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## Progress in Organic Coatings

journal homepage: [www.elsevier.com/locate/porgcoat](http://www.elsevier.com/locate/porgcoat)



# Structure-scratch properties relationships of acrylate photo-polymerizable protective coatings for thermoplastic substrates

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### ARTICLE INFO

*Article history:*  
Available online xxx

*Keywords:*  
Photo-polymerization  
Micro-scratch  
Bio-based monomers  
Nanoparticles  
Acrylates  
Polymer network

### ABSTRACT

The relationships between the composition and the scratch resistance of clear photo-polymerized protective coatings for thermoplastic substrates were studied in relation with their thermomechanical properties. For this purpose, dynamic mechanical analyses of free-standing films were compared to micro-scratch tests of thick or thin coatings deposited on polycarbonate. In these experiments, the depth indented by the tip, the elastic recovery of the material, the residual depth of the scratch, and the load at which the first crack appears, were analyzed. Different coatings close in formulation were studied. First, the proportion of a specific difunctional monomer featuring a hard structure was varied in order to change the crosslinking density of the polymer network. The thermomechanical properties were consequently modified at high temperature, but remained similar at 23 °C, whereas at this temperature, the scratch properties of the coating evolved with its composition. The addition of 5 wt% alumina or silica nanoparticles did not modify the thermomechanical properties or the scratch resistance of the coatings, even if a more concentrated filler layer was observed near the surface of the coating. Nevertheless, the consequent incorporation of a new diacrylate monomer in the polymer matrix delayed the ductile-brittle transition. Finally the substitution of petro-based monomers by slightly different bio-based compounds led to a change of the scratch behavior of the thickest coatings (150 μm-thick), and increased the critical load for the thinnest coatings (15 μm-thick). It comes out that micro-scratch tests allow a finer comparison of the samples.

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## 1. Introduction

In a view to save weight and thus to lower polluting emissions, many automotive pieces are made of plastic. Headlights made of polycarbonate are a good example. An important drawback of this thermoplastic is however its low resistance to damage. And yet everyone knows that during its life, an automotive headlight is strongly subjected to scratches, impacts, abrasion. . . That is why the use of a protective coating is required. To go further into a sustainable development approach, such coatings can be photo-cured [1–9]. Indeed, photo-polymerization is an environmentally-friendly technique, since it allows to work with mixtures containing no solvents, curing them at a very high rate, and it is an energetically economic process.

In the literature, many authors assess the efficiency of their coatings by hardness measurements [7–11], abrasion [1–3,7,10],

indentation [8,9] or scratch tests [6,10–14], amongst other experiments evaluating the damage resistance [8,9,11]. However, all these techniques are closely related. For instance, numerous hardness measurements exist, which are all based upon the scratching or the indentation of the sample [15]. But Caro et al. [12] demonstrated that hardness is not directly linked to the abrasion resistance of ophthalmic coatings on organic lenses as evaluated by usual standardized tests. On the other hand these authors managed to correlate the results of microscratch testing, provided that they were carried out under well-defined conditions, to the abrasion resistance of their coatings. More precisely, scratch hardness and residual depth proved to be especially relevant parameters to foresee the behavior of any ophthalmic coating submitted to abrasion.

The important characteristics which allow to evaluate the efficiency of a coating are indeed its resistance to indentation and its ability to recover its initial shape (elastic recovery). The load at which the first crack appears during the scratch is also a relevant parameter to assess the scratch resistance, since cracks constitute severe damaging that can worsen during the service life of the

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coating. It is easy to understand that a simple mechanical analysis cannot provide enough information to evaluate the damage resistance of coatings. On the contrary, micro- or nano-scratch experiments, often used in the literature to assess the scratch resistance of coatings [6,11–14], allow to evaluate all these characteristics when performed on well-defined samples, and thus provide a more comprehensive information about the resistance to damage. Thus, these tests are attractive to evaluate and compare protective coatings. Nano-scratch tests were used for example by Noh et al. [11] in order to determine the best curing sequence of UV-thermal dual-cure coatings; whereas Bautista et al. [13] used these tests to compare different nanocomposite coatings containing alumina or silica nano-fillers dispersed in various polymer matrices. These micro- or nano-scratch tests consist in applying a constant or increasing load on an indenter in contact with the surface of the sample while the latter moves. The indented depth is monitored in real time, whereas a pre-scan and post-scan allow to determine the initial relief and residual depth and to calculate the elastic recovery. An observation of the scratch, with an optical microscope for instance, allows to determine the critical load at which the first crack appears; this load is expected to be as high as possible. What is more, from an applicative point of view, the less visible the scratch is, the better. Of course, the scratch resistance of a material is related to its mechanical properties such as its modulus or its tensile behavior [16,17]. Nevertheless, because of the viscoelastic behavior of polymer materials, the scratch resistance also depends on the temperature, on the strain rate, and on the time elapsed between the test and the observation of the result. Even though these last two technical points can be controlled using the same protocol for each sample, the variation with temperature depends on the tested materials. Indeed, a material does not behave in the same way when it is in the glassy or in the rubbery state.

UV-curable coatings are mainly composed of multifunctional compounds, whose polymerization leads to the formation of a polymer network. The chemical structure between the crosslinks and their density play an important part in the properties of the resulting material. In particular, a lower crosslinking density is often associated with a lower elastic modulus at the rubbery plateau. Nevertheless, the damage resistance of UV-curable, 100% solids organic coatings is often not sufficient and many studies in the literature report the incorporation of nanoparticles in the systems. Nano-silica and nano-alumina are commonly used to improve the scratch or abrasion resistance of coatings [1,3–5,7–9,18], since they are high hardness materials (respectively, 7 and 9 on the Mohs' scale).

From an environmental point of view, the use of petro-based acrylate monomers is not representative of a sustainable chemistry, because of the depletion of fossil resources. Some authors published works concerning the use of bio-based acrylate compounds in UV-curable coatings. Nevertheless, these compounds were mainly obtained from triglycerides [19–23] and thus feature long fatty chains. This characteristic does not seem to be compatible with a protective efficiency. Nevertheless, there exist some commercially available bio-based acrylate compounds which are small molecules similar to their petro-based counterparts. Their evaluation as monomers for protective coatings could be of great interest.

The aim of this work was to study the influence of different raw materials on the scratch resistance of 100% solids polyacrylate photo-polymerizable coatings designed for thermoplastic substrates and more specifically polycarbonate. The formulation was varied in order to study its influence on the scratch resistance of the material, in relation with its thermomechanical properties.

First, the influence of a multicyclic monomer was studied, varying its percentage in the polymer matrix of the coating. Then, alumina and silica nanoparticles were incorporated in the coatings, to observe the efficiency of these fillers. Finally, in order to go further into a sustainable development approach, some petro-based

**Table 1**  
Composition of the coatings with varied percentages of TCDDA (wt%).

	U6A	MPDDA	TCDDA	Irgacure 184	Lucirin TPO-L
A1	37.4	58.8	0.0	1.5	2.3
A2	26.0	40.8	29.4	1.5	2.3
A3	23.2	36.5	36.5	1.5	2.3
A4	20.5	32.1	43.6	1.5	2.3
A5	17.6	27.7	50.9	1.5	2.3
A6	13.9	21.8	60.5	1.5	2.3
A7	0.0	0.0	96.2	1.5	2.3

monomers were substituted by commercially available bio-based equivalents and the consequences on the scratch behavior of the coatings were examined.

## 2. Materials and methods

### 2.1. Materials

U6A (proprietary hexafunctional aliphatic urethane acrylate, CN9010EU), MPDDA (3-methyl-1,5-pentanediol diacrylate, SR341), TPGDA (tripropylene glycol diacrylate, SR306) and TCDDA (tricyclodecane dimethanol diacrylate, SR833S) are petro-based oligomer and monomers provided by Arkema. DiPEPHA (mix of dipentaerythritol pentaacrylate and dipentaerythritol hexaacrylate, 15%BBC), PETA (pentaerythritol tetraacrylate, 10% BBC) and DDA (1,10-decanediol diacrylate, 60%BBC), are commercial partially bio-based acrylate oligomers and monomers also provided by Arkema. The structure of these compounds is detailed in Fig. 1. The percentage of bio-based carbon (%BBC) is calculated by the following equation:

$$\%BBC = \left( \frac{C_{\text{bio-based}}}{C_{\text{bio-based}} + C_{\text{petro-based}}} \right) \times 100 \quad (1)$$

The used nanofillers were Nanocryl<sup>®</sup> C145 (silica nanoparticles dispersed in TPGDA) provided by Evonik Industries, and NanoArc<sup>®</sup> AL-2260 (alumina nanoparticles dispersed in TPGDA) provided by Nanophase, respectively. According to the suppliers' data both types of nanoparticles, 20 nm in diameter, are surface modified.

Irgacure 184 (1-hydroxycyclohexyl phenyl ketone) and Lucirin TPO-L (ethyl-2,4,6-trimethylbenzoylphenylphosphinate) were used as photo-initiators; both were provided by BASF.

3,4,5-Trichloropyridine (purity 99%) was purchased from Aldrich. DMSO-*d*<sub>6</sub> (deuterated dimethylsulfoxide) and tetramethylsilane (TMS) were purchased from Euriso-Top.

### 2.2. Methods

#### 2.2.1. Preparation of the coatings

The mixtures (compositions specified in Tables 1–3), were prepared with the help of a Rayneri mixer. The used nano-filled additives consist of nanoparticles dispersed in TPGDA. Thus, the addition of nanofillers to the formulations also implies the incorporation of this new monomer into the polymer matrix. Therefore in order to rigorously study the influence of nanoparticles on the scratch resistance of the coatings, nano-filled coatings were compared to unfilled reference coatings having the same polymer matrix.

Amounts of 15 μm- and 150 μm-thick coatings on polycarbonate panels (PC; Makrolon AL 2447) were prepared for micro-scratch experiments, with a motorized film applicator Elcometer K4340 equipped with a spiral bar coater. They were polymerized through three passes under a Fusion F300S UV-lamp equipped with a conveyor belt. The mean total UV doses and irradiance peaks,

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