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Surface modification of Cr_2O_3 nanoparticles with 3-amino propyl trimethoxy silane (APTMS). Part 1: Studying the mechanical properties of polyurethane/Cr_2O_3 nanocomposites

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ABSTRACT

The surface of Cr_2O_3 nanoparticles was modified with various amounts of 3-amino propyl trimethoxy silane (APTMS). Thermal gravimetric analysis (TGA), turbidimeter and Fourier transform infrared (FTIR) spectroscopy were utilized in order to investigate APTMS grafting on the nanoparticles. Then, polyurethane nanocomposites were prepared using various loadings of silane modified Cr_2O_3 nanoparticles. The nanoparticles dispersion in the coating matrix was studied by a field emission scanning electron microscopy (FESEM). Dynamic mechanical thermal analysis (DMTA) and tensile test were utilized in order to investigate the mechanical properties of the nanocomposites. Results obtained from FTIR, TGA and turbidimeter measurements revealed that the organic functional groups of the silane were successfully grafted on the surface of the nanoparticles. The mechanical properties of the polyurethane were significantly enhanced using 2 wt% Cr_2O_3 nanoparticles modified with 0.43 g silane/5 g pigment compared with other samples.

1. Introduction

Polyurethane is a popular kind of coating used for different applications including decorative, automotive and industrial. A two component polyurethane coating can be obtained through the reaction between functional groups of polyol and isocyanate. A wide range of polyurethane coatings can be produced using various kinds of diisocyanate and polyols. In recent years, different kinds of polyurethane based coatings have been developed and used in different industries due to theirs superior properties, such as flexibility at low temperature, high abrasion resistance, high impact and tensile strength, high transparency, excellent gloss, color retention, corrosion protection properties, and good weathering resistance [1,2]. However, polyurethane has some disadvantages, i.e. low thermal resistance, low adhesion, low mechanical and anticorrosive properties [3]. In recent years, researchers have tried to conquest these disadvantages through different ways. Addition of pigments to the coatings has been introduced as an effective way to obtain polyurethane based coatings with enhanced mechanical and anticorrosion properties [4–6]. In this regard, nanoparticles have been introduced as a new brand of the materials to reach this target. Nanoparticles, owing small particle size and high specific surface area, can improve the mechanical and anticorrosion properties of the coatings [7]. There are a large number of reports in the literature indicating that the mechanical properties of the polyurethane based coatings can be significantly improved using nanoparticles such as: SiO_2 [8,9], Au [10], ZnO [1], grapheme [11], MWCNT [12], TiO_2, and nano clay [13]. Zhou et al. [14] showed that addition of the nano silica particles to the polyurethane coating could improve tensile strength and Young's modulus of the coating significantly. Chou et al. [15] showed that the mechanical properties of the polyurethane coating were significantly improved in the presence of silver nanoparticles. However, nanoparticles have a large tendency to form large size aggregates in the polymeric coating matrix. The presence of agglomerated nanoparticles in the coating matrix can negatively influence its properties [16,17]. Therefore, attempts have been carried out to enhance nanoparticles compatibility with the coating matrix. The surface modification of the nanoparticles is one practical way to make them compatible with the coating matrix [18,19]. In this regard, many different surface modifying agents are used to make nanoparticles more compatible with the

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coating matrix. Silane coupling agents are well known materials used to modify the nanoparticles due to their unique bifunctional structure. The surface modification process includes hydrolysis and condensation reactions between the silane and the surface of the nanoparticles. Surface modification of the particles by silane coupling agents changes the surface chemistry of the particles from hydrophilic to hydrophobic [20,21].

There are various reports showing that the surface modification of the nanoparticles could improve the mechanical properties of the coating [22–26]. Rostami et al. [27] showed that the surface modification of the nano silica with an amino silane caused a significant improvement of the mechanical properties of the polyurethane coating. Guo et al. [28] compared the effects of modified and unmodified ZnO nanoparticles on the mechanical properties of a vinyl ester coating. They found that surface modification of the ZnO nanoparticles with methacryloxy propyl-tri methoxy silane plays an important role in improvement of the mechanical properties of the resulting nanocomposites. Sun et al. [29] showed that SiO_2 nanoparticles modified with methacryloxy propyl tri methoxy silane could improve the mechanical strength of the poly vinyl chloride composites higher than the one modified with dimethyl dichloro silane and also the unmodified SiO_2 nanoparticles. Wu et al. [30] studied the effects of surface modification of nanosilica particles via different silane coupling agents including methyltriethoxysilane (MTES), octyltriethoxysilane (OTES), vinyltriethoxysilane (VTES) and methacryloxypropyltrimethoxysilane (MATMS) on the properties of acrylic-based polyurethane/silica composites. They found that nanosilica particles modified with OTES and MTES dispersed homogenously in the polyurethane matrix due to the formation of thicker organic layer on the nanoparticles. It was shown that the size of silane chains is important factor affecting the mechanical properties of the polyurethane coating significantly. In fact, nanosilica particles modified with MTES and OTES could reduce the storage modulus due to the plastification of long-chain silane molecules. This means that both the chain size and chemical structure of the silane coupling agents are influential parameters affecting the nanoparticles properties in the coating matrix. In another work, Wu et al. [31] studied the effects of silica nanoparticles with different sizes and surface groups on the properties of polyester resin. They prepared the silica nanoparticles through the sol–gel process of tetraethylorthosilicate. They showed that preparing polyester/silica nanocomposite via in situ (IS) polymerization caused better polyester resin bonding with the surface of particles compared to the method of preparing nanocomposite by blending procedure. They understood that the procedure of preparation nanocomposite is so important which can affect the nanoparticle dispersability in the resin. It was shown that there is a logical relationship between the glass transition temperature (T_g) of the coating and the amount of resin chemically bonded with the nanoparticles surface. Nanoparticles could increase the T_g of the coating when the resin segment chemically bonded to the surface of particles. Depending on the surface nature of the nanoparticles, they could migrate to the surface of coating or remain in the bulk [32]. It has been also shown that [33] addition of silica nanoparticles could enhance the tensile strength, modulus, hardness, and abrasion resistance of the polyurethane coating.

Nanoparticles have been also used in the polyurethane coatings formulations in order to improve its anticorrosion properties [34]. Among different kinds of nanoparticles, the Cr_2O_3 nanoparticles [35] are widely used in the organic coatings formulations in order to enhance its anticorrosion properties. However, apart from the anticorrosion properties of the coating, the mechanical properties of the coating are also important. In fact, the nanoparticle which has been used to improve the anticorrosion properties of the polyurethane coating should not reduce its mechanical strength. Therefore, the current work has focused on studying the effects of the surface modification of Cr_2O_3 nanoparticles on the mechanical properties of the polyurethane.

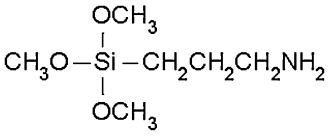

Fig. 1. The chemical structure of APTMS.

This work aims at surface modification of Cr_2O_3 nanoparticles by different amounts of 3-amino propyl trimethoxy silane (APTMS). Analytical techniques including FT-IR, TGA and turbidimetery are utilized to investigate the surface modification of the particles. FE-SEM is used to evaluate nanoparticles dispersion in the coating matrix. Tensile and DMTA tests are performed to evaluate the effects of the surface modification of the nanoparticles on the mechanical properties of the resultant nanocomposites.

2. Experimental

2.1. Materials

The spherical nano-Cr_2O_3 particles with the average particle size and density of 60 nm and 1.2 g/cm^3, respectively were provided from Alpha Nano Powder. In this study, surface modification of the nanoparticles was done by 3-amino propyl trimethoxy silane (APTMS) in order to enhance its compatibility with the polyurethane matrix. APTMS with the chemical structure given in Fig. 1 was purchased from Merck Co.

Polyurethane based nanocomposites were prepared using an acrylic polyol (1780 M) from DSM and a polyisocyanate hardener (Desmodur N75) from Bayer.

2.2. Surface modification of the Cr_2O_3 nanoparticles

The surface of Cr_2O_3 nanoparticles was modified with APTMS. The surface modification was done using various amounts of APTMS. The lowest amount of silane used was calculated according to Eq. (1).

$$M = \frac{M_p \times S_s}{MSC} \quad (1)$$

where M, M_p, S_s and MSC are the amount of silane (g), the amount of nanoparticles (5 g), the specific area of nanoparticles (38 m^2/g) and the lowest surface coverage (436 m^2/g), respectively. According to Eq. (1), the amount of silane calculated for surface modification of 5 g nanoparticles is 0.43 g. Therefore, the lowest amount of silane used in this study is 0.43 g.

For this purpose, Cr_2O_3 nanoparticles, ethanol, H_2O and hydrochloric acid were placed into a 3neck reactor. The reactor was placed in an oil bath and the suspension was dispersed with a homogenizer for 3 h. The suspension was kept under reflux at 80 °C for 3 h. The list of materials used and their amounts are given in Table 1.

Table 1
Surface modification bath components for the modification of 5 g of Cr_2O_3 nanoparticles with APTMS.

Silane (g)	Ethanol (g)	H_2O (g)	HCl (37%)[a] (cc)	NaOH (50 wt%)[b] (cc)
0.43	19.44	0.77	0.4	0.5
3	121.5	4.86	1.4	0.8
5	218	8.90	3.5	1.8

[a] Used for catalysis of hydrolysis reaction.
[b] Used for catalysis of condensation reaction.