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Graphene reinforced UV-curable epoxy resins: Design, manufacture and material performance

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ABSTRACT

Graphene and its derivatives (graphene oxide, reduced graphene, functionalised graphene oxide, and functionalised reduced graphene oxide) are found to improve the mechanical properties of the polymers in which they are dispersed. In the present work, the potential of graphene and its derivatives in terms of their anti-scratch performance is thus investigated. In particular, graphene oxides, as-is graphene nano-platelets and reduced graphene oxides that were functionalised with amino-propyl triethoxy silane (APTES) were blended as reinforcing phases in UV curable epoxy coatings on polycarbonates, and the resulting performances were comparatively evaluated. Additionally, UV curable epoxy coatings covalently bonded to amino-functionalised silica-nanoparticles were studied.

The experimental analyses involved FT-IR spectroscopy to study the chemical interactions that occurred among the different compounds in the investigated mixtures, progressive and constant load scratch tests and SEM images of the residual scratch patterns to evaluate the micro-mechanical response and scratch visibility of the coatings. APTES-functionalised reduced-graphene oxide was found to be able to reduce the scratch visibility, thus revealing its suitability to promote the effective anti-scratch properties of UV-curable bis cyclo-aliphatic epoxy resins deposited on polycarbonate.

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1. Introduction

In recent years, the applications of anti-scratch barriers on polymeric materials have stimulated a number of different research strategies. One of the most recurrent routes is the manufacturing of composite coatings consisting of a mineral filler, with a high degree of hardness and a superior mechanical performance, dispersed inside an organic matrix that acts as a binder. Hard fillers inside a softer polymeric material are usually able to withstand better external loads, absorbing much of the applied stresses. Kurkcu et al. [1] found that hard fillers were able to oppose applied stress fields more effectively, particularly compared with softer materials. Such fillers include silica, zeolites, aluminates or zirconates, as demonstrated by the recent investigations of [2–4]. Mineral fillers can also be dispersed as reinforcements in bulk materials, as shown by [3,5], or in surface overlaying coatings [6,7].

An increase in the scratch resistance and hardness by mineral fillers is often counterbalanced by a corresponding increase in a brittleness of the resulting polymeric material, particularly with

the reinforcement of protective coatings on soft and compliant substrates. Once brittle materials exhibit failure, they are often impaired much more than corresponding ductile counterparts, as confirmed by experimental evidence in [1,8]. Impact and scratch resistance of highly compliant materials such as polyolefins can be therefore pursued by modifying their toughness with fillers, which feature rubbery-like deformation responses [9]. However, adhesion between the fillers and the bulk materials plays a critical role in the failure of the material and is a weak point of the designed composite. An additional route to design anti-scratch barriers is the dispersion of lubricants inside the bulk or coating materials to reduce friction. A decrease in the friction coefficient modifies the interfacial conditions between the indenter tip and the underlying material. Therefore, the substrates yield a plastic deformation only for larger applied contact pressures and, correspondingly, exhibit a tougher response [10]. Toughness has been recently associated with the enhancements in the scratch resistance of polymeric coatings [11].

Carbon-based fillers and graphene derivatives in particular feature a high degree of hardness as mineral fillers do, but they also boast additional properties such as an outstanding elastic modulus (~1 TPa) and, accordingly, an enhanced toughness and an increase in the planar stiffness and ductility. Graphene derivatives are also

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often associated with the manufacturing of low friction materials [12]. Carbon-based materials express their full properties when they are designed as “pure” material (that is, without dispersing it in a binding phase) and assembled in the form of “papers” or, more appropriately, layers. Recently, Li et al. [13] showed a decrease in the friction coefficient of titanium alloys from 0.039 to 0.014 after the application of a single-layer of graphene oxide (GO) through an intermediate layer of APTES. Additionally, coatings of “pure” GO feature an elastic modulus between 18 and 36 GPa, as estimated by [14,15]. The properties of the graphene derivatives can be partially kept when graphene is dispersed inside the polymeric materials. Part of the graphene properties is thus transferred to the resulting composite materials. Establishing criteria to estimate how many of the initial graphene properties are transferred to the corresponding composite material is troublesome. However, the uniformity of graphene dispersion, the capability to covalently bond graphene to the organic matrix and the containment of the oxidation process can strongly affect the final properties of the composite material [16,17].

Graphene derivatives and polymeric matrices can be designed in composite materials that also involves the usage of grafting polymers. Grafting polymers are endowed with functional groups that can confer additional flexibility to the manufacturing, thus increasing the effectiveness of the dispersion process and the amount of graphene that can be added to the formulations without agglomeration when used at high concentrations [18,19]. In this respect, silanes are particularly promising. They feature highly reactive alkoxy groups that can combine with the hydroxyl counterparts on functionalised graphene, allowing for the ability to utilise a larger number of chemically compatible organic resins and the tailoring of the properties of the resulting composite material [19–23]. Composites of the graphene derivatives, silanes and organic polymers ensured an utmost performance of the mechanical properties [21,23], showing a response that is a function of the affinity between the selected silane and the organic polymer [22]. The formation of covalent bonds should be carefully calibrated to prevent the excessive stiffening of the molecular structure and the embrittlement of the resulting material [24].

An increase in the mechanical responses of polymeric materials reinforced by graphene derivatives is thus often found to be successful, opening new research challenges in the formulations of innovative materials with ever growing performances [13,25–28]. Although improvements in the hardness, Young's modulus, toughness, ultimate strength and friction of the polymeric materials that are covalently bound with graphene derivatives are associated with an increase in the scratch resistance and a decrease in the scratch visibility [1,29,30], only two papers have discussed the anti-scratch capabilities of graphene reinforced polymers. Cai et al. [31] investigated the anti-scratch resistance of a polyurethane resin reinforced with GO, and Shin et al. [32] studied the composite between polypropylene and GO. They found a significant increase in the scratch hardness (+189%) and a decrease in the penetration depth (–80%). However, they investigated bulk materials. In the literature, no studies have examined the anti-scratch performance of graphene reinforced polymeric coatings. In this respect, the present investigation was aimed at comparatively evaluating the graphene derivatives (GO, as-is graphene manufactured by mechanical exfoliation and reduced GO functionalised by amino-silane (amino propyl triethoxy silane-APTES)) to reinforce UV curable epoxy-based resins deposited onto polycarbonate. The experimental investigations utilised FT-IR spectroscopy to study the chemical interactions that occurred among the different compounds in the investigated mixtures, progressive and constant load scratch tests and SEM images of the residual scratch patterns and thereby evaluate the micro-mechanical responses and scratch visibilities of the coatings. APTES-functionalised reduced-graphene

oxide was found to be able to reduce the scratch visibility, thus revealing its suitability in promoting effective anti-scratch properties of UV-curable bis cyclo-aliphatic epoxy resins deposited onto polycarbonate.

2. Experimental procedures

2.1. Materials

Synthesis of the coatings involved a UV curable 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate (Sigma Aldrich, Milano, Italy) monomer (CE) and triarylsulfonium hexafluoroantimonate salts as the cationic catalyst. Reagent grade ascorbic acid, isopropyl alcohol and butyl acetate were supplied by Sigma Aldrich (Milano, Italy). Aminopropyl triethoxy silane (APTES) was supplied by Evonik (Evonik, Essen, Germany). Graphene oxide (GO) and graphene nano-platelets (GNP) were supplied by Nanesa (Arezzo, Italy). GO features a sheet thickness < 1 nm, while it is 1–6 μm wide. After reduction, the size of graphene oxide is further reduced. GNP features a sheet thickness of 10 nm (30 layers). The sheets are 10–60 μm wide. Specific surface area (BET) is approximately 30 m^2/g .

The substrates were achieved by the fine blanking of polycarbonate sheets (0.9 mm thick) in flat slabs of 20 mm \times 100 mm.

2.2. Filler preparation

GO fillers were prepared by centrifugation after water removal by a co-solvent mixing method according to the procedure by Liao et al. [33]. GNP fillers were prepared by centrifugation of 25 mg/ml of a GNP suspension. The resulting precipitate was washed and re-suspended in isopropyl alcohol.

Reduced graphene oxide (GOr) was prepared according to a procedure reported elsewhere (Fernandez-Merino et al. [34]). Briefly, 4 mg/ml of the GO suspension was added to a solution of 12% ascorbic acid and stirred for 48 h. After stirring, the resulting suspension was centrifuged and washed in water until the ascorbic acid was completely removed. GOr was then re-suspended in isopropyl alcohol.

Functionalisation of the reduced graphene oxide (fnGOr) fillers by APTES was achieved by hydrolysis and a condensation reaction between APTES and the residual –OH groups on GOr in excess of APTES. In particular, 1.72 g of APTES (approximately 10 times its stoichiometric amount evaluated respect to the potential reactive groups of GO before the reduction step) and 4.68 g of distilled water (approximately 300 times the stoichiometric amount) were added to the GOr that was prepared by the aforementioned reduction step of 50 mg of GO. The mixture was left to react for 2 h under sonication. The as-prepared fnGOr was washed to remove the unreacted and irregularly polymerised silane, centrifuged and re-suspended in isopropyl alcohol. Silica derivatives, which were still able to remain inside the solution at the end of the washing and centrifugation step, were therefore assumed to be bond with GOr by strong chemical bonds.

APTES functionalised silica particles (fnSiO₂) were prepared by a sol-gel reaction of APTES. Here again, 1.72 g of APTES was dispersed in isopropyl alcohol with 4.68 g of distilled water. Synthesis in an ultrasonic bath lasted 2 h. The reaction products were, then, used without further processing. Silica particles of approximately 20 nm are formed (Fig. 1).

2.3. Coating preparation

50 mg of the GO, GNP fillers, and fnGOr was prepared by the reduction and functionalisation of 50 mg of GO, and APTES

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