Progress in Organic Coatings 77 (2014) 1184–1190

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Optical and mechanical properties of transparent acrylic based polyurethane nano Silica composite coatings

Reza Eslami[a], Rouhollah Bagheri[a,*], Yasser Hashemzadeh[b], Mehdi Salehi[b]

[a] Department of Chemical Engineering, Polymer Group, Isfahan University of Technology, 84146 Isfahan, Iran
[b] Department of Materials Engineering, Isfahan University of Technology, 84146 Isfahan, Iran

ARTICLE INFO

Article history:
Received 17 January 2014
Received in revised form 30 March 2014
Accepted 5 April 2014
Available online 4 May 2014

Keywords:
Nano composite
Acrylic based polyurethane
Nano Silica
Silica nanoparticles
Fumed nano Silica
Precipitated nano Silica

ABSTRACT

The aim of this work is to investigate the effect of two types of nano Silica (precipitated and fumed) with various concentrations on the optical and mechanical properties of transparent polyurethane acrylic based nano composite coatings. Transparency, gloss, UV absorption, adhesion strength and impact resistance of the samples have been measured. The gloss of the film samples remains unchanged compared to the reference film sample up to 2 wt.% (weight percent) for both types of nanoparticles. The samples containing 4 and 6 wt.% nano Silica show reduction in the gloss property by 4.3% and 5.3%, respectively, for fumed samples and 1.8% and 23% for precipitated samples. The film samples show increase in light absorption in the wavelength region of 250–2000 nm by increasing the content of nano Silica. Also cross cut and pull-off test results show that a good adhesion to steel can be obtained (5B for cross-cut, 7 MPa for pull-off) and no changes in impact strength of the samples with respect to the reference have been observed.

1. Introduction

In recent years use of nano technology in coatings, especially in transparent ones, has been the focus of researchers' attention and much progress has been made. Among the reasons of such progress are the easy access to the different nano-materials and the knowledge of their effects on the properties of transparent coatings. These materials mostly enhance some characteristics such as life time, adhesion strength, resistance against UV ray and transparency without degrading other properties of the coatings. Use of nano-fillers also leads to the improvement of some properties of the coatings [1–3]. For example, employing metal oxide nanoparticles, such as nano Alumina and nano Silica, in polymer coatings offers a scratch resistance property such that the results of Mohs experiments for these nanoparticles prove hardness numerals of 7 and 9, respectively leading to the scratch resistance in the coatings [4,5].

Beside these advantages of using nano materials in the coatings, there are also some difficulties when mixing these nano materials with the polymer matrix which originate from high specific area of these nano materials. Inappropriate distribution of the nanoparticles in the coatings causes inhomogeneity in the properties of the coatings and even degrades their properties. To workout these problems, researchers proposed the surface treatments of nano materials [6]. Silica nanoparticles intrinsically contain OH functional groups on their surface which results in some type of hydrophilic character [7]. This is why surface treatments in nanoparticles by organosilanes are used to employ them in non-polarized matrix improvement of the interaction between matrix surface and nanoparticles [8,9]. Furthermore, adding Silica nanoparticles to acrylic based polyurethane matrix leads to the enhancement of scratch resistance, friction, abrasion resistance, tensile strength, adhesion strength and impact strength [10–14].

Comparison of the obtained properties for coatings with different nanoparticles seems necessary for choosing a nano material with acceptable characteristics. In this work, two types of nano Silica, named fumed nano Silica and precipitated nano Silica, have been used in polyurethane transparent coatings based on acrylic.

Fumed nano Silica is an amorphous powder that is produced by hydrolysis of high temperature vapor of Silicon tetrachloride in presence of oxygen–hydrogen radiation. The reaction for this process is written below:

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

Also precipitated nano Silica can be produced by a wet process. In this process Silicate and inorganic acids, such as acid sulfuric and

* Corresponding author. Tel.: +98 311 391 5613.
E-mail address: bagheri@cc.iut.ac.ir (R. Bagheri).

http://dx.doi.org/10.1016/j.porgcoat.2014.04.007
0300-9440/

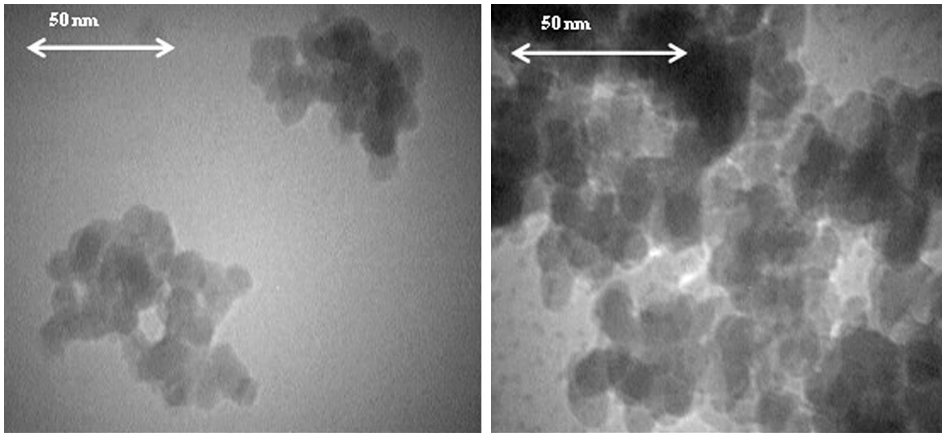

Fig. 1. TEM images for precipitated nano Silica particles.

Table 1
Properties of fumed and precipitated nano Silica particles.

Property	Fumed	Precipitated
Particle size (nm)	7–12	8–15
Surface	Hydrophilic	Hydrophilic
Specific surface area (m^2/g)	220 ± 20	220 ± 20
Purity	99.9%≤	98.31%
Bulk density (g/l)	50	50
Manufacturer	Tokuyama (Japan)	Fadak Chemistry Co. (Iran)
Product code	QS-20	F-110

hydrochloric acid, are used to produce particles of hydrated Silicate that precipitate in solution. The size of particles can be controlled by reaction conditions and drying processes.

The aim of this work is to investigate the differences between optical and mechanical properties of the acrylic based polyurethane samples containing fumed and precipitated nano Silica.

2. Experimental

2.1. Materials

The specifications of the two types of nanoparticles used as filler are summarized in Table 1. TEM images for employed nanoparticles show that they are actually nano-sized (see Fig. 1). Another investigation is conducted by XRD showing completely amorphous structure of these nanoparticles (see Fig. 2).

The employed polyurethane is composed of two parts, resin and curing agent. Resin is of acrylic- polyol type which is solved in Xylene. The curing agent contains isocyanate groups and dissolved in Butyl Acetate. Details of both parts of this polyurethane which are made by Bayer Co., Germany, are summarized in Table 2. Also Butyl Ester Glycol and Xylene as solvents are purchased from BASF Co., Germany.

For substrate, a carbon steel sheet ST-37 is used. This type of steel enjoys hardness of 140–150 Vickers and strength of 42–45 kg/mm^2 with the mixture of 99.5% of iron and 0.2% of Carbon in Pearlite and Ferrite microstructure.

Table 2
properties of resin and curing agent.

Acrylic based polyol resin (Desmophen A 650)	OH content	2/9 ± 0.4%
	Solid percent	65%
	Acid number (mgKOH/g)	7.5 ± 2.5
	Avg. molecular weight	586
Curing agent (hexamethylene diisocyanate) (desmodur N 75 BA/X)	NCO content	16.5 ± 0.3%
	Solid percent	7.5 ± 1
	Avg. molecular weight	255

2.2. Preparation of coating samples

Preparation of nano-Silica/polyurethane composite solutions and applying them on the surface of carbon steel are carried out as follows.

The first step is to mix fumed and precipitated nano Silica powder with the weight percentages of 2 and 4 in the Butyl Glycol Acetate solvent, which is done by a magnetic mixer rotating 1500 rpm, until reaching a smooth and homogenous solution. The volume of the solution is 100cc. This solution is called Silica sol.

In the second step, Silica sol is added to the acrylic based polyol resin by weigh percentages of 1, 2, 4 and 6 according to Eq. (1) and mixing is done by a rotation speed of 3000 rpm. The volume of the solution is 250cc. The resultant mixture is a composite resin.

$$\begin{pmatrix}\text{wt.\% of}\\ \text{nano Silica}\end{pmatrix} = \frac{\begin{pmatrix}\text{Sol}\\ \text{weight}\end{pmatrix} \times \begin{pmatrix}\text{solid}\\ \text{percent}\\ \text{of sol}\end{pmatrix}}{\begin{pmatrix}\text{Sol}\\ \text{weight}\end{pmatrix} \times \begin{pmatrix}\text{solid}\\ \text{percent}\\ \text{of sol}\end{pmatrix} + \begin{pmatrix}\text{Resin}\\ \text{weight}\end{pmatrix} \times \begin{pmatrix}\text{solid}\\ \text{percent}\\ \text{of Resin}\end{pmatrix}} \quad (1)$$

In the final step, a specific amount of curing agent is added to the composite resin such that the ratio NCO/OH = 1.2 is met. Then the final mixture is prepared for spraying operation.

PS1, PS2, PS4 and PS6 are named, respectively, for contents of 1, 2, 4 and 6 wt.% precipitated nano Silica while FS1, FS2, FS4 and FS6 are coded, respectively, for contents of 1, 2, 4 and 6 wt.% fumed nano Silica. It should be mentioned that a sample with no nano Silica is used as the reference.

The prepared solutions are sprayed on the surface of the carbon steel which has already been pre-treated by sand paper (No. 100) for 2 min. The drying process is carried out in 2 steps, such that in the first step it was subjected to the room temperature for 24 h and then transported to the oven with temperature of 50 °C, finally it was maintained at room temperature in a closed environment for the next experiments.

2.3. Characterizations and measurements

To investigate the size distribution of Silica nanoparticles in the background of acrylic based polyol, zeta sizer device is used which is a product of Malvern Co., England. and the process is done according to ISO2009:13320 standard.

A Turbidity Meter, Turbidimeter 2100 AN, Hach Co., USA, is used in order to measure the level of turbidity of different solutions by