



# A new resin for photocurable electrical insulating varnishes

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## Abstract

A new polyester resin for photocurable electrical insulating coatings was synthesized. The resin was diluted in hexanediol diacrylate (HDDA) monomer. 2-Hydroxy-2-methyl-1-phenyl-propane-1-one was aggregated to the coating formulation as a photoinitiator of the UV radiation curing. Coating film samples, 50  $\mu\text{m}$  thick, were prepared on copper plates using an appropriated extensor. Coating films were cured under different UV doses at room temperature using an UV tunnel. The UV doses of 400  $\text{mJ cm}^{-2}$  has promoted the higher curing degree without detectable coating degradation. Some samples were submitted to dual-cure (or hybrid cure) that means UV curing followed by thermal curing for 2 h at 240 °C in order to promote the improvement of some ultimate properties. Both samples, UV-cured and UV/thermal dual-cured, were evaluated.

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## 1. Introduction

Electrical insulating varnishes and wire enamels are products used as coatings in several electric and electronic equipment as electrical and chemical barriers. They also improve the mechanical properties of the end products. Nowadays, the applied technology for these coatings is based on the use

of thermally curable resins dissolved in 60–75% of organic solvents. Unfortunately, the use of these coating formulations generates VOC emission, toxicity and high inflammability risk. All these negative effects increase operation and post-operation costs of manipulating such chemical components in order to avoid environmental pollution. Furthermore, the loss of organic solvent by volatilization during the thermal cure reduces the thickness of the coating film applied on the substrate surface.

On the other hand, in ultraviolet (UV) or electron beam (EB) technologies, the oligomers are

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dissolved in reactive monomers. In other words, the UV/EB curable products are comprised of 100% reactive components, which provides for environmentally acceptable coatings. Electron beams are conventionally generated electron accelerators. The accelerated electrons are very energetic and reactive species. Thus, they are valuable in inducing chemical reactions by free radical curing and cross-linking mechanisms between oligomers and monomers to form a polymeric network containing 100% of the component materials without VOC emissions. For UV curing mechanism, photoinitiators are incorporated into the formulation. These materials absorb the incoming UV radiation, producing reactive species such as free radicals, which must be capable of rapidly initiating the curing process while participating minimally in the termination step [1].

UV and EB radiation curing are safe processes for the operating personal and also environmentally friendly technologies that save costs, energy and time. In the electrical and electronics areas, applications like soldering masks, photoresistors, conductive inks and development of flat wires for printed circuitry are examples of radiation-cured coatings usage [2,3]. Such coatings can also be applied to rigid and flexible printed circuitry wiring as a cover. Even though one patent about preparing magnet wire using radiation has already been registered [4], up to now, there are no products in the market to be used as UV/EB radiation curable wire enamels or electrical insulation varnishes. One of the main problems for the replacement of the thermal cure process by the UV/EB technology is to obtain end products with similar electrical insulating, and chemical and mechanical barrier properties. It must be considered that these coatings have to attain continuous thermal life of 20000 h, at least, at temperatures in the range of 155 and 240 °C, without losing its electrical insulating properties.

The most UV/EB curable coatings already in use in consolidated applications have their formulation based on acrylated compounds such as oligomers and diluents. According to technical literature, nonacrylated unsaturated oligomers are capable of absorbing UV radiation through their ethenic unsaturations but the rate they do

that and the rate of any subsequent photoinduced polymerization for film formation are so slow as to make this process uneconomic and technically unacceptable [5]. On the other hand, acrylic compounds are expensive when compared with the usual raw materials for conventional electrical insulating varnishes. Finally, the aim of the present work was to obtain and characterize a new resin based on unsaturated polyester diluted in acrylic monomer to be used in photocurable electrical insulating varnish formulations. Curing at different UV doses and also UV/thermal dual-cure processes were investigated, looking for an improvement in mechanical and electrical properties of the cured films.

## 2. Experimental

### 2.1. Synthesis of the resin

#### 2.1.1. Reagents

Ethylene glycol (124 kg), methylene propylenediol (0.720 kg), pentaerythritol (0.272 kg), tetrahydrophthalic anhydride (1.520 kg), Policat P-lítio<sup>®</sup> (produced by Miracema-Nuodex, Campinas-SP, Brazil) (0.001 kg) and hydroquinone (0.0005 kg) were used as raw materials for the resin synthesis. All chemicals were commercial products used without any further purification. The syntheses of different experimental polyesters were carried out according with the usual esterification technique [6].

#### 2.1.2. Instruments

For the syntheses, common equipment was used, such as round bottom glass reactors with four outlets, heating mantles, Vigreux type and straight condensers, and industrial stirrers with automatic control. The temperature was controlled by a “J” type thermocouple (iron-constantan, for temperature in the range of –190 to 870 °C).

#### 2.1.3. Synthesis procedure

Glycols were set in a glass reactor with 4 outlets. After heating to 130 °C, acid anhydride and catalyst were added, and the temperature was

increased up to 200 °C at a heating rate of 20 °C h<sup>-1</sup>. The reagent mixture was kept at this temperature to reach the acid index below 5.0 mg KOH g<sup>-1</sup>, measured according to the ASTM D1639 standard test method. Then, the temperature was reduced to 90 °C before adding hydroquinone.

## 2.2. Varnishes preparation

The obtained resin was dissolved in 1,6 hexanediol diacrylate (HDDA) monomer up to concentrations of 70%, 60%, 50%, 40% and 30%. Fractions of 1%, 2%, 3%, 4% and 5% of 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Darocur 1173<sup>®</sup> – Ciba Especialidades Químicas Ltd., São Paulo, Brazil) were added as photoinitiator to mixtures of resin/monomer with 50% and 70% of resin. The mixtures comprised of other resin/monomer relations were prepared with 3% of the same photoinitiator.

## 2.3. Dual-cure procedure

A Labcura<sup>TM</sup> UV tunnel (Germetec UV & IR Technology Ltd., Rio de Janeiro, Brazil) was used to cure the samples. The UV tunnel is composed of a medium pressure mercury lamp that operates at 50, 80 or 120 W cm<sup>-1</sup>. The UV doses were monitored using a 390B Light Bug radiometer (International Light, Inc., Newburyport, MA, USA). All samples with 3% concentration of photoinitiator and resin contents of 30%, 40%, 50%, 60% and 70% were cured in the Labcura tunnel up to UV dose of 400 mJ cm<sup>-2</sup>.

Half of the UV cured samples were processed with a complementary thermal cure at 240 °C for 2 h in a forced-air-circulating oven (Fanem Ltd., São Paulo, Brazil).

## 2.4. Test instrumentation and procedures

The Photo-DSC used was a Differential scanning calorimeter TA Instruments DPC 930/DSC 910, equipped with a medium-pressure mercury lamp (80 W cm<sup>-1</sup> operating power and irradiance of 80 mW cm<sup>-2</sup>). The uncured samples were poured in aluminum pans, and the photo-DSC

measurements were done at 25 °C, in nitrogen atmosphere, applying 1-min stabilization time and 7-min exposure time. These tests allow following the curing process by measuring the enthalpy of the reaction induced by UV emission, as a function of exposure time and sample composition.

The hardness of the cured samples was measured using a BYK-Gardner pendulum hardness tester (BYK-Gardner, Geretsried, Germany), in compliance with the ASTM D-4366 standard test method.

The *tangent delta* measurements were made in a DANSK TA9000 system adapted to analyze flat copper capacitors according to ASTM method D-150 at 1 MHz.  $\tan \delta$  gives an indirect measurement of the polymer electric dipole mobility as a function of the applied temperature.  $\tan \delta$  is calculated by the ratio between the loss index factor to its relative permittivity. To determine the dissipation factor of an enameled magnet wire an assembly with two electrodes and a bridge is required to measure the amount of loss of capacitance [7]. The measurements were made in calibrated oven in the range of room temperature up to 300 °C, applying a constant heating rate.

The thermal degradation of the cured samples was followed by thermogravimetry using a Shimadzu TG-50 thermobalance at a heating rate of 10 °C min<sup>-1</sup>, from room temperature up to 600 °C, in dynamic air atmosphere of 50 mL min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Determination of the optimum concentration of photoinitiator

Table 1 shows the photo-DSC data obtained from uncured samples with 50% and 70% of resin concentration as a function of different photoinitiator concentrations from 1% to 5%. The relatively lower value of curing enthalpy determined for samples with 1.0% PI represents that only a partial cure was reached due to insufficient photoinitiator concentration. Concerning to the curing enthalpy, data show that a 2% photoinitiator concentration is enough to promote the maximum cure of the

Table 1

Photo-DSC data from formulations containing 50% and 70% of resin dissolved in HDDA and different concentrations of photoinitiator

PI, %	Resin %		Induction time, s		Peak maximum, s	
	$\Delta H, \text{J g}^{-1}$					
	50	70	50	70	50	70
1.0	238	145	4.9	4.9	9.6	10
2.0	256	148	4.0	4.1	8.0	8.6
3.0	260	256	3.7	3.8	7.4	7.8
4.0	262	260	3.6	3.6	7.2	7.6
5.0	259	150	3.6	3.4	7.2	7.2

varnish, in the applied conditions of the photo-DSC (exposure time and lamp characteristics). On the other hand, the induction time (related to the conversion of 1% of reactive species [8]) decreases with the increase of PI concentration in the range of 1.0–3.0%, remaining constant from 3.0% up to 5.0%. Moreover, the peak maximum values (time between the opening of the lamp shutter and the peak maximum point in photo-DSC curve, when the reaction rate is the highest) have shown no variations with 3% or greater photoinitiator content. Thus considering costs and the fact that high content of PI must be avoided to keep the long-term performance of the cured film, 3% was elected as the suitable photoinitiator concentration for the subsequent studies.

Table 2 shows the photo-DSC results obtained from samples with 3% of photoinitiator and variable resin concentration from 30% to 70%. There is a remarkable variation in the reaction enthalpy values as a function of resin concentration. The data shows an approximate linear fitting as a function of the concentration of HDDA, indicating a predominance of acrylic functionality in the UV

Table 2

Photo-DSC data from formulations containing different concentrations of resin and HDDA at 3% photoinitiator concentration

% HDDA	$\Delta H, \text{J g}^{-1}$	Induction time, s	Peak maximum, s
30	151	3.8	7.8
40	199	3.7	7.7
50	256	3.7	7.4
60	309	3.5	7.2
70	351	3.4	7.1

curing mechanism over the polyester unsaturated functionality.

### 3.2. Principal properties of UV cured and UV/thermal dual-cured films

Figs. 1 and 2 show the behavior of the König hardness properties from UV cured samples and dual-cured samples, respectively.

In Fig. 1, a small hardness increase with the increase of photoinitiator concentration for both samples with 50% and 70% resin can be observed, even though these values are quite similar. On the other hand, the hardness increases considerably when resin concentration in the varnish is reduced

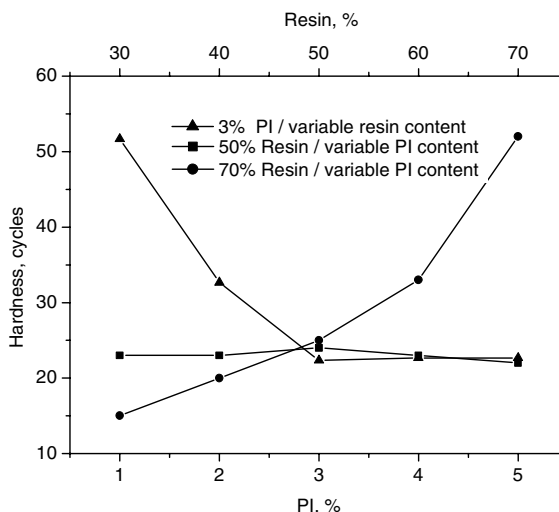


Fig. 1. Hardness values of UV cured films as a function of varnish composition.

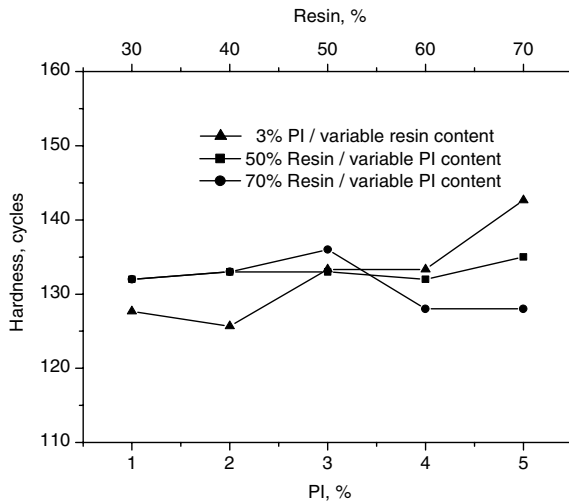


Fig. 2. Hardness values for UV cured films followed by thermal cure at 240 °C for 2 h, as a function of varnish composition.

to 40% or 30%, which correspond to the major concentration of acrylic monomer in the samples.

Fig. 2 shows that for samples submitted to UV/thermal dual-cure the hardness values increase and remain constant, and it independent of the varnish composition in the studied concentration range. The hardness values of the dual-cured samples are similar to those obtained for enameled magnet wire class “H”, which are thermally cured. In general, wire enamels presents better properties than electrical insulating varnishes.

Fig. 3 presents the dielectric properties of varnish with 70% resin, submitted to UV curing pro-

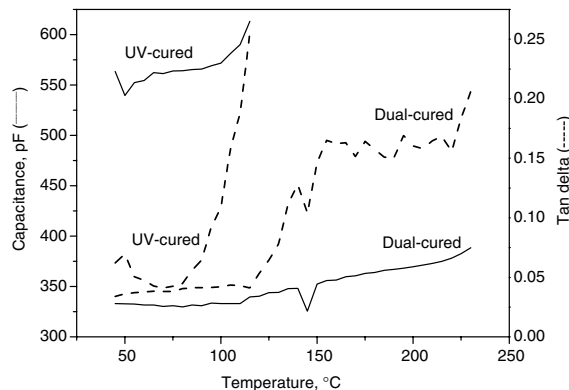


Fig. 3. Dielectric properties of UV cured and dual-cured 70% resin varnish samples.

cess and UV/thermal dual-cure as described above.  $\tan \delta$  is a revealing measurement and can be interpreted as follow. The UV-cured samples start losing their dielectric properties or their insulation capacity at about 90 °C. This behaviour can be attributed to the increase in the mobility of the dipoles present in the material activated by the temperature and induced by electromagnetic variant field, reaching the established measurement limits. In that condition, there is no physical restriction to the vibration of the dipoles. These effects cause the accelerated aging of the polymer and its rupture in a short time. On the other hand, the dielectric properties of the dual-cured (UV-thermal) samples remain inside the measurement limits. In the range of 115 °C and 165 °C, an increase in the dielectric loss factor can be observed, in the correspondent curve, as a function of the temperature. This indicates that part of polymeric chain begins to vibrate according to the increasing temperature profile, but these vibration modes were constrained leading to a constant dielectric loss factor at higher value. At 225 °C, there is another increase in loss factor but the equipment was programmed to stop the test at 230 °C. The observed behavior for the dual-cured samples is compatible with wire enamels class “H” based in organic solvent and thermally cured.

Thermogravimetry was performed to clarify the difference in the dielectric property behavior

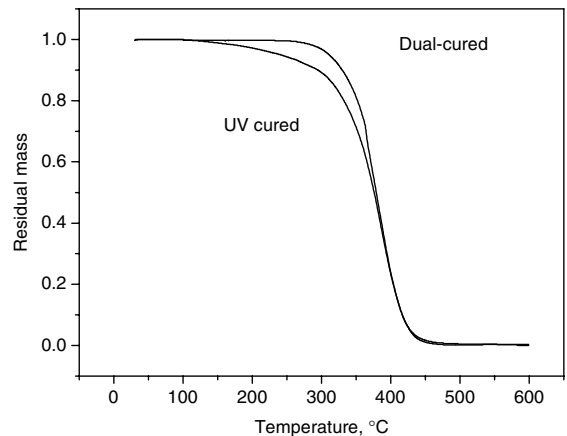


Fig. 4. TG curves from samples with 70% of resin after UV cure and UV-thermal dual-cure.

between UV-cured and UV-thermal dual-cured samples. Fig. 4 presents the TG curves for samples with 70% of resin, both UV-cured and dual-cured. It was observed that the dual-cured samples are thermally stable up to 250 °C. Meanwhile, the UV cured varnishes undergo through a weight loss starting at about 110 °C. This weight loss can be associated to the volatilization of the photoinitiator and the some residual molecules of monomer, trapped in the cross-linked network during the irradiation process. In addition, some products of low molecular weight from polycondensation reactions might be volatilized.

#### 4. Conclusion

The results show that the developed resin can be used in electrical insulating varnish formulations. The analyzed properties of UV-cured samples are in the same range as those from air-drying varnishes without any remarkable improvement. To improve them, a dual mechanism accomplishing UV and thermal curing is required. A good compromise between better properties and low costs was achieved with a formulation containing 70% of resin, because the polyester is cheaper than acrylated monomers used as a reactive diluent. With this alternative, the side effects of conventional technology in electrical insulating varnishes are surpassed.

Both UV-cured and dual-cured samples were evaluated. The results have shown that the UV-cured coating presents characteristics of electrical insulating varnishes. On the other hand, the hybrid

cure applied promoted the improvement of some ultimate properties and the cured products present similar characteristics as magnet wire enamels.

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