

# Ultrafast hardening of a modelling paste by UV-curing of a polyamide filled acrylic resin

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A modelling paste has been hardened within seconds upon exposure to intense UV-radiation at ambient temperature. The composite formulation was made of an acrylate functionalized oligomer, a radical-type photoinitiator (0.5 wt%), and an ultrafine polyamide powder (40 wt%). The polymerization process has been quantitatively followed by near-infrared spectroscopy and shown to proceed up to conversions above 90%. A more complete curing was achieved for 1 mm thick samples than for thin films, because of the greater increase in the sample temperature caused by the heat evolved in such ultrafast exothermal polymerization. Hardening of the paste by low-intensity visible light resulted slower and less extensive photocuring. The tensile properties of the photocrosslinked polymer were evaluated from stress-strain curves, and found to reach their optimum values for a UV-dose of  $5 \text{ J cm}^{-2}$ . The highest tensile strength (60 MPa) was obtained with a polyphenoxy-diacrylate oligomer. The addition of the polyamide filler has a negative effect on the tensile properties, depending on the granulometry of the powder. The best performing photocured composite fulfilled the specifications required for the considered moulding application, with respect to the tensile strength (40 MPa), the elongation at break (3%) and the calcination extent (100%). © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

UV-radiation curing has become a well-accepted technology which had found a large variety of applications because of its distinct characteristics: an ultrafast polymerization of a solvent-free resin performed at ambient temperature [1, 2]. Most of these resins consist of multifunctional monomers and telechelic oligomers, bearing generally the very reactive acrylate double bond [3]. Upon UV-exposure in the presence of a radical-type photoinitiator, the polymerization develops within seconds with formation of a tightly crosslinked polymer network. Because of the limited penetration of light, this environmental friendly technology has been mainly used to cure relatively thin films, in particular in the coating industry for the surface protection of various materials by fast-drying varnishes and printing inks [3, 4]. It also proved effective to cure some filled resins and produce rapidly composite materials at ambient temperature, such as dental cements [5, 6], fiber glass reinforced composites [7, 8], composite membranes and reinforced plastics [9], photopolymer nanocomposites [10, 11], prototype moulds and dental prosthesis models [12]. In all these applications, a deep through cure of up to a few millimeter thick samples can only be achieved by using transparent or light-scattering filler (such as silica, glass powder or organoclay), together with a photo-bleachable initiator promoting frontal polymerization [13].

The objective of the present study was to design a photocurable modelling paste to be used for the fabrication of a mould. After hardening by UV irradiation of a mould of desired shape and casting of the prototype, the mould should be completely removable by calcination. The composite must therefore be made of purely organic compounds, which prevents the use of a mineral filler. In addition, this photocurable paste has to fulfil a number of specifications:

- consistency of modelling clay for an easy forming of moulds of complex shapes;
- tack-free malleable paste before curing;
- fast hardening upon exposure to light (UV or visible) at ambient temperature;
- low elongation at break (<5%) and low shrinkage to maintain the mould shape and dimensions;
- high tensile strength (>40 MPa);
- low adherence of the cured material to allow an easy withdrawing of the model from the mould, without breaking;
- 100% calcinable photocured mould upon heating at 800°C.

In order to meet these stringent specifications, we have designed various UV-curable pastes made of well-selected acrylic resins and photoinitiators, by using as filler a finely divided polyamide powder. The performances of such modelling pastes have been evaluated

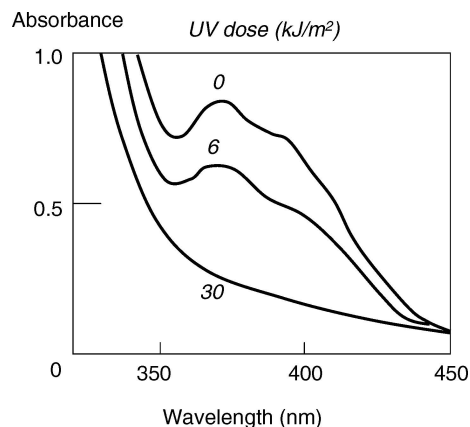


Figure 1 Photobleaching of a biacetylphosphine-oxide photoinitiator in an acrylate resin.

with respect to both the processing (UV-irradiation conditions) and the mechanical properties. They were compared to those of a commercial product developed for this application, but which is lacking the required tensile strength.

## 2. Experimental

### 2.1. Materials

The photocurable composite formulation was made of three basic components: a photoinitiator, an acrylate end-capped oligomer and an organic filler. An acylphosphine oxide (Irgacure 819 from Ciba Specialty Chemicals) was selected as photoinitiator for the curing by UV-radiation. This photoinitiator is not only very efficient [14], but it is also undergoing a fast photobleaching upon UV-exposure with formation of UV-transparent photoproducts, as shown in Fig. 1. The incident radiation can thus penetrate progressively deeper into the sample, thus allowing a few millimeter thick plates to be deep-through cured by such frontal polymerization process [15]. The photoinitiator concentration [PI] was set at 0.5 wt%, as it was found to be the best compromise between cure speed, which rises with increasing [PI], and light penetration, which grows with decreasing [PI]. For polymerizations induced by visible light, a xanthenic dye (0.5 wt% eosine) was used, in combination with a tertiary amine (5 wt% methyl-diethanol amine) acting as hydrogen donor molecule. Such association was previously shown to be a very efficient visible-type photoinitiating system for acrylate polymerization [16].

Among the large number of acrylate functionalized oligomers commercially available [17], we have selected three types having backbones of different chemical structures, in order to achieve the high tensile strength required for the photocured polymer:

- an polyphenoxy-diacrylate, PPA (Ebecryl 600 from UCB)
- an aliphatic polyurethane-diacrylate, PUA (Ebecryl 284 from UCB)
- an aromatic polyester hexaacrylate, PEA (Ebecryl 830 from UCB).

TABLE I Characteristics of the Orgasol® (ultrafine polyamide powder) used as filler in the photocurable acrylic composites

Filler	Type of polymer	Average size ( $\mu\text{m}$ )	Specific surface area $\text{m}^2/\text{g}$	Melting point $^{\circ}\text{C}$
PA-1	Polyamide 12	5	9	177
PA-2	Polyamide 12	10	4	177
PA-3	Polyamide 12	20	1	177
PA-4	Copolyamide 6/12	5	10	142
PA-5	Copolyamide 6/12	10	20	142
PA-6	Copolyamide 6/12	20	6	142

In some formulations, a multiacrylate monomer was added to increase the crosslink density and try to enhance the tensile strength of the cured polymer.

In order to obtain a non-tacky modelling paste, large amounts (up to 80 wt%) of a polymer powder like PVC or PMMA had to be introduced in the acrylic resin, with the expected drastic drop in the mechanical performance of the cured composite. It was possible to markedly decrease the filler content (down to 30 wt%) by using an ultra-fine powder, such as Aerosil 200 (Aerosil France). This is a mineral filler made of silica, so that the cured composite will not be completely calcinable, as required for the considered use of this material. In our search toward the ideal organic filler, we came across an ultrafine powder made of a polyamide (Orgasol from Atofina) which, mixed to the UV-curable resin, produced a non-tacky malleable paste at a filler content of less than 40 wt%. The detrimental effect of the filler on the mechanical properties was thus significantly reduced.

Orgasol ultra-fine polyamide powders are polymers and copolymers of lauryllactam and/or caprolactam obtained by direct polymerization. This process yields microporous spherical beads of specific size (between 5 and 60  $\mu\text{m}$ ) and specific surface area (between 1 and 20  $\text{m}^2/\text{g}$ ) [18]. The structure, the shape, the narrow size distribution and the properties of Orgasol powders make them significantly different from other powders made by grinding or precipitation. Among the various grades commercially available, we have selected those having the smallest particle size (between 5 and 20  $\mu\text{m}$ ), so as to reduce the filler content of the modelling paste. The characteristics of the Orgasol samples used in the present study are given in Table I. This type of organic filler is perfectly compatible with acrylic resins and was successfully used as matting agent in UV-curable epoxy-acrylate and polyurethane-acrylate formulations [19]. It is an important criterium in order to achieve an optimum wetting of the filler particles by the resin which must penetrate as far as possible into the micro-cavities. A commercial modelling paste (Palavit from Heraeus Kulzer) was used as reference for comparison of the performance of the products developed in the present study, specially regarding the tensile strength.

### 2.2. Processing

A typical formulation of the UV-curable paste was made of 0.5 wt% photoinitiator, 40 wt% Orgasol and 60 wt% of acrylic resin. The filler was progressively introduced in the liquid resin and thoroughly mixed

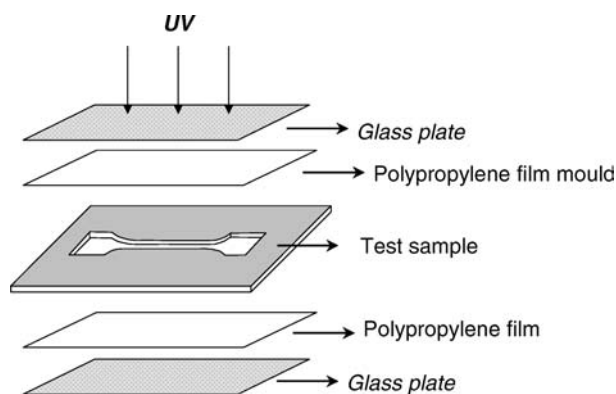
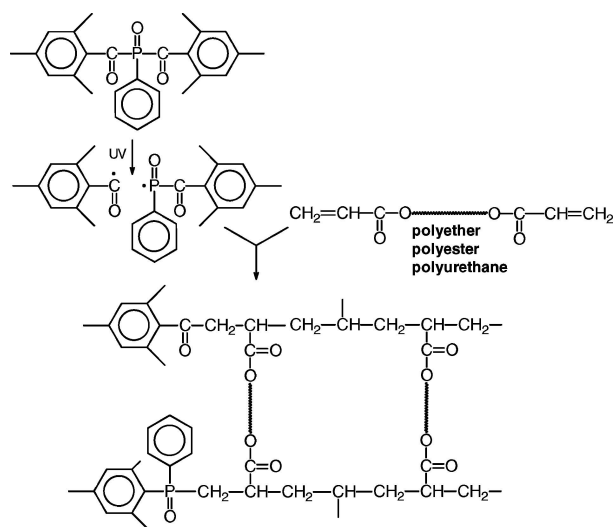


Figure 2 Experimental set-up for the preparation of test samples for mechanical analysis.



Scheme 1 Photoinitiated polymerization of telechelic acrylate oligomers.

until a non-tacky malleable paste was obtained. The 1 mm thick samples used for mechanical testing were prepared as shown in Fig. 2. The haltere shaped mould was filled with the UV-curable paste, and tightly pressed between two glass plates, intercalated by transparent polypropylene films to facilitate the release of the sample from the mould after photocuring. The complex assembly was exposed for a few seconds to the radiation of a medium pressure mercury lamp on a UV-curing line from IST (electrical power of 8 kW/m). The incident light intensity at the sample position was measured by radiometry to be on the order of 3 kW/m<sup>2</sup>.

To avoid an overheating of the sample due to the heat evolved by both the powerful light source and the ultrafast exothermal polymerization, the sample was not exposed continuously to UV radiation but passed several times under the lamp at a speed of 5 m/min, which corresponds to a 1 s exposure per pass. Moreover, the top glass plate is acting as a UV cut-off filter and also helps avoiding an excessive cure speed which would be detrimental for the polymer properties by imparting some brittleness. In practical applications where the paste will not be pressed between glass plates, it is thus recommended to use glass-filtered light to induce the polymerization. Some curing experiments were performed by means of the less intense visible light of an overhead projector or simply by sunlight. The exposure

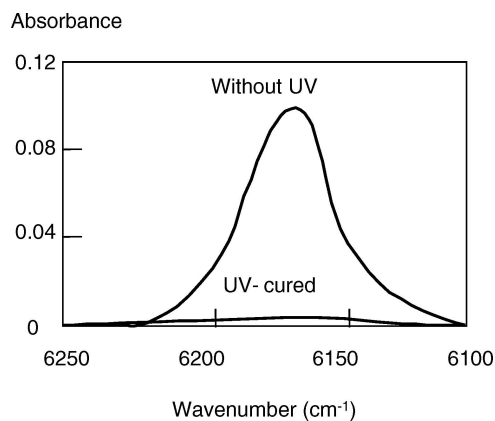


Figure 3 Near-IR spectrum of a photocurable acrylate resin, before and after UV exposure.

time had to be increased to several minutes because of both the decreased light intensity and the lower efficiency of visible-type photoinitiators [16].

The chemical processes occurring during the light-induced hardening of the modelling paste are represented in Scheme 1. It should be noted that the inhibitory effect of atmospheric oxygen, which is particularly pronounced in the UV-curing of acrylates [20], was prevented with the experimental set up used (Fig. 2), because the UV-curable paste is not in contact with air. An adequate surface cure of the paste was still achieved in the presence of air because of the very slow diffusion of atmospheric oxygen in the solid paste during the short UV exposure.

### 2.3. Analysis

The extent of the photoinitiated polymerization was evaluated quantitatively by near-infrared spectroscopy (Bruker IFS-66/S FTIR spectrophotometer) by following the disappearance of the acrylate double bond overtone IR band at 6160 cm<sup>-1</sup>. Fig. 3 shows a typical near-IR spectrum of an acrylic resin, before and after UV exposure. It should be noted that the near IR analysis of the cure extent can be performed directly on the complex assembly (Fig. 2), because glass and polypropylene are transparent to the infrared radiation of wavenumber above 3000 cm<sup>-1</sup>.

The surface cure of the UV-exposed sample was also determined by attenuated total reflectance FTIR spectroscopy, a technique which probes the 2 μm thick layer in contact with a diamond, reflecting the IR analyzing beam, by means of evanescent waves [21]. The degree of conversion ( $x$ ) was calculated from the decrease in IR absorbance ( $A$ ) after a given exposure:  $x = 1 - (A_t/A_0)$ . This analytical method permits to determine precisely the final conversion reached at the end of the UV exposure, and thus the amount of unreacted functionalities in the photocured polymer and its crosslink density, a crucial factor with respect to the tensile properties of the mould.

The mechanical properties of the photocured material were evaluated by recording the stress-strain curves by means of an Ingström (MTS) apparatus. Fig. 4 shows a typical curve recorded for a UV-cured polyether-acrylate paste containing 36 wt% Orgasol. From this

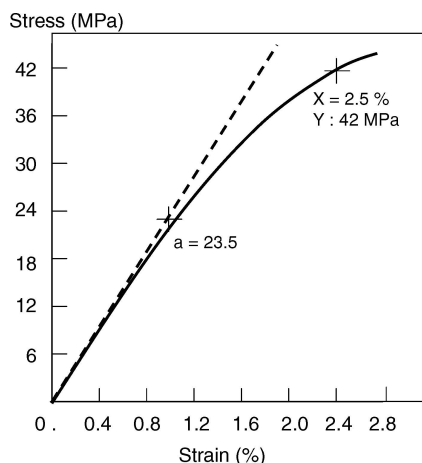


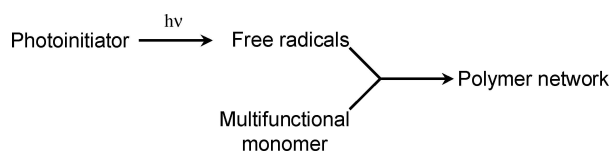
Figure 4 Stress-strain curve recorded for a photocured polyphenoxy-acrylate/polyamide composite.----: slope for Young modulus evaluation ( $E = 2.35$  GPa).

curve one can directly evaluate the elongation at break (typically on the order of a few percent) and the tensile strength, after accurate measuring of the test-sample width ( $\sim 5$  mm) and thickness (1 mm). The elastic modulus was obtained from the initial slope of the stress-strain curve.

### 3. Results and discussion

#### 3.1. Photocuring of the acrylic paste

The photoinitiated polymerization of multifunctional monomers, which leads to a highly crosslinked polymer, can be represented schematically as follows:



The disappearance of the reactive function, i.e., the acrylate double bonds, was followed quantitatively by infrared spectroscopy. A kinetic study of the photoinitiated polymerization was first carried out on the unfilled resins, taken as reference. Transmission near-IR spectroscopy was used to evaluate the average degree of polymerization of UV exposed 1 mm thick samples, while ATR-FTIR spectroscopy was used for the surface analysis of the UV-cured plates. Fig. 5 shows how the degree of conversion increases with the UV dose for the three resins investigated: polyurethane-acrylate (PUA), polyphenoxy-acrylate (PPA) and polyester-acrylate (PEA). A single pass under the lamp (1 s exposure) proved to be sufficient to polymerize more than half of the acrylate double bonds. Nearly complete polymerization was achieved upon further exposure up to 10 s for the aliphatic polyurethane-acrylate, which is the most flexible, while the conversion was levelling off at around 90% for the stiffer aromatic PPA and PEA samples. Premature ending of the polymerization is a well-known phenomenon in UV-radiation curing [1–3]. It was attributed to the severe molecular mobility restrictions brought upon by the build up of the tight polymer network and to vitrification. Indeed, polymer-

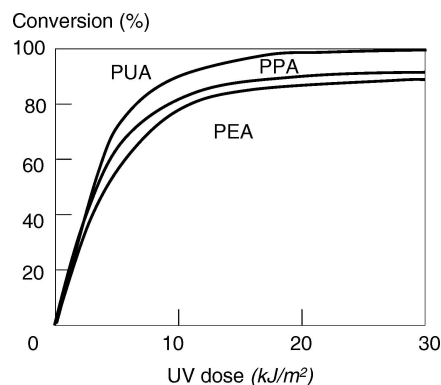


Figure 5 UV-curing of acrylic resins monitored by near-IR spectroscopy (overtone band at  $6160\text{ cm}^{-1}$ ). Sample thickness: 1 mm; Light intensity:  $3\text{ kW/m}^2$ .

ization does not occur anymore in a glassy polymer where reactive species are trapped.

Each of the two faces of photocured plates were found by ATR-FTIR spectroscopy to have similar degrees of conversion, quite comparable to those measured by near-IR spectroscopy. This means that a deep-through cure of the 1 mm thick sample has been achieved after a 10 s UV exposure, through a light-induced frontal polymerization. This is due to the fast photobleaching of the selected acylphosphine oxide photoinitiator (Fig. 1). It should be noted that a less complete polymerization was observed when the same resins were UV-cured as  $30\text{ }\mu\text{m}$  thick coatings, as monitored by mid-IR spectroscopy (band at  $812\text{ cm}^{-1}$ ). The cure extent of PEA and PPA sample was levelling off at around 70%, and that of PUA at 85%. This behavior was explained by a temperature effect which is more pronounced in thick samples undergoing an ultrafast exothermal polymerization, where the temperature can rise up to  $150^\circ\text{C}$  [3, 22]. For thin samples, the cooling off is more rapid and the temperature increase less pronounced [23]. The chain reaction is usually considered to stop when the glass transition temperature of the polymer undergoing curing reaches the temperature of the sample, so that polymerization will be more complete in thick samples which become hotter upon ultrafast curing.

The addition of the organic filler (36 wt%) in the UV-curable resin was found to have some slowing down effect on the photopolymerization (Fig. 6).

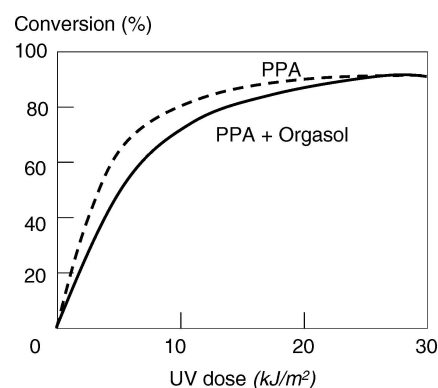


Figure 6 Influence of the organic filler (36 wt%) on the UV-curing of an acrylic resin monitored by near-IR spectroscopy (overtone band at  $6160\text{ cm}^{-1}$ ). Sample thickness: 1 mm; Light intensity:  $3\text{ kW/m}^2$ .

But the transparency of the polyamide above 320 nm, together with the light scattering by the Orgasol microparticles is limiting the importance of this UV-screen effect. Consequently, the same final cure extent was reached after a 10 s exposure for the modelling paste as with the clear resin.

Similar experiments have been performed by using as light source an overhead projector which emits in the visible range. As the acylphosphine oxide hardly absorbs light in this wavelength region, it proved to be poorly efficient to initiate the polymerization. It was replaced by a xanthenic dye (0.5 wt% eosine) associated to methyldiethanol amine (5 wt%) as hydrogen donor. This combination was previously shown to be a relatively efficient visible-type photoinitiator which undergoes some photobleaching upon exposure to light [15]. Under those conditions, the polymerization of the three selected resins proceeds rather slowly, in particular because of the less intense illumination, and it takes about 15 min to reach the final conversion. Their values were found to be significantly lower than for the polymers cured under intense UV illumination, and quite comparable to the values obtained for the 30  $\mu\text{m}$  thick coatings. Such incomplete cure can be explained by considering that the polymerization proceeds here at a lower temperature (about 40°C), the heat evolved during such slow polymerization being continuously dissipated.

### 3.2. Mechanical properties of the photocured paste

The photocured haltere-shaped sample was easily removed from the mould because of its poor adherence onto the polypropylene film. If necessary, its adhesion on a given substrate can be further decreased by lowering the surface energy of the cured polymer through the addition of a fluoro-acrylate monomer in the formulation. The contact angle of a water droplet on the photopolymer surface was increased from 60 to 110° by simple addition of 0.5 wt% of a fluoro-acrylate monomer and a concomitant drop to the surface energy from 52 to 32  $\text{mJ m}^{-2}$  [24, 25]. By using in the formulation some acrylate functionalized oligomers having relatively long backbone chains, shrinkage of the photocured paste was kept to a minimum ( $\leq 3\%$ ), as requested for the considered end-use. All the samples tested were completely calcinated upon heating at 800°C, as expected for these purely organic materials.

The hardness of the UV-cured polymer was measured by monitoring the damping of the oscillations of a pendulum (Persoz hardness). The pendulum hardness was shown to be a reliable measure of the viscoelastic properties of a polymer [26], and to be directly related to its glass transition temperature [27]. For the aromatic PPA and PEA glass samples, its value was in the 300–350 s range, on a scale which goes from 20 s for soft elastomers up to 400 s for mineral glass. As expected, the more flexible aliphatic PUA sample showed the lowest hardness value (250 s).

The main objective of this study was to design a modelling paste that would exhibit a higher tensile strength (superior to 40 MPa) after photocuring than the commercial material presently used (10 MPa). We have first

evaluated the tensile properties of the three unfilled resins to select the toughest system, and then try to maintain the highest tensile strength by a proper choice of the Orgasol filler, the use of multiacrylate monomers and the appropriate UV dose. All the results obtained are summarized in Table II which gives the sample composition, the tensile strength and the elongation at break for samples cured at a UV dose of 50  $\text{kJ/m}^2$ . The data reported correspond to average values of three measurements made for each formulation. It should be mentioned that the indicated monomer content refers to the UV-curable resin (e.g. 25 wt% monomer and 75 wt% oligomer), while the filler content refers to the modelling paste (e.g. 40 wt% Orgasol and 60 wt% UV-curable resin). All the UV-curable formulations contained 0.5 wt% Irgacure 819 as photoinitiator. The organic filler was added in such an amount as to get a tack-free malleable paste. To achieve this goal, higher amounts of Orgasol were required for fluid resins than for viscous resins, as expected.

In consideration of these results, the following comments can be made with respect to their mechanical properties:

- among the three unfilled samples, the polyphenoxy-diacrylate (PPA) exhibits the highest tensile strength (60 MPa) and was selected for further studies. One can note the relatively high value of the elongation at break of the polyurethane-diacrylate;
- the addition of a diacrylate or triacrylate monomer to the clear resin has no major effect on the tensile properties, while it has a detrimental effect on the shrinkage which is enhanced;
- the addition of the polyurethane-diacrylate (20 wt%) to PPA increases significantly the tensile strength (72 MPa);
- the polyamide filler has a drastic effect on the tensile strength which drops by a factor of up to 3. Among the six Orgasol powders tested, the copolyamide 6/12 with an average particle size of 20  $\mu\text{m}$  and a surface area of 6  $\text{m}^2/\text{g}$  (3502-D-Nat-1) gave the best result (41 MPa). The better performance of the copolyamide fillers may be due to their lower melting point;
- the detrimental effect of the filler on the tensile properties is as pronounced for the PEA formulations containing monomers or PUA as for the monomer-free samples;
- the tensile strength increases upon UV-curing to level off at a UV-dose of 50  $\text{kJ/m}^2$ , the elastic modulus reaching then values on the order of 2 GPa (Fig. 4).

In consideration of the given specifications of the photocurable modelling paste with respect to the tensile properties, elongation at break, shrinkage and reactivity, it turned out that the following simple formulation showed the best performance:

Irgacure 819:	0.5 wt%
Ebecryl 600:	64.5 wt%
Orgasol 3502-D-Nat-1:	35 wt%

It clearly outperforms the commercially available product at a much lower cost.

TABLE II Tensile properties of photocured polyamide/acrylate composites

UV-irradiation			([Irgacure 819] = 0.5 wt%)		
Oligomer <sup>a</sup>	Monomer <sup>b</sup>	Filler <sup>c</sup>	Tensile strength (MPa)	Break elongation (%)	UV dose (J cm <sup>-2</sup> )
PPA	–	–	60	1.8	5
PEA	–	–	45	1	5
PUA	–	–	36	2	5
PPA	HDDA (25%)	–	53	1.9	5
PPA	TPGDA (25%)	–	65	2.5	5
PPA	PETIA (25%)	–	55	1.5	5
PPA	PUA (20%)	–	72	3	5
PPA	–	PA1 (38%)	20	0.8	5
PPA	–	PA2 (42%)	18	0.7	5
PPA	–	PA3 (41%)	21	0.9	5
PPA	–	PA4 (32%)	28	1.2	5
PPA	–	PA5 (27%)	34	1.5	5
PPA	–	PA6 (35%)	41	2.4	5
PUA	–	PA6 (39%)	20	3	5
PPA	PUA (20%)	PA6 (35%)	38	2.2	5
PPA	TPGDA (25%)	PA6 (39%)	26	26	0.3
PPA	TPGDA (25%)	PA6 (39%)	33	1.9	1.2
PPA	TPGDA (25%)	PA6 (39%)	40	2.1	3
PPA	TPGDA (25%)	PA6 (39%)	42	2.5	6
	Visible Light			(Eosine (0.5 wt%) + MDEA (5 wt%))	
PPA	–	–	46	3.7	20 minutes
PPA	–	PA6 (37%)	31	2.5	20 minutes

<sup>a</sup>PPA: polyphenoxy-acrylate; PEA: polyester-acrylate; PUA: Polyurethane-acrylate.

<sup>b</sup>Monomer content (in weight %) in the photocurable resin.

<sup>c</sup>Filler content (in weight %) in the photocurable composite formulation.

For practical applications, it would be more convenient to perform the curing with some easily available visible light source, like an overhead projector or an incandescent desk lamp. The hardening of the paste takes then much longer than under intense UV illumination, typically 20 min for the overhead projector and 1 h with a 60 W incandescent desk lamp, eosine + MDEA being used as photoinitiator system. A faster polymerization could be achieved if needed by optimizing the photoinitiating system and by using a more intense lamp (halogen).

For the unfilled PPA resin, the tensile strength of the visible cured sample was measured to be 46 MPa, compared to 60 MPa for the same UV-cured sample, most probably because of some incomplete polymerization for a reaction occurring slowly at near-ambient temperature. Here again, the addition of the organic filler (37 wt% PA-6) makes this value drop to 31 MPa, which is still three times as high as that of the commercial product. By performing the visible illumination at a temperature well above ambient (e.g. 80°C), a more complete cure was accomplished and, consequently, an increase in the tensile strength of the final product. The faster and more complete polymerization achieved by means of visible light offers some interesting possibilities for future applications of this cost-effective and non-polluting technology. In this respect, it should be noted that the photocurable paste developed in this work was also successfully used as a mastic or sealant which could be hardened rapidly on order by UV-irradiation or by simple exposure to sunlight.

#### 4. Conclusion

The light-induced polymerization of a composite formulation made of an acrylate-based resin and an organic filler has been successfully used to promote the hardening of a modelling paste to be employed as a calcinable mould. The manifold specifications imposed for the considered application have been essentially fulfilled with respect to both processing and product characteristics. The best performance regarding the tensile properties has been obtained with a polyphenoxy-acrylate telechelic oligomer associated to an acylphosphine oxide photoinitiator and an ultrafine powder of a copolyamide 6/12. Under intense illumination the hardening of the photocurable paste occurs rapidly to yield a high modulus composite material. The rise in temperature due to the ultrafast polymerization, together with the use of a photobleachable initiator, is essential to achieve a nearly complete cure within seconds of 1 mm thick samples. It is also possible to harden the photocurable paste within minutes by exposure to less intense visible light, by using as photoinitiator a xanthene dye associated to a tertiary amine.

This environmental friendly technology appears to be very attractive to produce rapidly at ambient temperature purely organic composite materials to be used for the manufacturing of calcinable moulds. In consideration of its distinct features with respect to processing facility, low cost and product performance, one can reasonably expect radiation curing to find some new openings in various sectors of industrial applications, in particular in the areas of moulding, dental modelling and prototyping.

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