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

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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.

Keywords: photo-polymerization, micro-scratch, bio-based monomers, nanoparticles, acrylates, polymer network

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, photopolymerization 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 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 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 following Eq. (1):

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

The used nanofillers were Nanocryl ® C145 (silica nanoparticles dispersed in TPGDA) provided by Evonik Industries, and NanoArc ® 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*₆ (deuterated dimethylsulfoxide) and tetramethylsilane (TMS) were purchased from Euriso-Top.

Figure 1. Structure of the monomers and oligomers: TCDDA (a), MPDDA (b), TPGDA (c), DDA (d), DiPEPHA (e), PETA (f)

2.2. Methods

2.2.1. Preparation of the coatings

The mixtures (compositions specified in Tables 1 to 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.

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, measured with a Power Puck II (EIT), were respectively the following: UVA

(320-290 nm): 3837 mJ.cm⁻², 1747 mW.cm⁻²; UVB (280-320 nm): 3997 mJ.cm⁻², 1822 mW.cm⁻²; UVC (250-260 nm): 683 mJ.cm⁻², 321 mW.cm⁻². 150 µm-thick films on glass panels were also prepared under the same conditions, in order to peel them off to get free standing films that could be analyzed through mechanical experiments.

	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

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

	U6A	MPDDA	TCDDA	Nanocryl ® C145	NanoArc ® AL-2260	TPGDA	Irgacure 184	Lucirin TPO-L
C1	20.7	32.5	32.5	10.4		-	1.5	2.3
C1ref	21.8	34.2	34.2	-	-	5.9	1.5	2.3
C2	19.3	30.3	30.3		16.3	-	1.5	2.3
C2ref	20.3	31.9	31.9	-	-	12.1	1.5	2.3

Table 2: Composition of the coatings containing nanoparticles (named Cx) and their respective references (named Cxref) (wt%)

	DiPEPHA	PETA	DDA	TCDDA	Irgacure 184	Lucirin TPO-L
B1	23.2	-	36.5	36.5	1.5	2.3
B2	-	23.2	36.5	36.5	1.5	2.3

Table 3: Composition of the coatings containing bio-based materials (wt%)

2.2.2. Determination of the acrylate double bond density of the mixtures

As the used monomers might contain some impurities and as the chemical composition of oligomer U6A was not precisely known, it was first necessary to determine the acrylate double bond density (d_{ac}) for each monomer and oligomer. This was achieved by ^1H NMR, using 3,4,5-trichloropyridine as an internal standard [24]. In a NMR tube were placed a weighed mass of standard (m_s) of known molar mass (M_s) and purity (p), and a weighed mass of acrylate compound (m_{ac}). The spectra were acquired at 300K in DMSO- d_6 (+TMS), with a Bruker Avance III 400 US+ (400 Hz), 8 scans, a relaxation delay of 90 s and a sampling of $128 \cdot 10^3$ points. The integration of the signals related to the acrylate protons and to the protons of the standard (respectively I_{ac} and I_s) allowed to calculate d_{ac} (Eq. (3)):

$$d_{ac} = \frac{(2 \cdot I_{ac} \cdot m_s \cdot p)}{(3 \cdot I_s \cdot M_s \cdot m_{ac})}$$

Then, the acrylate double bond density of each mixture was calculated using d_{ac} and taking into account the weight percentage for each of its components.

2.2.3. Determination of the acrylate double bond conversion by Fourier Transform Infra-Red spectroscopy (FTIR)

The acrylate double bond conversion of the cured samples was determined by FTIR [8,11], using an Attenuated Total Reflectance (ATR) device equipped with a diamond crystal. For this purpose, the area of the acrylate band at 810 cm^{-1} was preferentially used. To avoid any bias related to an incorrect contact between the sample and the crystal, this area was normalized using the carbonyl band at 1720 cm^{-1} (constant throughout polymerization) as a reference. The comparison of the ratio of these areas for both the cured and uncured samples allowed to calculate the conversion degree after polymerization (Eq. 2). In order not to damage the device with a possible polymerization during the analysis, the uncured mixture was used without photo-initiator, after checking that this slight change did not have any influence on the results.

$$Conversion (\%) = 100 \times \left(1 - \frac{\left(\frac{A_{810 \text{ cm}^{-1}}}{A_{1720 \text{ cm}^{-1}}} \right)_{cured}}{\left(\frac{A_{810 \text{ cm}^{-1}}}{A_{1720 \text{ cm}^{-1}}} \right)_{uncured}} \right) \quad (2)$$

The analyses were carried out with a Nicolet™ iS10 spectrometer (ThermoScientific), equipped with a Smart iTR ATR unit. The spectra were acquired after 32 scans with a resolution of 4 cm⁻¹. If the conversion could be determined for each side of the free standing films, it could obviously only be determined on the side in contact with air during the polymerization of films deposited on PC.

2.2.4. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were carried out with a TRITON apparatus, in tension mode, using the following experimental conditions: temperature ramp: 3°C/min from -90°C to 300°C, frequency: 1 Hz, deformation: 0.1%, spacing between clamps: 2.5 mm. 150 µm-thick free standing films were analyzed, and at least three consistent analyses were carried out for each sample.

In all the graphics presented in this paper, tanδ curves have been vertically shifted in order to make the comparison easier; the absolute values should therefore not be taken into account.

2.2.5. Micro-scratch tests

Micro-scratch tests were carried out at 23°C and 50% relative humidity, with a CSM Micro-Scratch Tester equipped with a diamond Rockwell indenter featuring a 120° angle and a 100 µm-radius sphere. First, a pre-scan with a constant load of 0.03 N allowed to determine the initial topography on the path of the indenter before scratching the sample. Then, the 4 mm-long scratch was implemented at a speed of 8 mm.min⁻¹, applying on the indenter a progressive increasing load from 0.03 N to 10 N; the rate of the load increase was constant. During the scratch test, the indented depth (P_d) was followed in real-time. Finally, a post-scan was run in the same conditions as the pre-scan, which allowed to measure the residual depth (R_d) of the scratch. The elastic recovery (R_e) that expresses the ability of the material to recover its initial shape could be calculated following Eq. 3.

$$R_e = \left(\frac{(P_d - R_d)}{P_d} \right) \cdot 100 \quad (3)$$

After the test, the observation of the scratch with an optical microscope allowed to determine the critical load (L_c), i.e. the load at which the first crack appears. At least 5 micro-scratch tests were carried out for each sample. As the results (P_d , R_d , R_e and L_c) could not be statistically studied for each load between 0.03 and 10 N, we chose to focus on particular

normal loads: for 15 μm -thick coatings: 0.3 N and 1.5 N; for 150 μm -thick coatings: 1.5 N, 3.5 N and 9 N. The errors are given for a probability of 95%.

2.2.6. Transmission electron microscopy (TEM)

Transmission electron microscopy observations were carried out at the “Centre Technologique des Microstructures de l’Université Claude Bernard Lyon1” on a Philips CM120 microscope operating at 80 kV. The samples were cut up in their thickness into thin slices (50-60 nm) by ultra-microtomy performed at room temperature.

3. Results and Discussion

The photo-polymerization of the liquid mixtures (compositions given in Tables 1 to 3) led to clear, tack-free coatings. In every case, the mean acrylate conversion was about 95%, i.e. a rather high value. Considering the structure of the monomers and oligomers, it can be inferred that all the polymer networks have a high crosslinking density. Note that the real acrylate conversion of the coatings containing nano-silica could not be precisely determined because of a partial overlapping of the acrylate band at 810 cm^{-1} and the SiO_2 band at 820 cm^{-1} . Nevertheless, taking into account the high value of the received UV dose, this sample was considered to have a conversion degree similar to the others.

As can be noticed Fig. 2, which illustrates in particular the case of the coating A3, the damage of polycarbonate is higher without coating, since the indented and residual depths are more important than for the coated PC. Nevertheless, the latter features cracks contrary to the uncoated substrate. This evidences the fact that if a coating is indeed necessary, there are also drawbacks.

Figure 2: Evolution of the indented and residual depths for the uncoated PC and for the PC coated with A3; observation of the scratches with an optical microscope

3.1. Influence of the amount of a multicyclic monomer

The amount of monomer TCDDA was varied while maintaining the weight ratio between U6A and MPDDA constant; this percentage was increased from A1 to A7 respectively from 0 mol% to 100 mol%. The composition of all the studied coatings is summarized in Table 1. Considering the polymer network, the increase in the TCDDA proportion gets along with a decrease in the proportion of oligomer U6A and in the overall density of acrylate double bonds in the mixture, determined by NMR (Fig. 3). But since all the components are multifunctional, a higher density of acrylate double bonds increases the crosslinking density; the presence of increasing amounts of the oligomer as well, because of its high functionality. Since all the studied materials feature a similar conversion degree (95%), it comes out that the increase in the TCDDA proportion causes a decrease in the crosslinking density.

Figure 3: Evolution of the density of acrylate double bonds in the uncured coatings with the TCDDA weight proportion in the formulation

From a thermomechanical point of view, all the samples feature a high elastic modulus E' , higher than 10^8 Pa at the rubbery plateau (see Fig. 4). More precisely, sample A1 (the most highly crosslinked) indeed displays the highest value ($E' \approx 6.9 \cdot 10^8$ Pa at 280°C) while sample A7 (the less densely crosslinked) shows the lowest value ($E' \approx 2.8 \cdot 10^8$ Pa at 280°C). Ranking the intermediate samples according to their rubbery moduli is less easy, because the sensitivity of the used rheometer was apparently not sufficient to perfectly highlight such phenomenon; however, for this set of experiments the observed values are almost in the expected order: at 280°C , for A2 and A4: $E' \approx 5.4 \cdot 10^8$ Pa; for A3 and A5, $E' \approx 4.8 \cdot 10^8$ Pa; and for A6, $E' \approx 4.4 \cdot 10^8$ Pa.

Figure 5 shows that the maximum of the mechanical relaxation regularly shifts toward higher temperatures as the TCDDA percentage increases, due to the multicyclic structure of this monomer. The observed values go from 143°C (A1) to 218°C (A7), in agreement with the values found by Ye et al. for a TCDDA sample cured isothermally at 100°C (189°C for 85% conversion, at least 205°C estimated for 100 % conversion) [25]. Indeed, in order for such a rigid structure to move, it is necessary to provide it with a high amount of energy. Thus, the higher its proportion, the higher the temperature at which the mechanical relaxation occurs. However, it can be noticed that all the samples, even that without TCDDA (A1), are in the glassy state and have a rather similar elastic modulus at 23°C , temperature at which the micro-scratch experiments were carried out.

Figure 4. Evolution of the elastic modulus E' during dynamic thermomechanical analysis at 1 Hz, for materials containing increasing amounts of TCDDA

Figure 5. Evolution of $\tan\delta$ during dynamic thermomechanical analysis at 1 Hz, for materials containing increasing amounts of TCDDA

The results of the micro-scratch experiments are summarized in Figure 6. The percentage of TCDDA does not influence the initially indented depth. In contrast, the elastic recovery decreases as this percentage of TCDDA increases. Consequently, the residual depth increases along with the latter. Finally an increase in the critical load with the proportion of TCDDA is also observed. Following the literature [12,16], this critical load is related to the ductile-brittle transition of the material. Indeed, Jardret et al. [16] suggested the following mechanism for the formation of the partial cone cracks such as those observed in this work (see Fig. 2): as the scratch is performed, tensile stresses are created at the rear of the indenter. These stresses increase until they reach the ultimate tensile strength; then a crack is formed. The tensile stresses are partially released but as the indenter keeps on ploughing the sample, they increase again, until reaching the ultimate tensile strength once more. A new crack is formed, etc... Consequently, the results of the micro-scratch tests suggest that the ductile-brittle transition is delayed when increasing the amount of diacrylate monomer TCDDA in the polymer matrix.

At the same time, the evolutions of the elastic recovery and of the critical load are opposite. Yet both characteristics are equally important concerning the protective efficiency of the coatings, since a high elastic recovery decreases the visibility of the scratch, while the cracks are expected to appear at the highest possible load. Thus, a compromise must be found, and A3 could be suggested as a suitable coating.

The evolution of the elastic recovery, the residual depth and the critical load with the variation of the percentage of TCDDA is particularly remarkable for the extreme coatings A1 and A7 containing respectively 0 and 100 mol% of this monomer in their acrylate mixture. The evolution of these parameters between A2 and A6 is slightly less noticeable, but is nevertheless emphasized as the normal load increases. As stated before, as the TCDDA proportion increases, the network becomes less densely crosslinked. Moreover at the temperature at which the experiments were carried out, all the materials were in the same thermomechanical state. Thus, two points are underlined: first, the evolution of the scratch resistance with the percentage of TCDDA should be related to the evolution of the crosslinking density, but an influence of the specific rigid structure of this monomer must not be excluded. Secondly, the micro-scratch experiments allow a better differentiation of the samples comparing to DMTA.

Figure 6: Micro-scratch tests carried out on 15 μm -thick coatings containing varying amounts of TCDDA, deposited on PC: indented depth (a), residual depth (b), elastic recovery (c), critical load (d)

3.2. Influence of nanoparticles

As the introduction of the fillers gets along with the introduction of a new monomer in the mixture, in order to rigorously study the effect of the nanoparticles, the filled coatings must be compared to references having the same polymer matrix. Thus, C1 will be compared to C1ref and C2 will be compared to C2ref (see Table 2). Here the studied coatings contained 5wt% nano-alumina or nano-silica (respectively C1 and C2); this percentage is given considering the mixture without photo-initiators. C1 and C1ref contain 12.6 wt% TPGDA in their polymer matrix, whereas C2 and C2ref contain 6.1 wt% TPGDA. The respective mass ratio between the other acrylate compounds (U6A, TCDA and MPDDA) is the same as in A3. The filled coatings were compared with their respective reference, but also these references with A3, in order to observe the effect of the addition of TPGDA to the polymer matrix.

Before studying the properties of the coatings, the nanoparticles were first observed by TEM. The nano-alumina particles are more or less agglomerated, and have a broad size distribution, with diameters from 10 nm to 100 nm. The nano-silica particles are rather agglomerated and have a mean particle size of 25 nm. It appears in Figure 7 that both types of nanoparticles display a special organization within the thickness of the polymer matrix, which can be divided into four main zones: i) an enrichment in particles in a thin layer (1-2

μm) close to the surface (air side) of the coating, ii) a depletion zone; iii) in the middle of the film, a thicker layer where the concentration of the nanoparticles is medium; and iv) a layer in contact with the PC substrate, without any particle.

It can be assumed that during the processing of the coating, the nanoparticles migrate because of surface energy differences. The particle enrichment at the surface could also be related to the inhibition due to O_2 . Indeed, this phenomenon can cause the existence of a conversion gradient within the thickness, with a lower polymerization kinetics at the surface of the coating [26,27]. In this layer, the viscosity increases more slowly than in the bulk and the nanoparticles could have consequently more time to migrate toward the surface. The existence of the depletion zones is more intricate to explain, since many factors can act in addition to the oxygen inhibition; for instance, differences in polymerization kinetics within the thickness of the sample. Note that despite these observations, and consistently with the rather low amounts of incorporated nanoparticles, the coatings are perfectly clear.

Figure 7: Distribution of the nanoparticles throughout the thickness of the photopolymerized polymer matrix: nano-alumina (a), nano-silica (b)

No change related to the presence of TPGDA in the polymer matrix can be noticed on the mechanical relaxation or on the elastic modulus (coatings C1ref and C2ref, Fig. 8). The small amount of flexible oxypropylene units incorporated in the polymer network through the addition of TPGDA is not sufficient to noticeably change the thermomechanical properties of the material.

As seen in Figure 8, the incorporation of 5wt% nano-silica or nano-alumina in the coatings does not modify the mechanical relaxation or the elastic modulus of the materials. The relaxation remains broad whereas E' is always higher than 10^8 Pa at the rubbery plateau. The presence of nanoparticles could have been expected to increase the elastic modulus. Nevertheless, the unfilled materials already have a high modulus, thus maybe the small amount of particles cannot increase it anymore. In addition, these particles must have an influence on the relaxation times of the polymer chains, since they modify their environment. As there is no noticeable change in the mechanical relaxation after the incorporation of nanoparticles, it is likely that some relaxation times are modified but still remain in the existing range.

Thus, DMTA does not allow to distinguish differences between the mechanical properties of the different studied materials, filled or unfilled, containing TPGDA or not.

Figure 8: Evolution of $\tan\delta$ and of the elastic modulus during dynamic thermomechanical analysis at 1 Hz, for nano-filled materials and their references

Therefore the scratch resistance of 15 μm -thick coatings deposited on PC was then studied. As shown in Figure 9a to c, the indented depth does not change because of the addition of TPGDA in the polymer matrix, or because of the addition of nanoparticles. Having a closer look at the indented depth at the very surface of the samples (Fig. 10), no difference can be noticed between the unfilled and the filled coatings, despite the enrichment in nanoparticles in this particular zone for the filled samples.

Taking into account the statistical error, there is also no remarkable evolution of the elastic recovery or of the residual depth. The changes in the polymer network induced by the incorporation of TPGDA only have an influence on the critical load. Indeed, as can be seen in Figure 9d, all the coatings containing TPGDA feature a higher critical load (>2.5 N) than the

coating A3 (<2.5 N). In the same way as for previous results (3.1.), this suggests that the presence of TPGDA delays the ductile-brittle transition. The incorporation of TPGDA in the polymer matrix is thus beneficial, since the later the first crack appears in terms of load, the better. Comparing these results with those concerning the variation of the TCDDA proportion (3.1.), it seems that increasing the weight percentage of diacrylate monomers (whatever their structure, soft or hard) in the polymer matrix leads to an increase in the critical load. This may be related to the decrease in the crosslinking density, which delays the ductile-brittle transition.

The only noticeable effect of nanoparticles is the increase in the critical load for a filler content of 5% nano-alumina. Following the explanations from Caro et al. [12], this may be related to a better adhesion between the nanoparticles and the matrix, and/or to a lower stress concentration around the fillers. Excepting this point, nanoparticles do not enhance the scratch properties of the coating; this could be due to the already good performances of the unfilled coatings.

As a more global conclusion, it can be put forward that the micro-scratch experiments bring additional information in comparison with DMTA, since coatings containing TPGDA feature a better scratch resistance in terms of critical load.

Figure 9: Results of the micro-scratch tests run on the nano-filled 15 μm -thick coatings and their references, deposited on PC: indented depth (a), residual depth (b), elastic recovery (c), critical load (d)

Figure 10: Evolution of the indented depth close to the surface of the nano-filled coatings and of their unfilled references

3.3. Substitution of petro-based monomers by bio-based counterparts

Two bio-based coatings were developed, substituting in the petro-based coating A3 the monomer MPDDA by DDA, and the oligomer U6A by either DiPEPHA or PETA (respectively B1 and B2) (compositions given in Table 3). As seen in Figure 11, both bio-based coatings have the same thermomechanical properties. Their mechanical relaxation has a maximum at lower temperature than A3; this is attributed to the presence of DDA, featuring a long alkyl chain. The latter is supposed to favor long relaxation times and thus, according to the time-temperature equivalence, could shift the mechanical relaxation toward lower temperatures. B1 and B2, but also A3, also feature a similar elastic modulus.

An overall observation is that at the temperature of the micro-scratch experiments (23°C), all these 3 samples are in the same thermomechanical state and have a similar elastic modulus.

Figure 11: Evolution of $\tan\delta$ and of the elastic modulus E' during dynamic thermomechanical analysis at 1 Hz, for materials containing bio-based monomers (B1 and B2) or the corresponding petro-based monomers (A3)

The intrinsic scratch resistance of the materials was first considered, studying 150 μm -thick coatings deposited on PC. As the layer thickness is important, the effect of the substrate could be neglected. What is more, even if the indented depth was higher than the tenth of the total thickness at high load [6], no change was noticed in the scratch behavior of the samples. For these thick samples, no crack was generated along the scratch.

Both bio-based coatings (B1 and B2) feature a similar scratch resistance (see Fig. 12). Their oligomers (respectively DiPEPHA and PETA) both have a structure based upon pentaerythritol (see Fig.1); thus, the structure of the polymer networks in the coatings B1 and B2 is supposed to be rather similar. This could explain that the change of oligomer has no effect on the intrinsic scratch resistance of the studied bio-based materials.

Comparing B1, B2 and A3, it appears that the indented depth as well as the elastic recovery are higher for the bio-based coatings (see Fig. 12 a and c); as a result, the residual depth is lower (see Fig. 12 b). The coatings B1 and B2 thus feature a better intrinsic scratch resistance than the petro-based coating A3. From these results, it can be inferred that the indentation depth is not directly related to the elastic modulus of the materials. Indeed, even if A3, B1 and B2 feature a similar elastic modulus at the temperature of the micro-scratch tests, the indented depth is not similar for these three samples.

Figure 12: Results of the micro-scratch tests for the bio-based (B1 and B2) and the petro-based (A3) 150 μm -thick coatings deposited on PC: indented depth (a), residual depth (b), elastic recovery (c)

The case of 15 μm -thick coatings was finally addressed. In Figure 13 a, a similar indented depth is observed for B1 and B2. The latter has a slightly higher elastic recovery (Fig. 13 c), and its residual depth (Fig. 13 b) is also a very little lower. Comparing these bio-based coatings with A3, no great difference can be noticed in the scratch resistance, contrary to what is observed for 150 μm -thick coatings. This evidences the significance of the thickness of the samples on the results of the micro-scratch experiments. However, it appears in Figure 13 d that the critical loads are higher for the bio-based coatings (>2.5 N) than for the petro-based A3 (<2.5 N). This is clearly noticeable in Figure 14. This suggests that the ductile-brittle transition in the bio-based materials is delayed comparing to the petro-based matrix. Thus, the bio-based coatings feature a better scratch resistance than the petro-based reference.

The micro-scratch experiments allow a finer differentiation of the samples comparing to the DMTA analysis.

Figure 13: Results of the micro-scratch tests for the bio-based (B1 and B2) and the petro-based (A3) 15 μm -thick coatings deposited on PC: indented depth (a), residual depth (b), elastic recovery (c), critical load (d)

Figure 14: Observation with an optical microscope of the scratches on 15 μm -thick petro-based (A3) vs bio-based (B1, B2) coatings

Conclusion

This work studied the influence of different raw materials on the scratch resistance of polyacrylate clear photo-polymerizable coatings, dedicated to the protection of polycarbonate substrates. Dynamic thermomechanical analysis evidenced that all the studied materials displayed similar thermomechanical behaviors at room temperature (23°C). Micro-scratch tests were then carried out at this temperature. They first allowed a better differentiation of samples containing different amounts of a multicyclic diacrylate monomer, TCDDA: although the use of increasing amounts of this monomer increased the maximum temperature of the mechanical relaxation, it also decreased the overall crosslinking density and consequently increased the residual depth while decreasing the elastic recovery. However for the thinnest coatings this was accompanied by an increase in the critical loads, i.e. a rather beneficial effect; therefore a compromise can be found by using a medium proportion of TCDDA as it seems to delay the ductile-brittle transition.

The incorporation of nano-fillers in the coating did not improve its scratch resistance. Nevertheless, a study of the mechanisms which control the organization of the nanoparticles in the polymer matrix could complete this work, since the dispersion of the fillers in the whole sample has an impact on its properties. Finally, thin protective coatings featuring a good scratch resistance were obtained using bio-based monomers, with increased critical loads and a probably delayed ductile-brittle transition which could possibly be ascribed to their slightly different distribution of relaxation times observed by DMTA, and/or to their particular chemical structure. It can be noticed that contrary to the petro-based formulation the used bio-based monomers contain no urethane moiety, and therefore no hydrogen bonds; whether

this could be of significant importance should be considered in future studies. This result is nevertheless promising concerning the development of totally bio-based coatings.

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References:

- [1] F. Bauer, H.-J. Gläsel, U. Decker, H. Ernst, A. Freyer, E. Hartmann, V. Sauerland, R. Mehnert, *Prog. Org. Coat.* 47 (2003) 147–153
- [2] F. Bauer, R. Flyunt, K. Czihal, M. R. Buchmeiser, H. Langguth, R. Mehnert, *Macromol. Mater. Eng.*, 291 (2006) 493-498
- [3] R.H. Cayton, A. Farning, P.G. Murray, D. Nelson, *Coatings Technol.* 8(5) (2011) 34-39
- [4] J.-D. Cho, Y.-B. Kim, H.-T. Ju, J.-W. Hong, *Macromol. Res.* 13 (2005) 362-365
- [5] V. Landry, B. Riedl, P. Blanchet, *Prog. Org. Coat.* 61 (2008) 76–82
- [6] S. Roche, S. Pavan, J.-L. Loubet, P. Barbeau, B. Magny, *Prog. Org. Coat.* 47 (2003) 37-48
- [7] N.G.N. Salleh, M. F. Yhaya, A. Hassan, A.A. Bakar, M. Mokhtar. *Int. J. Polym. Mater.* 58 (2009) 422-451
- [8] H. Zhang, H. Zhang, L. Tang, Z. Zhang, L. Gu, Y. Xu, C. Eger, *Tribol. Int.* 43 (2010) 83-91
- [9] H. Zhang, H. Zhang, L. Tang, L. Zhou, C. Eger, Z. Zhang, *Compos. Sci. Technol.* 71 (2011) 471–479
- [10] Y.Z.K. Lahijania, M. Mohseni, S. Bastani, *Tribol. Int.* 69 (2014) 10-18
- [11] S.M. Noh, J.W. Lee, J.H. Nam, K.H. Byun, J.M. Park, H.W. Jung, *Prog. Org. Coat.* 74 (2012) 257-269
- [12] J. Caro, N. Cuadrado, I. González, D. Casellas, J.M. Prado, A. Vilajoana, P. Artús, S. Peris, A. Carrilero, J.C. Dürsteler, *Surf. Coat. Technol.* 205 (2011) 5040-5052.
- [13] Y. Bautista, J. Gonzales, J. Gilabert, M.J. Ibañez, V. Sanz, *Prog. Org. Coat.* 70 (2011) 178-185
- [14] V. Jardret, B.N. Lucas, W. Oliver, A.C. Ramamurthy, *J. Coat. Tech.* 72 (2000) 79-88
- [15] P. Fink-Jensen, *Pure Appl. Chem.* 10 (1965) 240-292
- [16] V. Jardret, P. Morel. *Prog. Org. Coat.* 48 (2003) 322-331

- [17] J.S.S. Wong, H.-J. Sue, in: ed. Wiley, Properties and Behavior of Polymers Vol. 2. Hoboken, New Jersey, 2011, pp. 1011-1030.
- [18] C. Roscher, European Coatings Journal (2003) (4) 138-142
- [19] Z. Chen, J.F. Wu, S. Fernando, K. Jagodzinski, Prog. Org. Coat. 71 (2011) 98-109
- [20] Y. Huang, L. Pang, H. Wang, R. Zhong, Z. Zheng, J. Yang, Prog. Org. Coat., 76 (2013) 654-661
- [21] K.I. Patel, R.J. Parmar, J.S. Parmar, J. Appl. Pol. Sci. 107 (2008) 71-81
- [22] S. Rengasamy, V. Mannari, Prog. Org. Coat. 76 (2013) 78-85
- [23] B.S. Rao, A. Palanisamy, Prog. Org. Coat. 67 (2010) 6-11
- [24] T. Rundlöf, M. Mathiasson, S. Bekiroglu, B. Hakkarainen, T. Bowden, T. Arvidsson, J. Pharmaceut. Biomed. Anal. 52 (2010) 645-651
- [25] S. Ye, N.B. Cramer, C.N. Bowman, Macromolecules 44 (2011), 490-494
- [26] K. Studer, C. Decker, E. Beck, R. Schwalm, Prog. Org. Coat. 48 (2003) 92-100
- [27] K. Studer, C. Decker, E. Beck, R. Schwalm, Prog. Org. Coat. 48 (2003) 101-111

Figure Captions

Figure 1. Structure of the monomers and oligomers: TCDDA (a), MPDDA (b), TPGDA (c), DDA (d), DiPEPHA (e), PETA (f)

Figure 2. Evolution of the indented and residual depths for the uncoated PC and for the PC coated with A3; observation of the scratches with an optical microscope

Figure 3. Evolution of the density of acrylate double bonds in the uncured coatings with the TCDDA weight proportion in the formulation

Figure 4. Evolution of the elastic modulus E' during dynamic thermomechanical analysis at 1 Hz, for materials containing increasing amounts of TCDDA

Figure 5. Evolution of $\tan\delta$ during dynamic thermomechanical analysis at 1 Hz, for materials containing increasing amounts of TCDDA

Figure 6. Micro-scratch tests carried out on 15 μm -thick coatings containing varying amounts of TCDDA, deposited on PC: indented depth (a), residual depth (b), elastic recovery (c), critical load (d)

Figure 7. Distribution of the nanoparticles throughout the thickness of the photopolymerized polymer matrix: nano-alumina (a), nano-silica (b)

Figure 8. Evolution of $\tan\delta$ and of the elastic modulus during dynamic thermomechanical analysis at 1 Hz, for nano-filled materials and their references

Figure 9. Results of the micro-scratch tests run on the nano-filled 15 μm -thick coatings and their references, deposited on PC: indented depth (a), residual depth (b), elastic recovery (c), critical load (d)

Figure 10. Evolution of the indented depth close to the surface of the nano-filled coatings and of their unfilled references

Figure 11. Evolution of $\tan\delta$ and of the elastic modulus E' during dynamic thermomechanical analysis at 1 Hz, for materials containing bio-based monomers (B1 and B2) or the corresponding petro-based monomers (A3)

Figure 12. Results of the micro-scratch tests for the bio-based (B1 and B2) and the petro-based (A3) 150 μm -thick coatings deposited on PC: indented depth (a), residual depth (b), elastic recovery (c)

Figure 13. Results of the micro-scratch tests for the bio-based (B1 and B2) and the petro-based (A3) 15 μm -thick coatings deposited on PC: indented depth (a), residual depth (b), elastic recovery (c), critical load (d)

Figure 14: Observation with an optical microscope of the scratches on 15 µm-thick petro-based (A3) vs bio-based (B1, B2) coatings

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

Table 2: Composition of the coatings containing nanoparticles (named Cx) and their respective references (named Cxref) (wt%)

	U6A	MPDDA	TCDDA	Nanocryl ® C145	NanoArc ® AL-2260	TPGDA	Irgacure 184	Lucirin TPO-L
C1	20.7	32.5	32.5	10.4		-	1.5	2.3
C1ref	21.8	34.2	34.2	-	-	5.9	1.5	2.3
C2	19.3	30.3	30.3		16.3	-	1.5	2.3
C2ref	20.3	31.9	31.9	-	-	12.1	1.5	2.3

Table 3: Composition of the coatings containing bio-based materials (wt%)

	DiPEPHA	PETA	DDA	TCDDA	Irgacure 184	Lucirin TPO-L
B1	23.2	-	36.5	36.5	1.5	2.3
B2	-	23.2	36.5	36.5	1.5	2.3

Highlights:

- Micro-scratch tests enable a finer differentiation of the coatings than DMTA
- The crosslinking density plays a part in the scratch resistance
- Nanoparticles did not modify the properties of the coating
- Bio-based coatings show a better scratch resistance than petro-based counterparts

Graphical abstract