

# Light induced curing of Clay/Polymer nanocomposites.

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## ABSTRACT

Clay nanocomposites have been synthesized by UV-curing with organic and waterbased resins. The effect of the chemical structure of the organophilic layer of the clay on the dispersibility in the photocurable resins, the photocuring efficiency and the final properties of the UV-cured nanocomposites are discussed.

## 1. INTRODUCTION

The introduction of mineral charges such as silica particles or glass fibers into a curable resin leads to hard and abrasion resistant materials<sup>1</sup>. Composites in which the mineral particles have a micron scale leads often to insufficient adhesion between the organic matrix and the mineral filler. Using nanoscale fillers have been shown to afford remarkable property enhancement like stiffness and strength, heat resistance and gas barrier properties<sup>2</sup>.

Silicate layered nanoparticles like phyllosilicate clays are found in form of stacked platelets of about 200nm lengths and 10 to 50nm thick. Each platelets having a thickness of near 1nm. The interlayer galleries contains cationic counter-ions. High performance nanocomposites can be obtained if the curable resin is able to penetrate into the galleries (intercalation) and make them ultimately fall apart (exfoliation). Exfoliation can be obtained by melting of the clay/organic resins mixtures. However, in thermoset micro- and nano- composites, the melting of the polymer in the presence of the mineral nanoparticles leads often to thermodegradation, thus affecting the composite heat stability. By using light induced polymerization, the curing proceeds without external heating, at low temperature, and produce rapidly and in a inexpensive way, the nanocomposite material<sup>3</sup>.

Moreover, UV-curing allows to prepare nanocomposites with essentially: no emission of volatile organic compounds ; a fine control of the swelling time to ensure a perfect interpenetration of the resin into the lattice layers of the clay mineral ; a precise control of the polymerization onset, simply by switching on the light ; an ultrafast curing by using the highly reactive acrylate-based resins and adequate photoinitiators ; a fine control of the polymerization rate in a large domain, simply by controlling the light intensity ; a large range of mechanical properties, from soft and flexible composite materials to hard organic glasses, by a proper choice of the telechelic oligomer.

In this work, we describe the effect of the the chemical structure of the organophilic layer of the silicate clay on their dispersibility and stability in the polymerizable resins and waterbased dispersions, the curing process and the properties of the cured acrylate nanocomposite materials.

## 2. EXPERIMENTAL

### 2.1. Materials

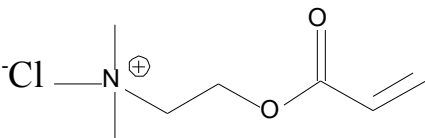
A typical UV-curable resin was made of a telechelic acrylate oligomer (Ebecryl 8402 from UCB), a reactive diluent (25 wt% of hexanediol-diacrylate) and a photoinitiating system (a combination of Darocur 1173 and Irgacure 819 from Ciba SC). Experiments with waterbased dispersions were conducted with LR 9005 (WD1) and LR8949 (WD2) (BASF). The selected clays were an industrial grade bentonite (Impersol V, Süd-Chemie, Germany) and a synthesized clay with known chemical composition and structure, beidellite<sup>4</sup> ( $\text{Na}_{0.6}(\text{Si}_{3.4}\text{Al}_{0.6})(\text{Al}_2)\text{O}_{10}(\text{OH},\text{F})_2, n\text{H}_2\text{O}$ ). Natural clays contains often metal ions like  $\text{Fe}^{2+}$  or  $\text{Al}^{3+}$  which, even at very low level of concentration, lead to coloured products. Impersol V (ImpV) is a very slightly greenish powder. Moreover, the presence of catalytic amounts of metal cations could infer the weathering resistance of the cured nanocomposite.

The clays were made organophilic by treatment with ammonium salts (AS). The chemical structures of the ammonium salts used are given in Table 1. Two methods were used for the treatment: the classic method in which the AS is mixed with the clay under heavy stirring for about 3 hours at 80°C. The best exchange yields are obtained if the amount of AS in contact with the clay is at least two times the value of the Cation Exchange Capacity of the clay (CEC). In the second method, instead of 3 hours at 80°C, the mixed solution is sonificate for 5 minutes at room temperature (Sonifier Branson 400W, Power level 1, duty 50%). The two steps can be successively used in case of the waterbased dispersions. After treatment with the AS, the organophilic clay filler was mixed in the dark with the UV-curable resin or waterbased acrylic dispersions under heavy stirring.

### 2.2. Irradiation

Samples were exposed to the UV radiation of a medium pressure mercury lamp, either on a Minicure line from IST (power output of 80 W/cm and light intensity of 500 mW cm<sup>-2</sup>), or on a Novacure irradiation device from EFOS equipped with an optical guide where the light intensity could be varied between 15 and 400 mW cm<sup>-2</sup>. All the irradiation experiments were performed at ambient temperature in the presence of air.

Table 1: Chemical structures of the ammonium salts used as organophilic layer

	<i>Name</i>	<i>Chemical structure</i>
<b>C19</b>	Hexadecyl-N,N,N-triméthyl ammonium chloride	$\text{CH}_3-(\text{CH}_2)_{15}-\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$
<b>C10</b>	Decyl ammonium chloride	$\text{CH}_3-(\text{CH}_2)_9-\text{NH}_3^+, \text{Cl}^-$
<b>C6</b>	1-amonium-dodecanoic acid chloride	$\text{HOOC}-(\text{CH}_2)_{11}-\text{NH}_3^+, \text{Cl}^-$
<b>C8A1</b>	[2-(Acryloyloxy) ethyl] tri methyl ammonium chloride	

## **2.3 Analysis**

The conversion yield of the acrylate double bonds was evaluated by infrared spectroscopy through the decrease of the IR band at  $810\text{ cm}^{-1}$  for thin films ( $\leq 50\text{ }\mu\text{m}$ ) or at  $6160\text{ cm}^{-1}$  for 2 mm thick plates. The presence of the clay filler did not affect the monitoring of these bands. In some experiments, the sample was exposed simultaneously to the UV beam and to the IR beam, thus allowing conversion *versus* time curves to be directly recorded by this technique (real-time IR spectroscopy).

The exchange process was followed by FTIR spectroscopy and the washed and dried samples were further analyzed by X-ray diffraction spectroscopy (XRD) to evaluate the efficiency of the organophilic treatment of the mineral filler by quantification of the widening of the clay galleries, as well as to assess the complete defoliation after incorporation of the organoclay into the UV-curable resin. Thermal Gravimetric analysis (TGA) is used to follow the weight loss as a function of the temperature. The weight loss recorded between  $150^{\circ}\text{C}$  and  $800^{\circ}\text{C}$  can be attributed solely to the decomposition of the organic AS present in the sample.

## **3. RESULTS AND DISCUSSION**

### **3.1. Organophilic treatment of the clays**

Layered silicate clays show usually a strong hydrophilic character due to hydroxyl groups at the external surface of the platelets and by the presence of cationic counter-ions like  $\text{Na}^+$  or  $\text{Ca}^{2+}$  in the interlayer galleries. To obtain a true nanocomposite material, it is essential that the 1 nm thick silicate platelets be uniformly dispersed within the polymer matrix. One of the key step in the preparation of clay nanocomposites is therefore the lypophilization of the clay in order to become dispersible in an organic polymerizable matrix. Moreover, the organophilic layer of the clay platelets should allow the UV-curable resin to penetrate into the clay galleries and make them full apart.

Exchanging the alcali cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$ ) by cationic surfactants, such as alkylammonium salts (AS), proved to be an effective way to make the clay compatible with the acrylate resin. This treatment leads to a widening of the clay galleries, as shown by the shift toward small angles of the X ray diffraction pattern. The nature of the ammonium salt will have an effect on the exchange yield, and therefore on the dispersion of the filler in the resin, but could also have an effect on the photocuring process and on the final properties of the cured nanocomposite.

The preparation process of the cured nanocomposites is depicted in Figure 1.

When a complete exfoliation occurs, the three following observations can be made :

- a total disappearance of the X ray diffraction band of the organoclay, which is not the case for the untreated clay (microcomposite);
- a much slower sedimentation of the mineral particles in the nanocomposite resin than in the microcomposite resin;
- a greater transparency because light scattering by the nanoparticles is much reduced, compared to the microparticles in the non-exfoliated sample (Figure 3, right upper sample of beidellite/C19).

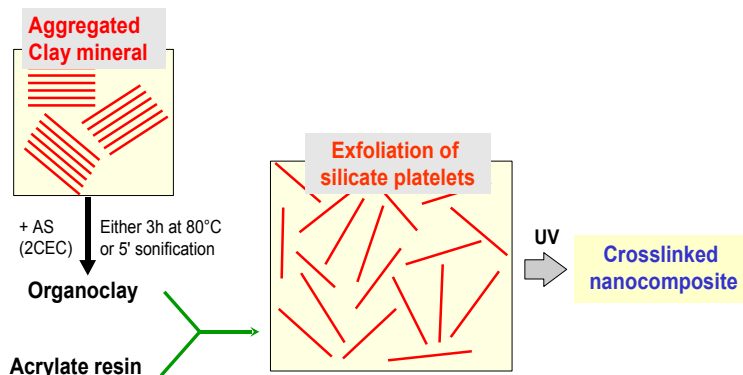


Figure 1: Preparation steps of the photocured nanocomposites.

The clays ImpV and Beidellite were treated with four different ammonium salts (Table 1). After washing and drying, the FTIR spectra of the treated clays show that organic AS is contained in the clay (Figure 1). Both methods of treatment, either a few hours at 80°C or 5' under sonification, lead to the same maximum exchange yield.

The mixing of the organophilic clays with telechelic acrylic oligomers leads in most cases to homogeneous and stable mixtures. The sedimentation rate measured by following the light absorption at 500 nm is very slow compared to the mixture with the untreated clay (Figure 2 right).

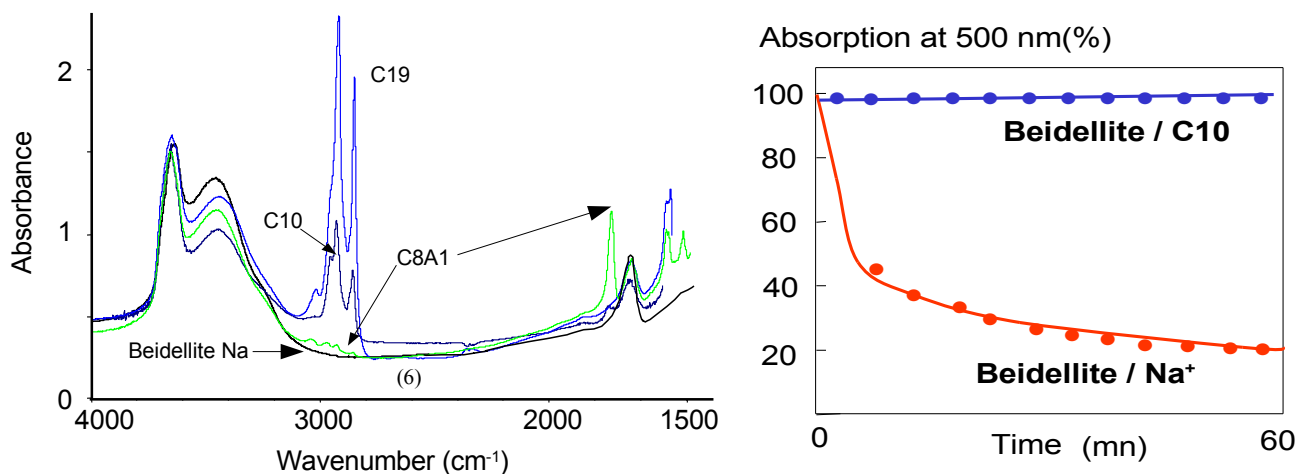


Figure 2: *Left*: Normalized Infrared absorption spectra of the beidellite clay dispersed in a KBr pellet before and after treatment with C19, C10 or C8A1. *Right*: Changes in the UV absorption at 500 nm of a mixture of the organophilic clay beidellite/C10 and hydrophilic clay beidellite/Na<sup>+</sup> in a curable acrylic resin (HEMA: Hexadecylmethacrylate).

Moreover, by X-ray diffraction analysis and weight loss measurements, it can be seen that beidellite contains up to 39% of C10 AS after the cationic exchange (Table 2) and the interlayer space distance increases, from 2.2 Å with Na<sup>+</sup> as counter-ion to 9.8 Å in the case of the C19 AS. The AS C10, C19 and C8A1 are therefore well suited for the organophilic treatment of the clays (Table 2).

Table 2: XRD and TGA analysis of beidellite and ImpV organoclays.

Clay	AS	$d_{001}$ (Å)	weight loss 150-800°C (%)	Interlayer distance (Å)
Beidellite	/	12.2	5.7	2.2
	C10	17.6	38.5	7.6
	C19	19.8	17.3	9.8
	C8A1	14.5	14.8	4.5
ImpV	/	12.6	7.5	2.6
	C10	/	18.3	/
	C19	19.4	33.1	9.4
	C8A1	14.3	12.6	4.3
	C6	17.5	15.3	7.5

### 3.2. UV-curing of the filled Acrylic resins

An UV-curable polyurethane-acrylate (PUA) resin known to polymerize rapidly upon UV irradiation, with formation of tight tridimensional polymer network was used in this study. Several millimeter thick samples can be obtained under UV light in the presence of air (Figure 3).

In case of exfoliation of the clay in the resin, leading to a hazeless curable mixture, the addition of the organoclay treated with n-alkylammonium salts like C10 and C19 was found to have no significant effect on the polymerization kinetics (Figure 3). Similar conversion *versus* time curves being recorded by RTIR spectroscopy upon UV-exposure for the samples containing or not the clay filler (Figure 3). However, in case of a partial exfoliation, a turbid mixture is obtained and the curing rate decreases like it was the case for the not optimal C19/Beidellite sample in Figure 3.

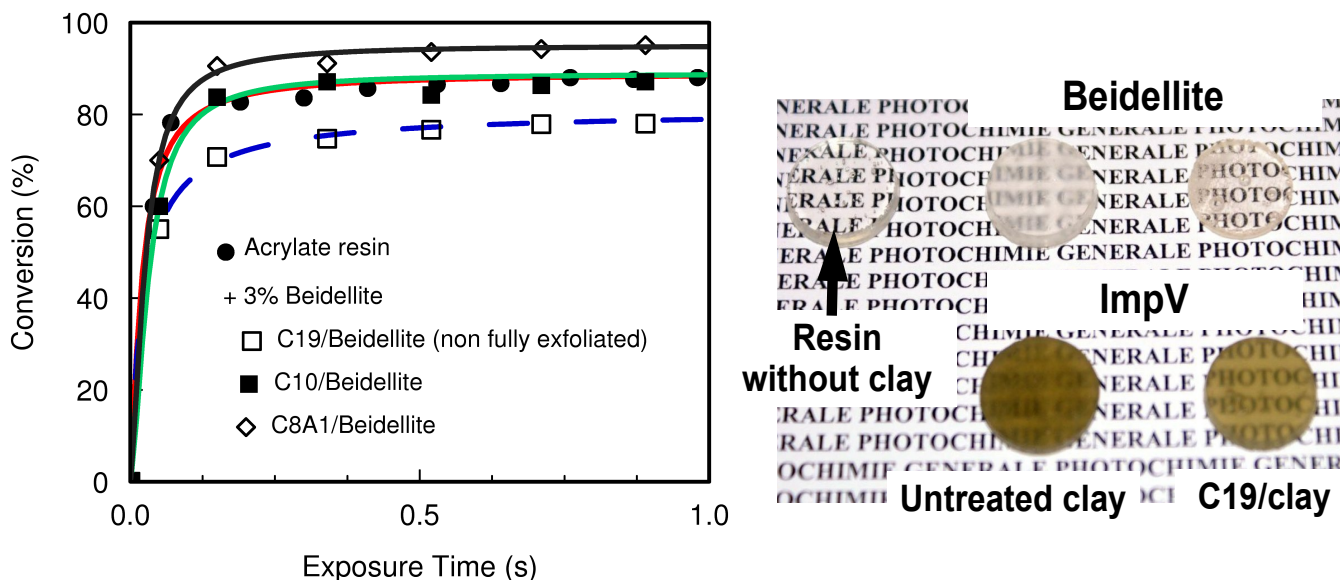


Figure 3: Left: UV-curing rates of a PUA/HDDA mixture in the presence of 3% organophilic clay filler. UV light source (100mW/cm<sup>2</sup>, UV-A/B). Right: View of 2 mm thick cured samples containing no clay (left top) and 3% of untreated clay (left column) or C19 organophilic clay (right column). UV Light intensity 400mW/cm<sup>2</sup>.

But with the clay having a reactive organophilic layer like C8A1, the curing rate is faster and the final conversion yield is increased. The reason for such a behavior is under examination and could be related to the tight and ordered disposition of the C8A1 acrylic double bonds surrounding the silicate platelets.

Under irradiation with UV light, the samples containing ImpV become colored whereas the samples containing beidellite remain transparent (Figure 3). The apparition of dark colors under irradiation with UV-light can be related to the presence of catalytic amounts of heavy-metals in the natural clay.

### 3.3 Curing of the waterbased urethane dispersions

The organophilic clays were dispersed in the waterbased curable polyurethane dispersions containing the photoinitiating system. The films were dried either at room temperature or at 80°C and cured either at room temperature (RT) or at 80°C.

It is observed that the clay/AS organoclay can have a greater effect on the curing efficiency than in the case of solventless resins. The curing extent recorded upon UV irradiation at room temperature can be better, depending on the composition of the dispersion and the AS (Figure 4). At 5% (and 7%) load of beidellite/C19 filler, the final conversion yield of the dry WD1 dispersion is better than for the unfilled resin. One of the greatest effect was observed with the WD2/beidellite/C6 nanocomposite (Figure 4). The curing extend at room temperature in the presence of 7% of the clay filler reaches nearly the value observed at 80°C in case of the pure dispersion.

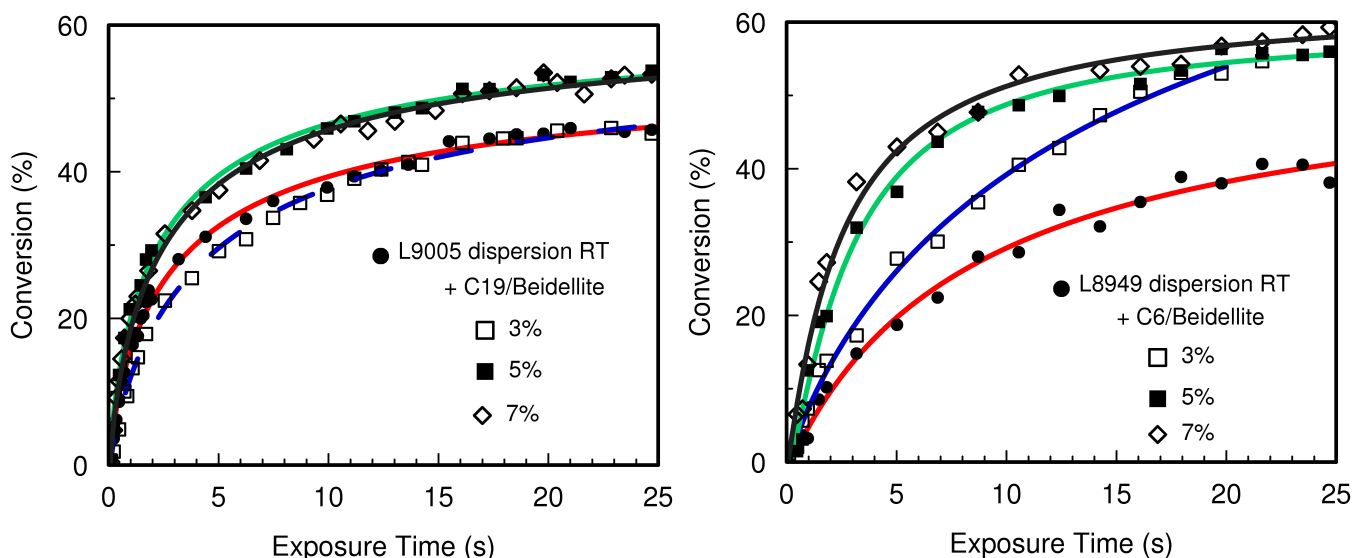


Figure 4: Conversion of acrylic double bond upon irradiation time for WD1 and WD2 in the presence of increasing amounts of C19/beidellite and C6/beidellite respectively. In air at room temperature.

One reason for such a behaviour could be the effect of the organophilic clay nanoparticles on the viscosity and polymer chain mobility in the dried resin which is of great importance as shown by the effect of the curing temperature on the curing. Another effect could arise from a ionic exchange mechanism. The counter ions of the carboxylate groups of a typical dispersion are usually sodium ions. Replacing it by ammonium salts enhance the reactivity of the dispersion. A part of the C6 AS used in the organophilic treatment of the clay could be exchanged with the sodium ions during the mixing of the clay with the waterbased dispersion.

### **3.4. Properties of UV-cured nanocomposites**

#### **a) Mechanical and rheological properties**

According to recent morphology and rheology investigations<sup>5</sup>, *in situ* generated anisotropic nanoparticles assemble to form a skeleton like superstructure, which is considered to account for the enhanced properties. The true nanocomposites synthesized by UV-radiation curing will therefore exhibit the distinct characteristics which are typically found in this kind of materials<sup>2</sup>. Compared to the conventional microcomposites made of the same components, nanocomposites show :

- a lower permeability to gas due to a labyrinth effect,
- an excellent chemical resistance owing to their high crosslink density which made them totally insoluble,
- a greater thermal resistance,
- a higher flame retardancy,
- improved stiffness and strength.

The mechanical properties of the nanocomposite will depend mainly on the type of UV-curable resin selected, and they can therefore be modulated in a large range, depending on the considered application. One can thus produce either flexible and impact resistant nanocomposites, or hard and scratch resistant materials. Figure 5 shows some typical stress-strain curves obtained with a UV-cured polyurethane-acrylate (Ebecryl 8402) film containing 3 wt% of a clay filler (microcomposite) or of an organoclay filler (nanocomposite).

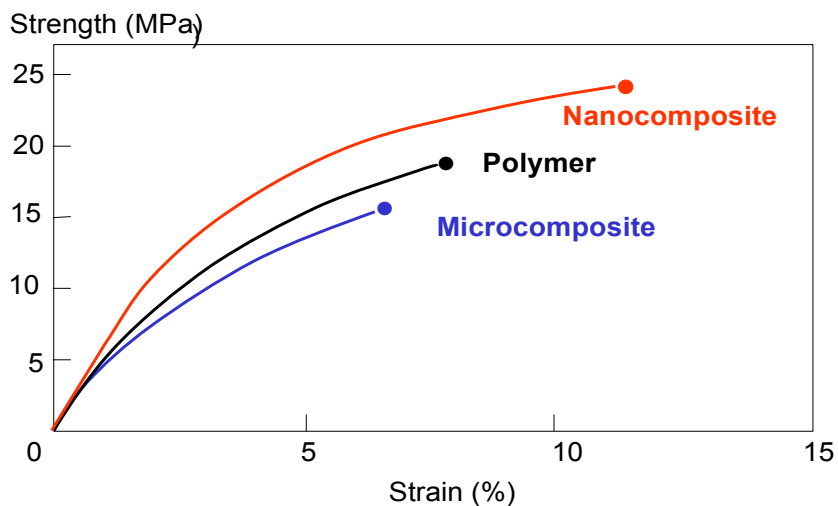


Figure 5: Influence of the mineral filler (3wt%) on the viscoelastic properties of a UV-cured PUA polymer (Eb8402/HDDA). Microcomposite: untreated beidellite. Nanocomposite C19/Beidellite.

The Persoz hardness of the acrylic resins are not strongly affected by the presence of less than 7% of clay filler (Table 3). The hardness of the coatings obtained from waterbased dispersions can be much more affected. In fact, in the case of the C19/clay, the hardness of a coating obtained from WD1 is reduced by a factor two, whereas if the C6/clay is used, the hardness drop remains low compared to the clay-free coating. Softer nanocomposites can be obtained by using a monoacrylate as reactive diluent.

Table 3: Pendulum hardness of the cured resins and the nanocomposite containing 3% of organophilic clay. Temperature 25°C. Film thickness 100µm. Curing under UV light at room temperature.

<i>Resin PUA/HDDA</i>	<i>No filler</i>	<i>C19</i>	<i>C10</i>	<i>C6</i>	<i>C8A1</i>
	148	150	159	/	144
<i>Dispersion WDI</i>	350	200	/	300	/

Figure 6 shows the water uptake, followed by IR spectroscopy through the increase of the OH absorption band, for a UV cured polyurethane-acrylate film placed in a closed chamber at relative humidity of 100% at 25°C. Within 2 hours, the hardness and the polymer was significantly decreased due to the plasticizing effect of water. It can be seen that the decrease is much less pronounced for the nanocomposite sample.

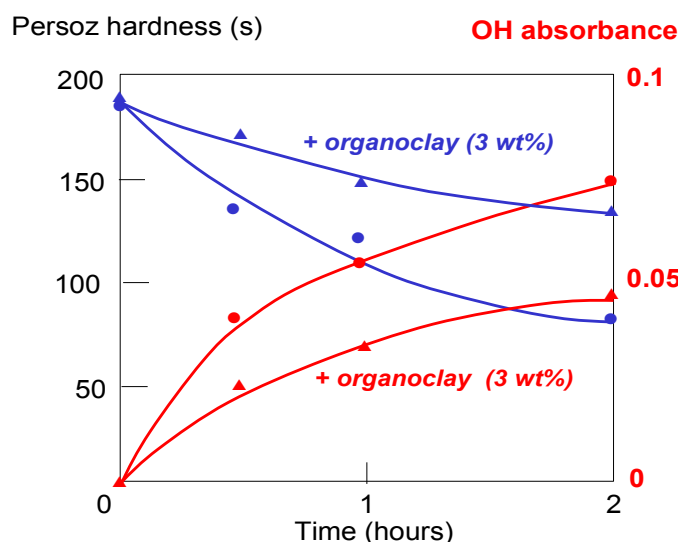


Figure 6: Influence of the organoclay on the water uptake followed by the increase of the OH absorbance at 3500cm<sup>-1</sup> and the hardness of the UV-cured PUA coating placed in a 100% relative humid atmosphere. Film thickness 40µm.

### **b) Effect on gloss**

Another effect of nanoparticles is to reduce the gloss of the UV-cured coating, as shown in Figure 7. An organoclay content of 5 wt% can be already sufficient to make the gloss value drop from 85% to 20% (Montmorillonite/C19 in ref. 6). While this effect may be a drawback for some applications where glossy materials are desired, it can be an advantageous in some others like for wood coating or floor finishes. Low gloss UV-cured coatings are unusually difficult to obtain without increasing too much the formulation viscosity. In this respect, organoclay appears as an effective and cheap matting agent, low amounts of this filler being sufficient to reduce sharply the gloss because of the uniform distribution of the nanoparticles.

Within the organoclays studied, the same effect on gloss is observed for C10, C19 and C8A1, both on PUA resins and dispersions. However, the drop of the gloss was not observed in the case of some other copolymerizable AS.

The loss of gloss can be attributed to the surface roughness as shown with optical topographic analysis of the surface (Figure 8).



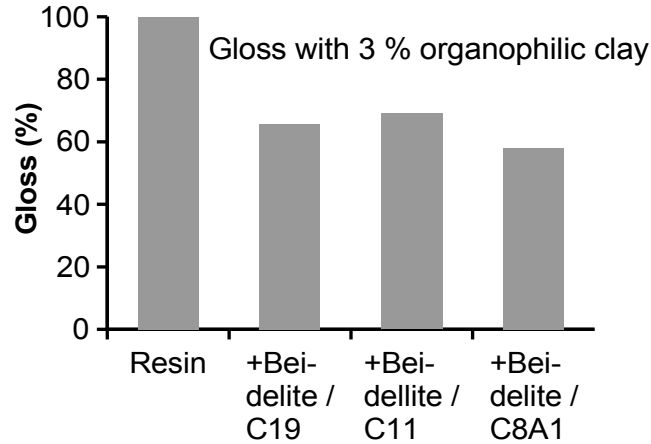


Figure 7: Effect of the organoclay on gloss of the PUA coating.

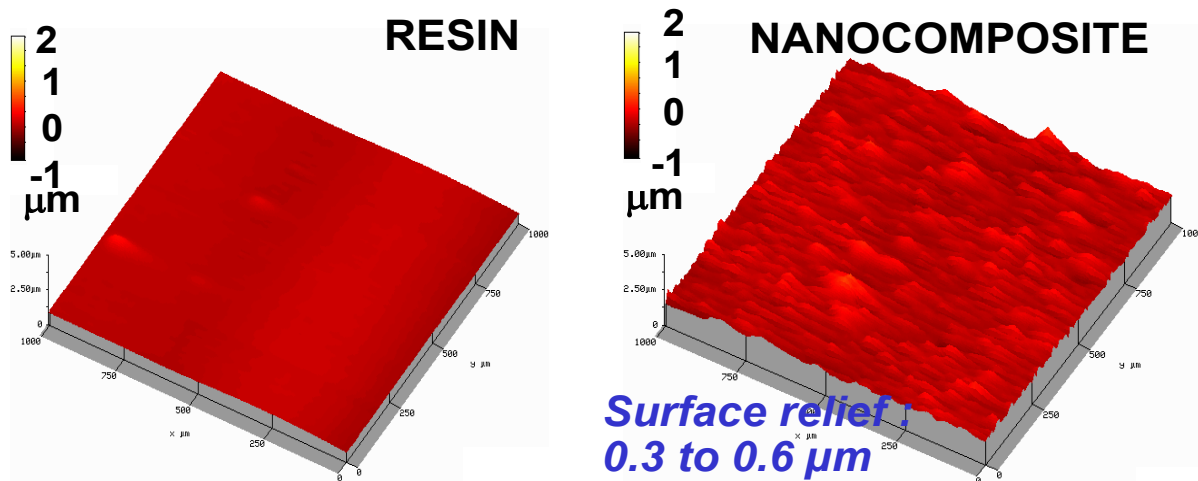


Figure 8: Influence of the organoclay on the surface roughness of a UV cured PUA coating.

#### 4. CONCLUSION

Nanocomposite materials made of silicate platelets dispersed in a crosslinked polyurethane-acrylate matrix have been readily produced at ambient temperature by photoinitiated polymerization. The clay mineral was made organophilic by treatment with alkylammonium salts to allow the acrylate resin to penetrate into the expanded galleries. Complete exfoliation of the layered silicate was demonstrated by X-ray diffraction spectroscopy and sedimentation analysis. The 1 nm thick silicate particles are randomly dispersed in the polymer matrix, which accounts for the significant improvement in properties achieved already at a low filler content (3-7 wt%). The UV-curing reaction was followed in real time by IR spectroscopy and shown to proceed at least as fast and as extensively as in the clay-free formulation mainly because of the remarkable transparency of the nanocomposite material. Moreover, depending on the nature of the ammonium salt, the curing efficiency can be increased, especially in the case of waterbased curable acrylic dispersions.

- 1 a) A. Eranian, Proc. RadTech Europe Conf. (Berlin), p.523 (2001); b) C. Decker, *Chimia*, **47**, 378 (1993)
- 2 Alexandre M., Dubois P., *Mater.Sci.Eng.*, **28**, 1 (2000).
- 3 C. Decker, K. Zahouily , L. Keller, S. Benfarhi, T. Bendaikha, Baron J., *J.Mater.Sci.*, **37**, 1 (2002); L. Keller, C. Decker, K. Zahouily, S. Benfarhi, J.M. LeMeins, J. Miehe-Brendle, *Polymer*, **45**, 7437 (2004)
- 4 J. Miehe-Brendlé, L. Khouchaf, J. Baron, R. LeDred, M.H. Tullier, *Microporous Material* **11**, 171-183(1997).
- 5 R. Mülhaupt, *European Polymer Federation*, AIM Magazine, July 2001, p.50; J.H. Choy, S.J. Kwon, S.J. Hwang, Y.I. Kim and W. Lee, *J.Mater.Chem.* **9**, 129 (1999)
- 6 C. Decker, L. Keller, K. Zahouily , S. Benfarhi, *Polymer*, **46**, 6640 (2005).