tough organic glasses. The performance of different types of photocured polymers (epoxides, vinyl ethers, acrylates) containing organically modified clays has thus been recently examined and shown to be superior for the nanocomposite (organoclay) than for the microcomposite (unmodified clay) [20].

Since our early work on photopolymer–clay nanocomposites [21], a few similar studies have been reported. Wang et al. [22] produced intercalated nanocomposites by photopolymerization of a methacrylate or *m*-cresol resin filled with montmorillonite, but the slow cure and the deep color of the final product make such system ill-suited for industrial use. Uhl et al. [23–25] reported a moderate enhancement of some of the properties of UV-cured acrylate films containing layered silicates as nanomaterial. Paczkowska et al. [26] have synthetized polymer–clay nanocomposites by sunlight or laser-induced polymerization of methacrylate monomers in the presence of a xanthenic dye, but the composite materials thus obtained had poor mechanical properties. Poly(*N*-vinylcarbazole)-clay nanocomposite materials were prepared by Yu et al. [27] by cationic photoinitiated polymerization, and their morphology thermal stability and optical properties were examined as a function of the filler content.

The present study is a follow-up of our previous work on the ultrafast synthesis of polymer–clay nanocomposites by UV-radiation curing, in an attempt to enhance the performance of both the processing operations and the final product properties, and to explore the industrial potential of these novel materials in various sectors of applications, in particular in the coating industry.

2. Experimental

2.1. Materials

Two types of UV-curable resins were used as binders to produce the polymer nanocomposite: an acrylate-functionalized resin which undergoes radical-type polymerization, and an epoxy-functionalized resin which undergoes cationic-type polymerization. Table 1 shows the various compounds used for the resin formulation: the photoinitiator at a total concentration of 3 wt%, the telechelic oligomer and the monomer (hexanediol diacrylate, HDDA) used as reactive diluent to adjust the formulation viscosity (500–2000 mPa s) at a weight content of 27%. In some formulations, light stabilizers were added in order to improve the weathering resistance of the UV-cured polymers, for possible use in outdoor applications, namely, a hydroxy-phenylbenzotriazine (Tinuvin 400 from Ciba) and a hindered piperidine radical scavenger (Tinuvin 292 from Ciba).

The mineral fillers selected were natural clays which were made organophilic by a treatment with hexadecyl trimethylammonium chloride, as described previously [16]. The same treatment was applied to a synthesis clay (Beidellite) to make it organophilic. The characteristics of the various organoclays, used at a typical concentration of 3 wt%, are also reported in Table 1. Values of the interfoliar space, before and after treatment, were determined by X-ray diffraction. The mineral filler was dispersed into the liquid UV-curable resin and exposed to ultrasound (Bransonic 2250-100W—42 KHz) for 7 h in the dark to ensure an effective exfoliation of the silicate platelets.

Transmission electron microscopy (TEM) was used for visual observation of the exfoliation extent of the silicate platelets in the UV-cured nanocomposites. Circa 100 nm thick samples were cut by means of a microtome (LKB model 8800) and placed on a mesh copper grid for analysis. The TEM investigation was performed on a Philips CM 200 apparatus operated at an acceleration voltage of 200 kV.

2.2. Photopolymerization

Nanocomposite formulations were UV-cured as 50 μm or 2 mm thick samples coated on a baryum fluoride crystal or a glass plate, respectively, for evaluation of the polymerization kinetics or of the viscoelastic properties, respectively. Two types of medium pressure mercury lamps were used: a Novacure lamp from EFOS equipped with an optical fiber where the fluence rate at the sample position could be varied between 10 and 200 mW cm^{-2}, and a Minicure set up from IST operated at a belt speed between 5 and 50 m min^{-1} (exposure time between 1 and 0.1 s) and a fluence rate of 500 mW cm^{-2}. All the irradiation experiments were performed at ambient temperature in the presence of air.

The extent of the polymerization upon UV irradiation was evaluated by means of infrared spectroscopy (Bruker IFS-66 FTIR spectrophotometer) by monitoring continuously, or immediately after UV exposure, the disappearance of the characteristic bands of the reactive group: at 790 cm^{-1} for the epoxy ring, and at 1410 or 6160 cm^{-1} (near-IR overtone) for the acrylate double bond. The monomer conversion (x) after a given exposure time was calculated from the relative decrease of the absorbance of the corresponding IR band: $x=(A_0-A_t)/A_0$. No correction was made for shrinkage because the thickness decrease is compensated by a concomitant increase of the functional group concentration. Exotherms of samples undergoing photopolymerization were measured by optical pyrometry (Testo 825-T2). The infrared beam analyzes the 5 μm top layer of the sample.

2.3. Properties of UV-cured nanocomposites

The viscoelastic properties of 2 mm thick samples of UV cured nanocomposites were determined by dynamic mechanical analysis (DMA-Q 800 from TA-Instruments), by operating at a 1 Hz frequency and a 20 μm amplitude, with a 2 ° min^{-1} temperature rising rate. From the variation of the storage modulus (E') and of the tensile loss factor (tan δ) with temperature, values of the Young modulus and of the glass transition (or relaxation) temperature (T_g or T_α) were obtained, respectively. The tensile properties of the photocured material (tensile strength and break elongation) were evaluated by recording the stress–strain curve by means of an ADAMEL LHOMARGY apparatus (Model 400M). The hardness of 50 μm thick coatings was measured by monitoring the damping time of the oscillations of a pendulum placed on the UV-cured sample coated onto an horizontal glass plate, with the pendulum swinging in a vertical plane from an initial angle of 12° to a final angle of 4° (Persoz hardness). Persoz values are ranging from 30 s for soft elastomeric materials up to 350 s for hard and glassy polymers. The scratch resistance of UV-cured samples was measured by means of a scratch/shear Tester from Taber Industries on 100 μm thick films coated onto glass plates. A single scratch is generated by a conical diamond indenter with an angle of 90° under a constant load, at a speed of 3 cm s^{-1}. The scratch resistance value (expressed in grams) corresponds to the minimum load applied to the indenter which produce a 75 μm wide and 37 μm deep scratch.

The influence of the mineral filler on the optical properties (transparency and gloss) of UV-cured samples was determined by means of a UV–visible spectrophotometer (Beckman model DU-7000) and by a 20° glossmeter (Erichsen glossmaster), respectively. The surface roughness of the UV-cured sample was evaluated by scanning with a laser beam (UBM microfocus) which provides a topographic picture of the relief. For evaluation of their weathering resistance, 50 μm thick UV-cured nanocomposites films were placed in a QUV-accelerated weatherometer (Q-panel) equipped with fluorescent UV-A-340 lamps and operated under wet cycle conditions: 8 h UV exposure at 70 °C and 50% relative humidity, followed by 4 h in the dark at 50 °C and water condensation. The photodegradation extent was evaluated from the changes in the IR absorption spectra of the films upon QUV-A exposure for up to 3800 h, which allow one to quantify the light-induced chemical modifications.

3. Results and discussion

3.1. Synthesis of nanocomposites by photopolymerization

The different types of UV-curable resins used in this study were previously found to polymerize rapidly upon UV exposure with formation of a tight tridimensional polymer

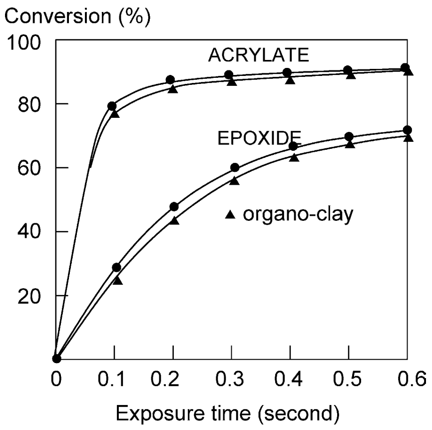


Fig. 1. Influence of the organoclay (PUA) (+) on the photoinitiated polymerization of a polyurethane-acrylate containing 27 wt% HDDA and a cycloaliphatic epoxide. Light intensity: 500 mW cm^{-2}; film thickness: 40 μm. [Organoclay] = 3 wt%. Radical-type photoinitiator [Darocur 1173] = 3 wt%; Cationic-type photoinitiator: [Cyracure UVI-6976] = 3 wt%.

network [15]. Fig. 1 shows the conversion versus time profiles obtained by infrared spectroscopy analysis performed immediately after UV exposure, for a polyurethane-acrylate resin (radical-type) and an epoxy resin (cationic-type) exposed as 40 μm thick coatings to intense UV radiation on the Minicure line. It can be seen that the polymerization proceeds rapidly in both samples to reach its maximum conversion within 1 s. As expected from molecular mobility considerations, the polymerization develops more extensively in the soft low modulus polyurethane than in the hard and glassy epoxy-polymer. The slower polymerization of the epoxide is in full agreement with previous observations on the photoinitiated polymerizations of multifunctional monomers [15] and is attributed to a lower rate constant of propagation for the epoxide than for the acrylate monomer.

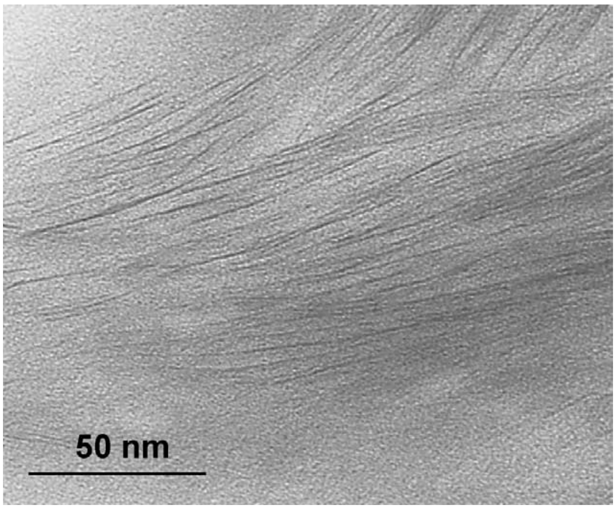


Fig. 2. Transmission electron microscopy picture of an intercalated clay/PUA nanocomposite photopolymer.

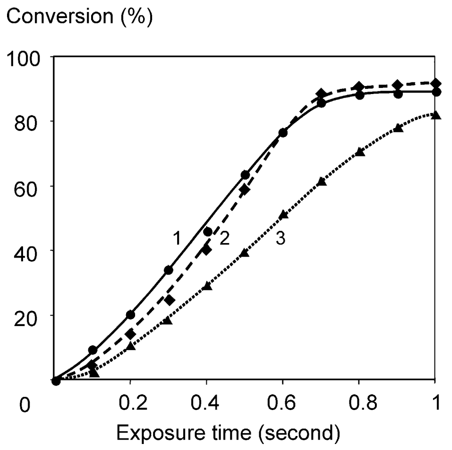


Fig. 3. Influence of the organoclay on the UV-curing of a thick PUA sample, monitored by near-IR spectroscopy. **1**: neat PUA resin; **2**: +7 wt% Montmorillonite K10; **3**: +7 wt% Nanomer I-30E. Plate thickness: 2.5 mm. Light intensity: 500 mW cm^{-2}.

The addition of the organoclay (3 wt%) to the liquid resin was found to hardly affect the polymerization kinetics of both types of resins, UV-irradiated under the same conditions and by using the same amount of photoinitiator as in the clay-free resin (Fig. 1). The similarity between these curves indicates that the penetration of UV radiation into the 40 μm thick sample is not reduced significantly by the presence of the organoclay. It also means that the mineral filler is not acting as a radical scavenger or a proton trap. Similar results have been obtained by using as telechelic oligomer a polyester-acrylate (PEA) or a polyphenoxy-acrylate (PPA). It should be noted that the curing of the resin could also be achieved upon exposure to a violet light emitting diode (LED), but the hardening required a 5 s irradiation because of both the lower fluence rate (10 mW cm^{-2}) and the low absorbance at 400 nm of the sample (0.1 for a 50 μm thick film).

When the organoclay (Beidellite) was introduced in the UV-curable acrylic or epoxy resin, intercalation and exfoliation did occur, as shown by the total disappearance in the UV-cured nanocomposite of the X-ray diffraction band at 28.5 Å of the organoclay, while the characteristic band at 12.5 Å remained clearly visible in the microcomposite containing natural clay. Transmission electron microscopy picture of the acrylic nanocomposite (Fig. 2) have confirmed that both intercalated and exfoliated structures are present in the UV-cured nanocomposite photopolymer.

While the most important applications of the UV-curing technology are to be found in the coating industry where the film thickness ranges typically between 5 and 50 μm, up to a few millimeter thick samples are needed in some specific applications (moulds, sealants, dental fillers, composites). A deep-through cure of such thick samples can still be achieved by means of UV radiation, by using a photobleachable initiator which allows the incident light to penetrate progressively into the sample, thus inducing a frontal photopolymerization [28,29]. The addition of

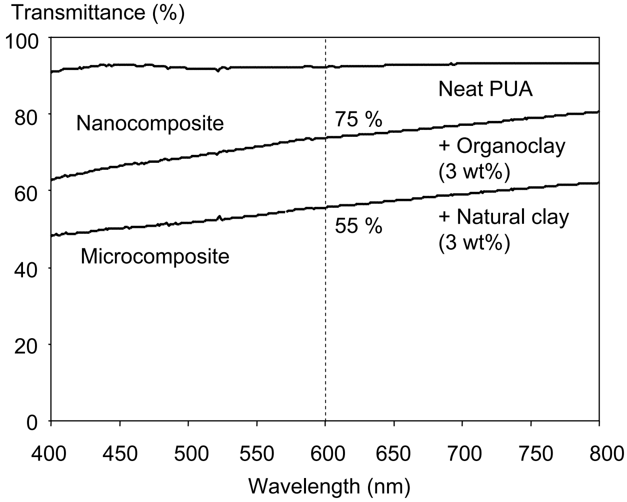


Fig. 4. Influence of the clay filler on the transparency of a 2 mm, thick UV-cured PUA sample. [Beidellite] = 3 wt%.

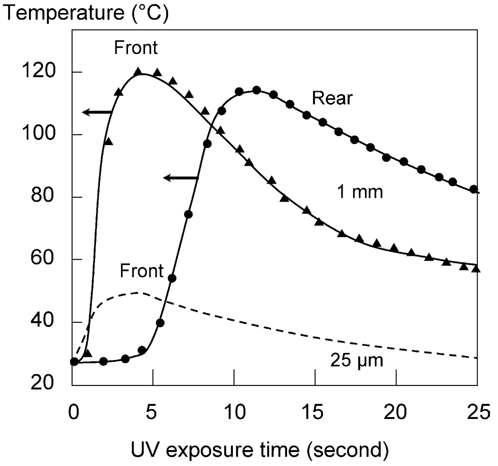


Fig. 6. Temperature profiles recorded by pyrometry for a PUA sample undergoing UV-curing. Influence of the sample thickness. $I = 50$ mW cm^{-2}.

opaque mineral particles to the clear UV-curable resin was expected to hinder this process and thus restrict the field of applications of nanocomposite photopolymers. Actually, a slowing down effect in the 2.5 mm thick samples was only observed with the Nanomer I-30E filler at a load of 7 wt% (Fig. 3), the same final conversion being reached for an exposure time twice as long as for the unfilled resin. At a low filler content (3 wt%), as well as with the other more transparent organoclays, nearly similar polymerization profiles were obtained with the nanocomposite and the clear resin (Fig. 3). The best optical properties, with respect to color and transparency, were obtained with the synthetic phillosilicate (Beidelitte). For a 2 mm thick PUA sample containing 3 wt% of mineral filler, the transmittance at 600 nm was measured to be 75% for the nanocomposite (organoclay), compared only to 55% only for the micro-composite (unmodified clay), as shown in Fig. 4, and less than 50% for the commercial Nanomer I-30E. For organic coatings, where the thickness is typically in the 20–50 μm range, the UV-cured nanocomposite films are essentially as transparent as the unfilled clearcoat.

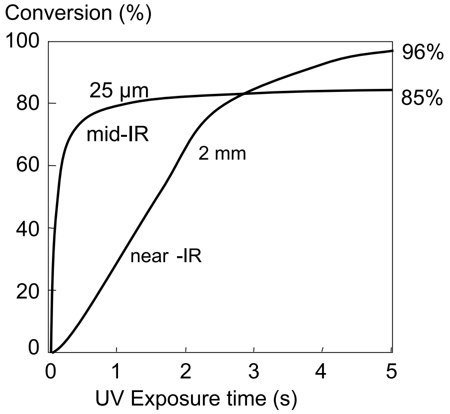


Fig. 5. Influence of the sample thickness on the polymerization profile of a PUA nanocomposite exposed to UV-radiation. Light intensity: 100 mW cm^{-2}. Profiles were recorded by real-time infrared spectroscopy.

In such fairly transparent samples, the incident UV radiation can penetrate deep enough to ensure a uniform through cure of a few millimeter thick nanocomposite polymer plates. We observed an interesting behavior by comparing the polymerization profiles of thin (25 μm) and thick (2 mm) samples (Fig. 5). The final conversion was found to be significantly higher for the thick plate (98%) than for the thin film (85%), albeit it required a longer UV exposure-time (6 s versus 2 s) because of the photoinduced frontal polymerization [28,29]. We have attributed such behavior to a thermal effect, the rise in temperature caused by the exothermic polymerization being more pronounced in thick samples than in thin films [30]. Indeed, an increase in the sample temperature is expected to prevent the premature ending of the polymerization due to vitrification

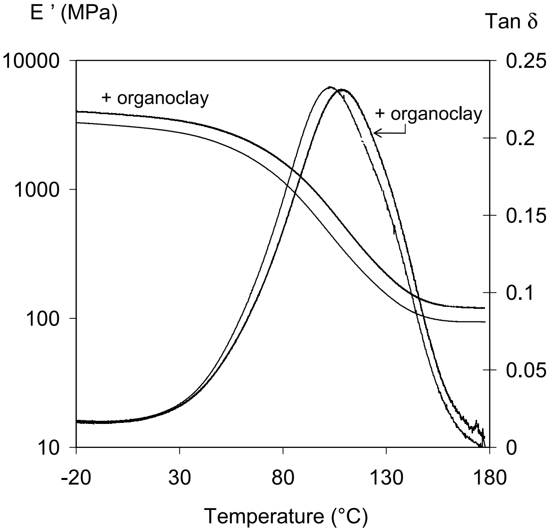
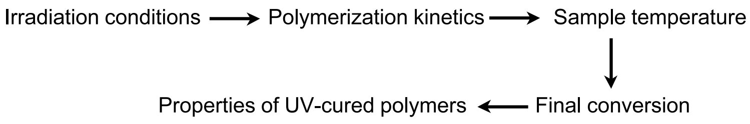


Fig. 7. Influence of organoclay on the viscoelastic characteristics of a UV-cured polyphenoxy-acrylate polymer. [Beidellite] = 3 wt%.

Table 2
Influence of organoclay (3 wt%) on the viscoelastic properties of UV-cured acrylate and epoxy polymers

UV-cured resin	T_g (°C)	Young modulus (MPa)
Polyphenoxy-acrylate	105	2750
Polyphenoxy-acrylate + Beidellite	115	3520
Polyurethane-acrylate	53	1110
Polyurethane-acrylate + Nanomer I-30E	53	1320
Polyester-acrylate	57	2650
Polyester-acrylate + Nanomer I-30E	58	2200
Cycloaliphatic epoxide	93	1320
Cycloaliphatic epoxide + Montmorillonite K10	30	910

which is observed in thin films. By recording the temperature of a sample undergoing photopolymerization by means of a pyrometer, we found that the temperature was rising from ambient to about 50 °C for the 25 μm thick film, but up to 120 °C for the 2 mm thick plate (Fig. 6). In a systematic study to be reported later on, we have demonstrated that the irradiation conditions (sample thickness, light intensity, initial temperature, type of substrate) have a critical effect on the polymerization kinetics specially on the final conversion, and consequently on the viscoelastic and tensile properties of the UV-cured polymer, as shown schematically below:



3.2. Properties of nanocomposite photopolymers

The physico-chemical properties of photocrosslinked polymers depend not only on the cure extent, but also on the chemical structure of the telechelic oligomer, as well as on the functionality of the monomer used as reactive diluent [15]. They can be varied in a large range depending on the considered application, from soft aliphatic polyurethane elastomers to hard and tough polyphenoxy glassy materials. The addition of clay nanoparticles was found to affect, to a certain extent, some of these properties by imparting to the nanocomposite polymer a greater tensile strength, a higher flame retardancy and a lower permeability to gas [11]. We provide here some further evidence of the beneficial effect of small amounts of a nanoclay filler on some of the properties of UV-cured acrylate and epoxy polymers.

The viscoelastic characteristics of the various nanocomposite photopolymers were evaluated by dynamic mechanical analysis (DMA) on 2 mm thick samples. Fig. 7 shows some typical profiles recorded by DMA for a UV-cured polyphenoxy-acrylate by monitoring the variation of the storage modulus (E') and the tensile loss factor (tan δ) with increasing temperature. The addition of the silicate nanoparticles (3 wt%) causes a small rise of the glass transition temperature and a 25% increase of the storage modulus. At the rubbery plateau ($T > 100$ °C), an E' value of 120 MPa was measured for the nanocomposite, compared to 94 MPa for the clay-free UV-cured polymer. For the polyurethane-acrylate and polyester-acrylate nanocomposites, the T_g value was not affected at all, while the elastic modulus of the polyester-acrylate was slightly decreased (Table 2). A more pronounced effect was observed with the UV-cured cycloaliphatic epoxide [20], where both the T_g and E values dropped substantially in the presence of organoclay (Table 2), thus making the nanocomposite epoxy polymer more flexible and resistant to shocks, with an increase of the resiliency from 19 to 46 kJ m^{-2}. Concerning the tensile properties, the addition of

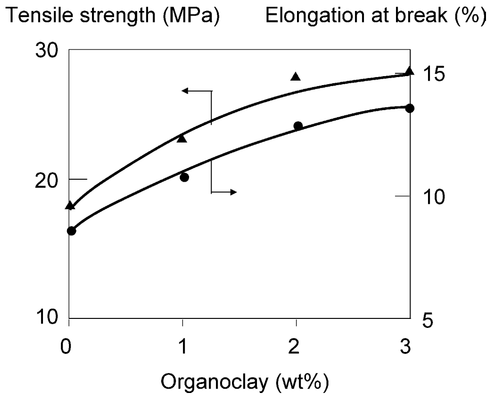


Fig. 8. Influence of the organoclay [Montmorillonite K10] content on the tensile properties of a UV-cured polyurethane-acrylate nanocomposite.

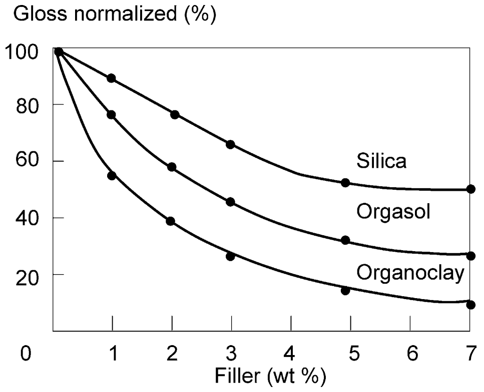


Fig. 9. Influence of the filler content on the gloss of a UV-cured PUA composite polymer.

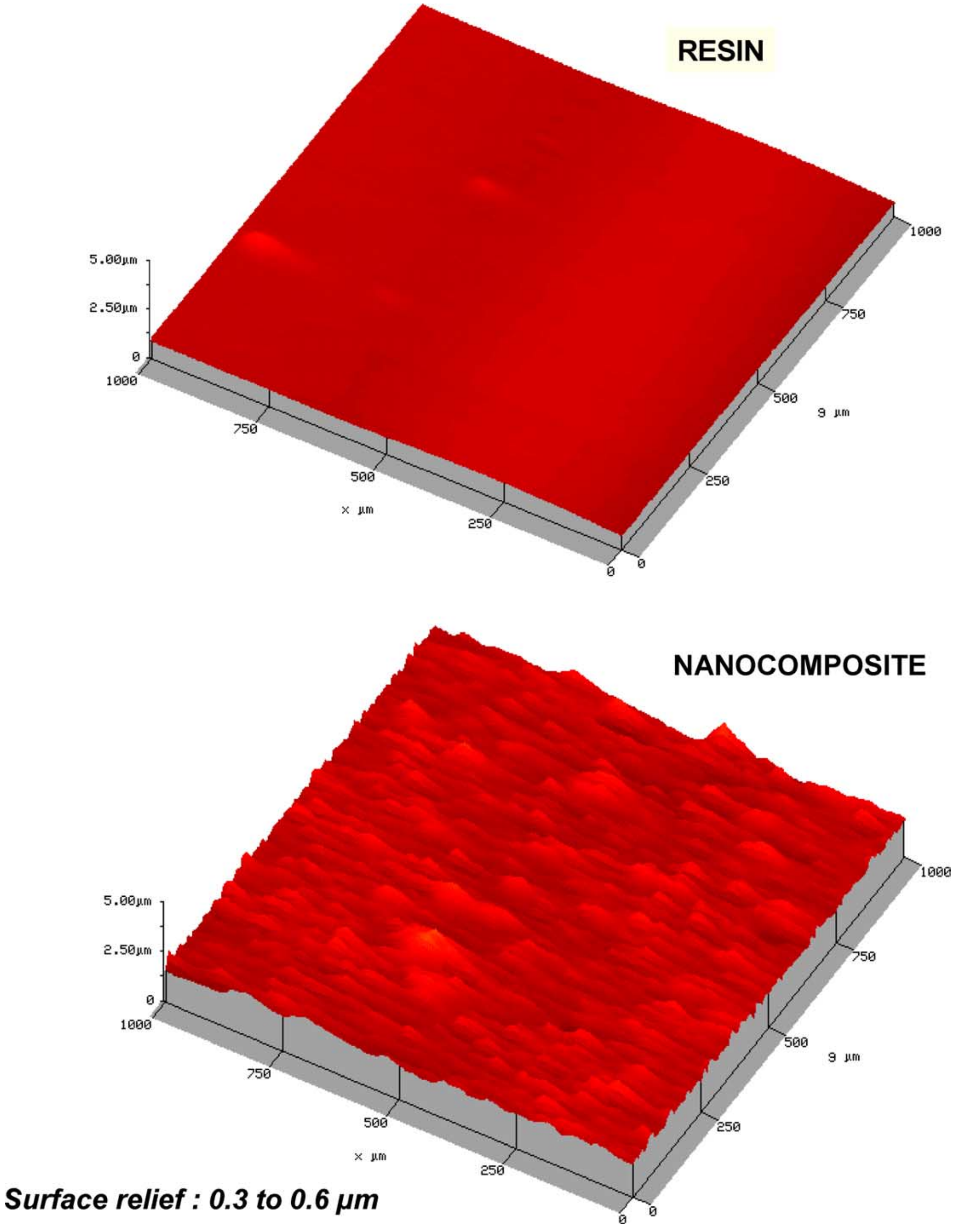


Fig. 10. Influence of the organoclay on the surface roughness of a UV-cured PUA coating.

organophilic montmorillonite (2 wt%) to a hard polyurethane-acrylate containing hexanediol diacrylate as reactive diluent was found to have some beneficial effect on the mechanical strength of the UV-cured nanocomposite, in comparison to the microcomposite, with an increase of the elongation at break from 9 to 14% and of the tensile strength from 19 to 29 MPa (Fig. 8). Such UV-cured clay/acrylic nanocomposites were also found to be quite resistant to scratching, depending on the chemical structure of the telechelic oligomer (polyurethane < polyphenoxy < polyester) and on the functionality of the monomer (monoacrylate < diacrylate < triacrylate). The Taber scratch values of the UV-cured samples were typically ranging between 150 and 300 g.

It was already mentioned that the nanocomposite photopolymers containing as filler the synthetic Beidelitte are not colored and fairly transparent, specially for less than 100 µm thick coatings. But the addition of the nanoparticles was found to cause a drastic loss of the gloss of these UV-cured acrylic coatings, even at a relatively low load of

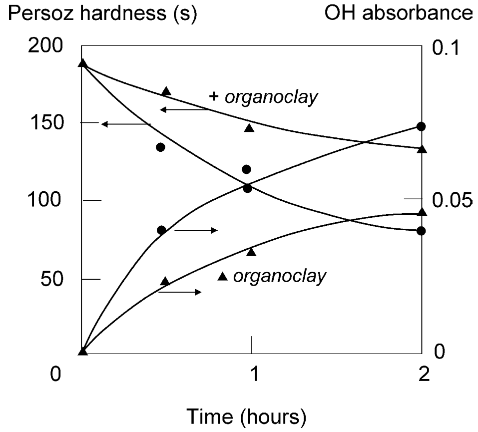


Fig. 11. Influence of the organoclay (+) on the water uptake (OH infrared absorbance at 3500 cm^{-1}) and on the hardness of a UV-cured PUA coating placed in a humid atmosphere. [Montmorillonite K10] = 3 wt%. Temperature: 25 °C. Relative humidity: 100%. Film thickness: 40 μm.

organoclay, as shown in Fig. 9. For some coating applications, such matting effect is highly desired, like for wood furniture and floor finishes. It can be achieved at a lower filler content than with the conventional matting agents, like finely powdered silica or polyamide (orgasol), as shown in Fig. 9. This loss of gloss was attributed to a surface roughness created by the clay nanoparticles, mainly the intercalated aggregates. Such roughness is clearly apparent on the pictures shown in Fig. 10 representing the surface mapping of the nanocomposite in comparison to the unfilled clearcoat. It can be seen on the picture borderlines that the relief height is on the order of 0.5 μm for the nanocomposite polymer, thus implying the presence of stacks of clay nanoparticles. The addition of clay nanoparticles is also making the surface of the UV-cured coating less slippery, as expected from the increased roughness.

A distinct feature of UV-cured polymers lies in their great chemical resistance which results from their high crosslink density, i.e. a branch point concentration of 4 mol kg^{-1}. The nanocomposite photopolymers were not only totally insoluble in organic solvents like chloroform or tetrahydrofuran, but some of them hardly undergo swelling, specially the PEA and PPA samples when associated to a diacrylate or triacrylate monomer. Acrylic polymers are known for their hydrophilic character and to pick up water when they are placed in a humid atmosphere. Fig. 11 shows the water-uptake, followed by IR spectroscopy through the increase of the OH band, for a UV-cured polyurethane-acrylate film placed in a closed chamber at a relative humidity of 100% at 25 °C. It can be seen that water is mainly absorbed during the first two hours and is less important for the nanocomposite sample containing 3 wt% organoclay. Concomitantly, the hardness of the polymer was significantly decreased, as expected from the plasticizing effect of the absorbed water, the decrease being much less pronounced for the nanocomposite sample (Fig. 10). When these samples were placed in a dry atmosphere, the water was released within 2 h and the polymer recovered its original hardness, without any detrimental effect on its resistance to moisture. Indeed, a PUA coating kept in a humid atmosphere at 70 °C for 2 months did not suffer significant degradation and chemical modifications (monitored by IR spectroscopy), unlike melamine-acrylate thermoset clearcoats commonly used as automotive finishes which appeared to be less resistant to moisture [31], as illustrated in Fig. 12 which shows the decay of the two most sensitive functional groups, the ether bond of the melamine-acrylate thermoset and the amide bond of the polyurethane-acrylate photoset.

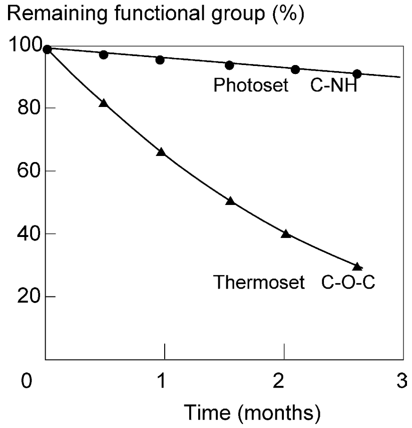


Fig. 12. Resistance of a UV-cured PUA nanocomposite in a hot (70 °C) and humid atmosphere, in comparison to a melamine acrylate thermoset.

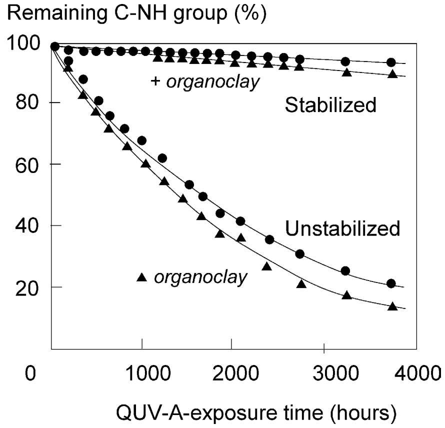


Fig. 13. Weathering resistance of UV-cured PUA coatings. Influence of organoclay (+) and of light stabilizers. [Beidellite] = 3 wt%; [Tinuvin 400] = 1 wt%; [Tinuvin 292] = 1 wt%. QUV-A accelerated weathering.

The resistance to accelerated weathering of such UV-cured PUA nanocomposites proved to be outstanding in the presence of adequate light stabilizers, and it was not affected by the presence of the organoclay filler [32]. Fig. 13 shows the decay of the C–NH group for a PUA clearcoat and a clay/PUA nanocomposite upon accelerated wet cycle

QUV-A ageing. The stabilizing effect of the UV-absorber (Tinuvin 400) and HALS radical scavenger (Tinuvin 292) used is particularly impressive. This quite remarkable feature is in marked contrast with the results reported in some recent studies [33–35] on the light stability of clay/polyolefins nanocomposites which was found to be drastically decreased by the presence of both the organoclay and the alkylammonium salt. Such UV-cured acrylic nanocomposites can therefore be used as non-glossy coatings to effectively protect organic materials against photodegradation upon outdoor exposure.

4. Conclusion

A novel method has been developed to synthesize highly resistant nanocomposite polymers by photoinitiated polymerization of multifunctional acrylate or epoxy monomers containing small amounts (3 wt%) of an organophilic clay. It offers the unique advantages of the UV-curing technology, namely, a high speed hardening of a solvent-free resin at ambient temperature to produce a highly crosslinked polymer showing a great resistance to chemicals and heating. The silicate filler does not affect at all the polymerization process, neither the radical-type or the cationic type, thus allowing a few millimeter thick samples to be extensively cured within seconds by a light-induced frontal polymerization.

In the UV-cured nanocomposite, the clay platelets are either packed together in a disordered arrangement (intercalated morphology) or dispersed as isolated nanoparticles (exfoliated morphology). They were found to have no major effect on the viscoelastic properties of acrylate based nanocomposites, while they make the epoxy-based nanocomposite more flexible and impact resistant. The surface roughness caused by the clay nanoparticles leads to a sharp drop of the gloss, thus providing the matting effect desired for some coating applications. These highly crosslinked nanocomposite polymers are quite resistant to organic solvents, moisture and weathering, as well as to mechanical aggression (scratching, shocks). They are therefore well suited for coating applications to protect and improve the surface properties of different types of materials, in particular those used in outdoor applications.

References

[1] Alexandre M, Dubois P. Mater Sci Eng 2000;28:1.
[2] Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Karauchi T, Kamagaito O. J Mater Res 1993;6:1185.
[3] Vaia RA, Giannelis EP. Macromolecules 1997;30:7990–8000.
[4] Le Baron PC, Wang Z, Pinnavaia TJ. Appl Clay Sci 1999;15:11.
[5] Reichert P, Kressler J, Mülhaupt R, Stöppelmann G. Acta Polym 1998;49:116.
[6] Zhang Q, Fu Q, Jiang L, Lei Y. Polym Int 2000;49:1561.
[7] Kato M, Usuki A, Okada A. J Appl Polym Sci 1997;66:1781.
[8] Dubois P, Alexandre J, Hindrycks F, Jerome R. J Macromol Sci 1998; C38:511.
[9] Akelah A, Moet A. J Mater Sci 1996;31:1064.
[10] Doh JG, Cho I. Polym Bull 1998;41:511.
[11] Wang Z, Pinnavaia TJ. Chem Mater 1998;10:3769.
[12] Messersmith PB, Gianellis EP. Chem Mater 1994;6:1719.
[13] Lan T, Pinnavaia TJ. Chem Mater 1994;6:2216.
[14] Zily C, Mülhaupt R, Finter J. Macromol Chem Phys 1999;200:661.
[15] Decker C. Prog Polym Sci 1996;21:1319.
[16] Decker C, Zahouily K, Keller L, Benfarhi S, Baron J. J Mater Sci 2002;37:4831.
[17] Zahouily K, Decker C, Benfarhi S, Baron J. Proc RadTech Am 2002;309.
[18] Decker C, Keller L, Zahouily K, Benfarhi S. Proc RadTech Asia 2003;516.
[19] Decker C. Macromol Rapid Commun 2002;23:1057.
[20] Benfarhi S, Decker C, Keller L, Zahouily K. Eur Polym J 2004;40: 493.
[21] Zahouily K, Benfarhi S, Bendaikha T, Baron J, Decker C. Proc RadTech Eur 2001;583.
[22] Wang H, Mei M, Jiang Y, Zhang X, Wu S. Polym Int 2001;51:7.
[23] Uhl FM, Hinderliter BR, Davuluri SP, Croll SG, Wong SC, Webster DC. RadTech North America 2004.
[24] Uhl FM, Hinderliter BR, Davuluri SP, Croll SG, Wong SC, Webster DC. Polym Prepr 2003;44(2):247.
[25] Uhl FM, Davuluri SP, Wong SC, Webster DC. Chem Mater 2004;16: 1135.
[26] Paczkowska B, Stzelec S, Jederzejewska B, Linden LA, Paczkowski J. Appl Clays Sci 2004;25:221.
[27] Yu Y, Lin C, Yeh J. J Appl Polym Sci 2004;91:1904.
[28] Ivanov V, Decker C. Polym Int 2001;50:113.
[29] Decker C. Polym Int 2002;51:1141.
[30] Decker C, Elzaouk B, Decker D. J Macromol Sci 1996;A33:173.
[31] Nguyen T, Martin J, Byrd E, Embree N. Polym Prepr 2001;42(1):420.
[32] Keller L, Decker C, Zahouily K, Benfarhi S, Le Meins JM, Miehe-Brendle J. Polymer 2004;45:7437.
[33] Qin H, Zhao C, Zhang S, Chen G, Yang M. Polym Degrad Stab 2003; 81:497.
[34] Maillhot B, Morlat S, Gardette JL, Boncard S, Duchet J, Gerard JF. Polym Degrad Stab 2003;82:163.
[35] Morlat S, Mailhot B, Gonzalez D, Gardette JL. Chem Mater 2004;16: 377.