Progress in Organic Coatings 90 (2016) 178–186

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Hard transparent coatings on thermoplastic polycarbonate

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ARTICLE INFO

Article history:
Received 4 July 2015
Received in revised form
26 September 2015
Accepted 14 October 2015

Keywords:
Polycarbonate
Epoxy
Acrylate
Organo-silane
Coatings

ABSTRACT

Thermoplastic polycarbonates are widely used in several manufacturing domains because of their extraordinary combination of transparency, toughness, ductility and chemical inertness at low and moderate temperature. They are, thus, ideal candidates to substitute float glasses, where lightweight and safety are of utmost relevance. In contrast, polycarbonates feature limited scratch and mar resistance, being characterized by very low surface hardness. This suggests the protection of polycarbonates with hard transparent coatings. However, poor interfacial adhesion between conventional coatings and polycarbonates, reduced cohesive strength of some hard coating materials and, in particular, their limited compliance when deposited on ductile substrates often reduce significantly their performance. In this respect, the present work analyzes the *pros* and *cons* of protecting thermoplastic polycarbonates with specialty coatings, emphasizing the real advantages of applying surface overlying layers and their drawbacks. Different formulations of the coatings were herein studied to optimize their interfacial adhesion with polycarbonates and cohesive strengths. Tribological (scratch, wear and mar) tests were, thus, performed to assess the performance of the coatings. After appropriate designing, specialty coatings might be useful to increase hardness and mar resistance of polycarbonates. Nevertheless, they are still largely ineffective to improve wear resistance of polycarbonates.

1. Introduction

Thermosetting and, especially, thermoplastic polycarbonates are largely involved in the design and manufacturing of components for several industrial domains. Thermoplastic polycarbonates are of particular relevance as they could be formed at low costs and in a multitude of shapes by conventional melt processing as extrusion and injection molding. Being thermoplastic polycarbonates, usually, highly transparent, flexible and tough, they are often used to replace large sized float glasses, where lightweight and operational safety are of utmost importance. In contrast, thermoplastic polycarbonates feature limited hardness and, thus, mar resistance [1–3]. Haziness of polycarbonates by marring is thus the main drawbacks that might arise, especially when thermoplastic polycarbonates come in touch with highly abrading materials (sharp objects, dusts, soils, . . .). Thermoplastic polycarbonates can be improved *in-mold* by modifying their formulations during compounding and pelletizing using as-is or reinforced (with fillers) amides, silicone oils, organic modified siloxanes, grafted polymers or mixture of those provided as additives [4]. Additives can interfere with the chemical composition of polycarbonates, improving sometimes abrasion resistance (often by limiting their surface friction), but often deteriorating the workability and visual appearance of the resulting compounds and increasing the environmental impacts [5,6]. Surface protection of thermoplastic polycarbonates might be also achieved by applying surface overlying coatings. For example, surface protection might be implemented by the application of thin laminates on polycarbonates surface. In this case, marring is often only transferred on the laminates just placed on top of the thermoplastic polymers. Accordingly, laminates should be systematically replaced to restore the original features, especially transparency and visual appearance, of the underlying substrates. This route is, however, of limited interest, being it extremely expensive, unpractical and suitable only to simple shaped substrates. Surface protection might be, thus, obtained by the application and, eventually, drying of surface overlying layers deposited by vacuum process or starting from liquid-driven formulations. In this respect, Chen et al. emphasized how protection of ductile polymers with hard coatings could be complicated by the mismatch in the flexibility of the two materials, especially when submitted to highly concentrated loads [7]. Highly concentrated loads can significantly deform the thermoplastic polymers, forcing the overlying brittle coatings to follow the ductile substrates and causing their early failure. Vacuum deposition by CVD or PVD

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http://dx.doi.org/10.1016/j.porgcoat.2015.10.014

is thus often ineffective as it is able to deposit only thin (<5–10 μm) brittle inorganic coatings, which can be a reliable protection only when minimal deformation of the underlying polycarbonates is involved [8–10]. Wet-based coating formulations are very easily to manage, cheap if compared with vacuum processes and are suitable to be applied on large shares of substrates. Nevertheless, coating of thermoplastic polycarbonates with wet-based formulations keeps on being extremely troublesome, as polycarbonates are extremely ductile and flexible, while the coatings much more brittle. In addition, thermoplastic polycarbonates feature very low surface tension, are, therefore, difficult to wet and interfacial adhesion with topcoats is often a severe issue to face. Starting from liquid-driven formulations, sol–gel route is a widely explored technique to deposit thin protective layers on polycarbonates. Wu et al. emphasized the possibility to improve abrasion resistance of polycarbonates by the application of hybrid organic inorganic materials via the sol–gel route [11]. The resulting coatings showed to be very promising, however their limited toughness due to the massive presence of inorganic moieties was often found to compromise the coatings deformation response in case of large local loads, thus leading to early fragile failure and/or coatings delamination. Liquid-driven organic coatings, eventually reinforced with nano- or micro-fillers, might be an effective alternative to protect thermoplastic polycarbonates, being, usually, more flexible than their hybrid organic inorganic counterparts. Seung et al. showed the efficacy of organic coatings in the protection of automobile paints, showing their suitability to reduce significantly surface damage by marring [13]. Similarly, Noble, first, and Barletta et al., later, showed the potentiality of polyurethanes to protect thermoplastic polymers from abrasion damage [14,15]. However, organic coatings were often found to be rather brittle, too, and their protection against mar or, more in general, abrasion damage less effective than hybrid organic inorganic or fully inorganic counterparts do.

In this respect, the present work tries to combine the advantages of organic coating materials and sol–gel route to define new class of multi-layer coatings suitable for the protection of high performance thermoplastic polycarbonates. The final purpose is, therefore, to achieve a coating system, which can mediate between high hardness, typical of inorganic materials and fillers, and acceptable compliance, typical of organic resins. Accordingly, several formulations of the coating materials were investigated to identify the optimal combinations to get multilayer coatings featuring acceptable interfacial adhesion and cohesive strengths. The coatings were thus manufactured by superimposing an organic layer of high chemical affinity with the underlying polycarbonate, an intermediate bridging layer consisting in a hybrid organic inorganic material synthesized by the sol–gel route and a hard and tough topcoat consisting in an organic matrix/silica nano-composite. Once designed, the most promising coating formulations were applied in the form of liquid-driven materials by spraying on polycarbonate substrates and, subsequently, dried by combined thermal and UV curing. Tribological (scratch, wear and mar) tests on the resulting materials were, thus, performed to assess the performance of the coating-substrate systems. Based on the experimental findings, hard transparent coatings were found to increase significantly hardness and mar resistance of polycarbonates. In contrast, the designed multi-layers were found to be highly ineffective to improve wear endurance of polycarbonates.

2. Experimental

2.1. Material

40 × 60 mm^2 substrates were achieved by fine blanking of high-flexible 1.2 mm thick polycarbonate 2 × 1 m^2 (PC) sheets (Makrolon GP, Bayer, Munich, Germany). The protective coatings of the polycarbonate substrates were designed by superimposing an organic layer of high chemical affinity with the underlying polycarbonate, an intermediate bridging layer consisting in a hybrid organic inorganic material synthesized by the sol–gel route and a hard and tough topcoat consisting in an organic matrix/silica nanocomposite.

An epoxy cycloaliphatic UV curable resin, that is, a 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EC) (Sigma Aldrich Italia, Milano, Italy) were chosen to formulate the first layer (i.e., primer) of the multi-layers coating system. A (50% wt.–50% wt.) mixture of pre-hydrolyzed 3-methacryl oxypropyltrimethoxysilane (MEMO) (Dynasylan, Evonik, Essen, Germany) and amino propyl triethoxy silane (AMEO) (Dynasylan, Evonik, Essen, Germany) were selected for the formulation of the bridging-layer (i.e., intermediate layer). Lastly, a mixture of monomeric, polymeric and oligomeric UV-curable trimethylolpropane triacrylate (TMPTA) (Sunchemical, NJ, USA) reinforced by the addition of different kind of silica nano-particle was chosen to formulate the topcoat (i.e., outermost layer). Among different classes of fillers, finely dispersed silica were chosen as they were expected to ensure better levels of dispersion within the coatings. Three different types of silica were involved in the formulation of the topcoat:

(i) pyrogenic silica (supplied as loose powders, Sigma Aldrich Italia, Milano, Italy) with a surface area of 200 $\mathrm{m}^2/\mathrm{g} \pm 25\ \mathrm{m}^2/\mathrm{g}$;
(ii) hydrophobic pyrogenic silica (supplied as loose powders, made hydrophobic by after-treatment with hexamethyldisilazane (HMDS) and chosen to increase affinity between filler and organic matrix) (Aerosil R 812, Evonik, Essen, Germany), with a surface area of 195–245 m^2/g and declared single crystallite dimension of 7 nm;
(iii) colloidal silica (supplied as suspension, Nanocryl C150, Evonik, Essen, Germany), which forms a stable suspension of individual nanometric silica particles in an active matrix of TMPTA with a silica content of 50% wt.

Different combinations of silica concentration (0.5, 1, 3, 7.5% wt.) and coating thickness (30, 50 μm) were tested during the experimental investigations.

2.2. Coating process

The formulations were applied layer-by-layer on the polycarbonate surface by air-mix spraying. Spraying process was carried out by an air-mix gun equipped with a nozzle of 0.8 mm and setting the feeding pressure at ∼1.75 bar. First, the primer was sprayed on the as-received polycarbonates. The resulting layer was dried 10 min in a static oven at 60 °C. The bridging layer (AMEO + MEMO) was, subsequently, sprayed on the primer and the resulting double-layer was re-dried in the static oven for 10 min more at 60 °C. After that, the unreinforced acrylate or the acrylates reinforced by the different types of nano-silica were deposited on the top of the double-layer. The resulting multi-layers were UV cured (two 120 W/cm lamps, 1 m/min belt speed) until full drying was attained.

2.3. Coating characterization

Coatings thickness was measured using a magnetic inductive gauge (Mega-Check 5FN-ST, List-Magnetik, Echterdingen, Germany) by the difference of the coated to the uncoated substrates. To ensure data reliability, the measurements were performed on three different points equally spaced over the substrates. The coating thickness was accurately controlled to achieve two sets of samples, 30 μm and 50 μm thick, respectively. All the coatings failing to agree to the above specifications more than 10% were