



Scratch behavior of epoxy coating containing self-assembled zirconium phosphate smectic layers

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ABSTRACT

A facile but efficient spray-coating method was recently developed to manufacture thin, flexible, and transparent epoxy films reinforced with well-exfoliated and highly-aligned α -zirconium phosphate (ZrP) nanoplatelets in smectic liquid crystalline order. Here, we investigate the scratch resistance of ZrP/epoxy nanocomposites prepared following the same spray-coating process. Comparison was made with neat epoxy coating to determine the impact of ZrP nanofillers. Tests were conducted with accordance to ASTM D7027/ISO 19252 scratch standard and scratch mechanisms were studied using different experimental tools. Results show that scratch resistance is considerably improved after introducing ZrP nanofillers to the epoxy coating. This was reflected by the delay in microcracking and plowing damages and the decrease of scratch coefficient of friction. This result is attributed to the significant role of exfoliated and aligned ZrP nanofillers in enhancing the mechanical properties of the epoxy matrix. The usefulness of the current study in developing new coating systems for high-performance applications is discussed.

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1. Introduction

Thanks to the emerging advanced materials with highly attractive properties, new devices and applications are being introduced in an ever-increasing pace. Many of these new devices and products contain significant polymeric components, such as electronic devices and energy efficient automobiles. These polymeric components are subjected to tribological damages, thus reducing their functional and aesthetic performance. One of the most commonly challenging tribological damages for polymers is scratch damage. Consequently, improvement in scratch performance has become one of the most sought after desire among polymer producers and component manufacturers. Unfortunately, the time-dependent and non-linear constitutive behaviors, coupled by the complexity of polymer deformation and damage during scratch, make these efforts daunting.

After significant concerted efforts between academia and

polymer industry through an industrial consortium operation [1], an ASTM D7027/ISO 19252 standard was developed to perform consistent, straightforward, and meaningful scratch tests [2,3]. The standardized scratch test has since been increasingly adopted by industry and academic institutions globally. The new scratch test has now been used to study the effect of different surface properties like roughness [4–6], friction [7], and perceptual attributes [7], mechanical properties like constitutive parameters [8,9], and test conditions like aging time [10,11], humidity [12], and test speed [13] on the scratch resistance of polymeric systems. Results show that scratch performance is generally related to friction, gloss, thermal treatment, surface roughness, yield stress, and strain hardening coefficient. Based on these findings, better scratch performance has been practiced by adding slip agents [7,14], increasing mold temperature [15], decreasing gloss level [7], and introducing surface texture [7]. Furthermore, better fundamental understanding of polymer scratch behavior is gained through finite element methods (FEM) modeling which provides mechanistic interpretations of scratch through extensive stress and parametric analysis [16–18]. This FEM modeling suggests that materials with greatly improved mechanical integrity and drop in friction coefficient are expected to exhibit significantly better scratch resistance.

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In an effort to develop such scratch-resistant materials, more and more interest is given to high-performance polymeric materials [19] and nanocomposites reinforced with a variety of nanofillers such as graphene [20,21], glass fibers [22], rubber [23], and metallic pigments [24]. Previous studies investigated the scratch response of these nanocomposites and showed that scratch and chemical resistance of neat polymers are improved after introducing graphene [21], metallic pigments [24], or natural montmorillonite (Na^+MMT) nanoclay [25]. This makes these nanocomposites good materials for scratch-resistant coatings, like epoxy/graphene coating on a polycarbonate substrate [21]. Nevertheless, improvement in scratch resistance was not always obtained when nanofiller was incorporated [23]. There is still much to learn about how nanoparticles can be incorporated in a polymeric matrix to exert maximum improvement in scratch performance [26].

Clay has been extensively utilized as a nanoparticle of choice for preparing polymer nanocomposites for its low cost, relatively easy preparation, and fairly predictable stiffening behavior when introduced into polymers [27,28]. Previous studies showed that polymers with exfoliated clay nanoplatelets have remarkably improved barrier [29,30], optical [29,30], electrical [30], mechanical [30], and thermal [27,31] properties. Based on Halpin–Tsai and Mori–Tanaka composites theories, Fornes and Paul demonstrated that, for the same polymer matrix and loading, clay nanoplatelets show better performance than glass fibers [22]. This was explained by their high modulus, high aspect ratio, and ability to reinforce in two directions. Therefore, polymer/clay nanocomposites can be effectively used in many industrial applications such as food packaging [32], photovoltaics and flexible optoelectronics [30], and flame retardation [33].

An in-depth fundamental understanding on structure–property relationship in polymer/clay nanocomposites has been acquired through a series of investigations based on epoxy and synthetic α -zirconium phosphate (ZrP) nanoplatelets [34–41]. The simple and versatile synthesis and functionalization of ZrP nanoplatelets make these model systems ideal for unambiguous study of structure–property relationship of polymer nanocomposites. For instance, ZrP exhibits well-controlled size, high crystallinity, relatively narrow size distribution, well-defined chemical structure, high purity, and facile exfoliation [34–36]. Similar to other clay nanofillers, exfoliated ZrP improves barrier properties [37] and increases strength and stiffness values even at low concentration levels [22,42], without compromise to fracture toughness [38]. An earlier study has indicated that 2 vol% of ZrP nanoplatelets did not show improvements on polymer scratch resistance [23], which was attributed to a reduction in ductility in the nanocomposite [22]. Also, viscosity build-up at a ZrP concentration above 2 vol% led to entrapment of air bubbles in the epoxy matrix, thus preventing further improvement in mechanical performance [34,39,40]. To overcome this limitation and obtain good ZrP exfoliation even at high concentration levels, a recent study showed that this could be achieved by introducing an amphiphilic monoamine surfactant that does proton exchange with acid groups in ZrP monolayers in acetone [41]. As a result, the inter-layer binding weakens and the exfoliation of the layered structures is promoted into individually dispersed 2D nanoplatelets in acetone. This method was employed in a recently-developed spray-coating technique to obtain smectic epoxy/ZrP films with good ZrP exfoliation at high loading levels [4]. This technique showed promising results and will be employed in this study.

A characteristic property of exfoliated ZrP nanoplatelets is the remarkable and proportional increase of their alignment in polymer matrix with increasing loading levels [34]. This increase in ordered orientation is attributed to the geometric confinement of

the surrounding ZrP nanoplatelets at higher amount of exfoliated ZrP particles [38]. This unique architecture, known as *brick-and-mortar* architecture, is similar to nacre biomaterial [43]. Nacre has alternating layers of soft proteins and aligned calcium carbonate platelets, leading to significantly high stiffness and strength values [44]. Likewise, high alignment and overlapping arrangement of ZrP nanoplatelets in epoxy matrix leads to improved mechanical [34] and barrier [4] properties. The spray-coating method previously described is one of the most practical and effective techniques recently developed to obtain good brick-and-mortar structures of large-scale self-assembled clay smectic layers [4]. Thanks to the spray-coating technique, epoxy/ZrP nanocomposite with highly exfoliated and aligned ZrP fillers can be produced on an industrial scale and utilized for high-performance structural and functional applications. However, more studies should be conducted to better investigate the tribological performance of this material, especially its scratch resistance.

In this study, we consider determining the scratch resistance of epoxy coating containing self-assembled ZrP nanoplatelets. The impact of these nanofillers on epoxy scratch behavior is investigated. The relevance of the present study for potential industrial applications is also discussed.

2. Experimental

2.1. Materials and sample preparation

2.1.1. Synthesis and exfoliation of ZrP nanoplatelets

ZrP nanocrystals were synthesized using a refluxing technique as was previously reported [35]: 20 g of Zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%, Aldrich) was refluxed with 200 mL of phosphoric acid (chemical formula 3.0 M H_3PO_4 , 85%, EM Science) for 24 h in a Pyrex glass flask at 110 °C. The recovered ZrP product was then washed and collected three times by centrifugation at 10,000 rpm. The exfoliation of ZrP nanoplatelets was performed in aqueous solution by adding polyoxyalkyleneamine with a nominal molecular weight of 1000 g mol^{-1} (Jeffamine[®] M1000, Huntsman Chemical) at a molar ratio of M1000: ZrP = 1:1. The obtained mixture is designated as ZrP-M1000. It was fully exfoliated as individual hexagonal crystals with monodisperse thickness of 0.76 nm in organic solvent [45], and remained exfoliated in an epoxy suspension [4].

2.1.2. Preparation of model coating systems

Three coating systems, namely neat epoxy, epoxy-M1000, and epoxy/ZrP-M1000 were investigated in our study. Neat epoxy was made by adding 2.33 g of bisphenol-F epoxy (DER 354, The DOW Chemical Company) to 0.62 g of diethyltoluene diamine (DETDA) curing agent (Epikure[®] W, Momentive) in 2.5 mL of acetone (ACS grade, EMD). To obtain epoxy-M1000 system, the prepared neat epoxy was added with 18.6 wt% of M1000 monoamine. Finally, epoxy/ZrP-M1000 system was prepared using ZrP-M1000 mixture described previously. This was performed by dissolving 2.33 g of epoxy in 5 mL of acetone to form a clear solution which was later added dropwise to a dispersion containing 0.5 g of ZrP and stirred homogeneously for at least 4 h. Then, 0.62 g of DETDA curing agent was added to the solution and homogenized by stirring. After this procedure, epoxy/ZrP-M1000 coating system with 10 wt% (volume fraction $\phi = 0.044$) of ZrP nanoparticles was obtained. Its concentration in acetone solution was adjusted to 20 wt% to achieve good spray coating condition.

2.1.3. Spray coating process

In most applications, epoxy coating should be sufficiently thick to ensure uniform coverage of the substrate surface and consistent

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