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Effect of nano-silica on the mechanical properties of acrylic polyurethane coatings

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ABSTRACT

A special focus has recently been made on the enhancement of the mechano-tribological properties of the clearcoats commonly used in several industries such as the automotive manufacturing sectors. However, still further investigations are needed for the better understanding of the behavior of such clearcoats in different working conditions. The purpose of the current research was investigating the erosion resistance, adhesive strength, micro-hardness and weathering stability of the acrylic-based polyurethane nano-composites which were reinforced by precipitated and fumed nano-silica particles. To achieve this, Zeta Sizer, scanning electron microscope (SEM), X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) analyses were used. Furthermore, a series of experimental tests including the adhesive strength, toughness, micro-hardness and erosion resistance were carried out to measure the mechanical response of the fabricated clearcoats. It was concluded that the nano-silica additives significantly improve the adhesive strength, and highly increase the micro-hardness as well as the erosion resistance. It is also found that the precipitated nano-silica is able to create an inexpensive, hard and tough coatings rendering it very durable against wear, weathering conditions, and, thus, can be potentially employed as a reinforcing filler and as a replacement to the fumed clearcoats that are usually much more expensive than the proposed reinforcement.

1. Introduction

Polymer based coatings are widely used in a variety of applications in order to protect surfaces underneath against impact, scratch, wear, corrosion and weathering conditions, solvents, etc. One of the most common coatings used as protection against the aforementioned issues is polyurethane. Epoxy based coatings are specific types which are extremely transparent and possess good to excellent weathering stability, high toughness, and excellent resistance against wear and corrosive chemicals [1,2].

One of the key applications of the acrylic-based polyurethane is its use in the top clearcoat of automobile body. As a final coating, the top layers are to be as much glossy, transparent and resistant against harsh weathering conditions as possible. Ley et al. [3] studied the optimization of acrylic polyols for two-component water-based polyurethane top coatings offering an excellent hardness and mechanical strength. Apart from the several downsides of the polyurethane clearcoats, further investigations are highly required. It is mostly because these clearcoats do not offer enough resistance against impact and wear, as well as appropriate protection against chemical corrosive/erosive substances.

The use of inorganic particles such as Al_2O_3, TiO_2, $CaCO_3$ and SiO_2 as reinforcements added to clearcoats has been an interesting topic of a great body of research work, yet the utilization of these fillers has been shown a pressing issue due mainly to the unavoidable challenges mentioned earlier. These particles are however added into a neat polymer and are expected to considerably enhance mechanical, chemical and or even optical properties of the filled materials.

Silica particles are divided into three groups: (1) precipitated silica, (2) fumed silica, and (3) colloidal silica among which the former is synthesized by a wet chemical method. In this process, silica is produced when H_2SO_4 or HCl is reacted by silicate resulting in a precipitated type of nano-silica. The fumed silica is synthesized thorough the hydrolysis of $SiCl_4$ in the flame of oxygen-hydrogen [4]. The reaction is expressed as follows:

$$SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4HCl$$

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A high quality clearcoat needs to be as glossy as possible and hence light scattering parameter (P_{scat}) must be known. According to the Rayleigh's equation expressed by Eq. (1), the refractive indices of the nano-particles should be equal to those of the polymeric matrix; moreover, the particle size should not exceed the light wavelength [5].

$$P_{scat} = 22\pi^4 P_0 \rho \left(n' - n\right) \left(V^2/\lambda^4\right) \quad (1)$$

where P_{scat} is the light scattering parameter, P_0 and λ are the light power and the light wavelength, respectively, ρ and V are respectively the portion and the size of suspended particles, and n and n' are the refractive indices of the polymer matrix and the suspended particles, respectively.

Mixing and the degree of homogeneity are of high importance in the reinforced polymer composites. Lack of an effective mixing/dispersion, a myriad of defects and insufficient interfaces created between the reinforcing particles and the matrix are expected. The aforesaid drawbacks, unfavorably, result in a significant reduction in the overall mechanical properties of the fabricated clear coatings.

Extensive work has been reported by Zhou et al. [6,7] in respect of the acrylic and polyester based polyurethane/colloidal nano-silica coatings. It is indicated that the preparation route and different silane couple agents leave underlying significant effect on redispersibility as well as the mechanical performance of the clearcoats. Arena et al. [8] studied the solid particle erosion and the viscoelastic properties of thermoplastic polyurethanes by the study of the morphological, tribological, viscoelastic response of clear coatings. It was shown that thermoplastic polyurethane dissipates the impact energy of the erodent materials. Petrović et al. [9] investigated the structure and properties of polyurethane-silica nanocomposites. Maganty [10] et al. found that the mechanical properties of polyurethane composite coatings are improved upon the addition of nano-silica. The mar resistance of automotive clearcoats was experimentally studied by Scrinzi et al. [11]. The results indicate that both mar resistance and hardness improve when nano-silica particles are added to the neat polymer. Eslami et al. [5] studied the optical properties of the transparent acrylic based polyurethane nano-silica composite coatings by the turbidity and UV–vis absorption tests. Kotnarowska et al. [12] examined the wear resistance of epoxy-polyurethane coating modified by TiO_2. It was indicated that the erosion resistance was remarkably improved by the addition of TiO_2 nanofiller.

For the fabrication of turbine blades, polyurethane coatings reinforced by boron carbide (B_4C) or silicon carbide (SiC) nanoparticles on a 16Cr-5Ni martensitic stainless steel substrate was examined by Syamsundar et al. [13]. It is indicated that the samples reinforced by the B4C nanoparticles outperform those filled with the SiC nanoparticles. The improvement observed was correlated to the higher hardness of the B4C nanoparticles than that of SiC fillers. The effect of non-polar nano-silica particles on the electrochemical properties of 2-pack polyurethane matrix was studied by Mills et al. [14]. They represent that the abrasion resistance is enhanced by higher curing temperatures or the addition of nano-silica particles. The use of precipitated silica with silanol groups as an inorganic chain extender in polyurethane was reported by Chen et al. [15]. Das et al. [16] studied the effect of nano-silica additives on the physicochemical, morphological and curing characteristics of transesterified castor oil based polyurethane coatings. Eslami et al. [5] examined the optical property of the nano-silica/polyurethane clearcoats. According to their turbidity results, the addition of nano-silica below 2 wt% of powder will not result in a decrease in the degree of the transparency. They concluded that the gloss of such a nano-silica/polyurethane clearcoats remained unchanged. However, upon the addition of further amount of nano-silica, the gloss level reduced. For example, 1.8% and 23% reductions in the gloss level were reported respectively for the 4 wt% and 6 wt% of the precipitated nano-silica/polyurethane clearcoats. Accordingly, 4.3% and 5.3% reductions were respectively observed for the fumed type of nano-silica/polyurethane clearcoats.

In the present work, two types of precipitated and fumed nano-silicas are added to an acrylic-based polyurethane clear coating to examine possible improvement in mechanical, optical and tribological properties. The adhesion, microhardness, and erosion resistance behavior of clearcoats are discussed and examined. The effect of addition of fumed and precipitated nano-silica reinforcements are thoroughly compared and discussed.

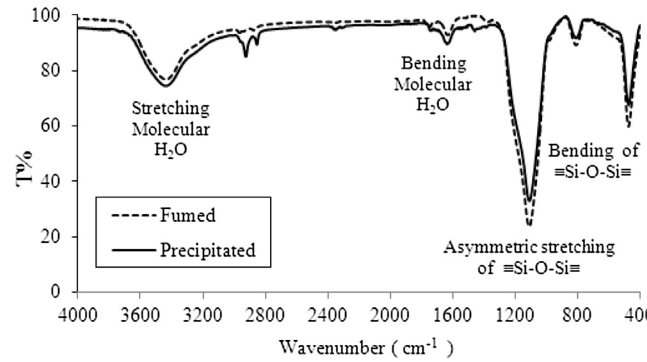

Fig. 1. The FTIR spectroscopy of the fumed and precipitated nano-silica particles.

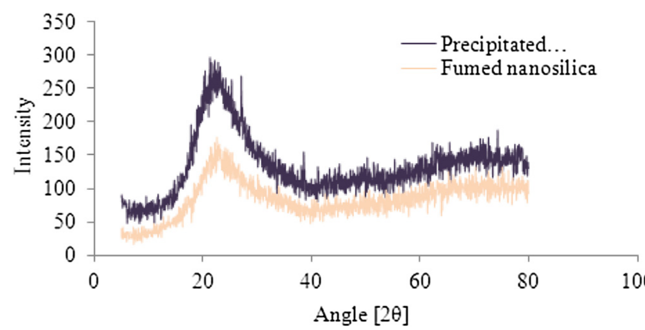

Fig. 2. The X-ray diffraction (XRD) of nano-silicas.

2. Experiments

2.1. Materials

Two types of nano-silica were used as fillers in the reinforcing process of the polyurethane clearcoats. Table 1 shows the material properties of the fillers used in this study.

The fourier transform infrared spectroscopy (FTIR) of the fumed and precipitated nano-silica particles is shown in Fig. 1. Surface hydroxyl groups are shown in both fumed and precipitated nano-silicas. Silanol group density of the fumed nano-silica particle is rather lower than that of precipitated samples which is shown in Fig. 1. Fig. 2 represents the X-ray diffractions that support the presence of the amorphous structure of the two types of nano-silica particles. Fig. 3 shows a representative TEM image of the fumed nano-silica particles. The image clearly supports the expected geometry and average dimensions of the reinforcements being at a nano-size level. Moreover, the image represents aggregated and agglomerated fillers already present in the synthesized nano-fillers. The TEM image was recorded by a TEM Zeiss EM-10C instrument to examine the structure by passing electrons through the samples.

The polyurethane used in this research consists of two parts, an acrylic-based polyol resin solved in a solution of butyl acetate/xylene and a hardener from poly isocyanate aliphatic group