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Acidic hydrophobic nanosilica particle-induced mechanical dissipation and adhesion promotion of acrylate-based photopolymeric nanocoatings

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ABSTRACT

In this paper, some photopolymeric nanocoatings with various contents of the hydrophobic nanosilica were prepared to be chosen for the morphological assessments and the mechanical dissipation behavior. When the nanosilica content was increased, both the glass transition temperature and the cross-link density of the coating decreased. It showed that the photopolymerization-induced structurally heterogeneous domains formation like microgel domain was reduced with addition of the nanosilica particles. The mechanical dissipation nature and the adhesion energy of the nanocoatings were determined to be higher than that of the coating without the nanosilica. This corresponded to the reduction of the internal stress caused by the photo-cure shrinkage because of the surface acidity nature of the nanosilica particles.

1. Introduction

The photopolymeric materials have been well-known as a category of the products possess a variety of the controversial arguments in the base. These complexities have corresponded to different dynamic and structural heterogeneities in this kind of materials [1–3]. The existence of these heterogeneities like chemical defects such as dangling chain, unreacted potentially-reactive sites and linear chain extension make it difficult to be well-informed about structure-property relationships leading to some unsolved problems [4,5]. So, there has been a great deal of interest in this research area to solve these problems in order to better material engineering. The main reason of the presence of different types of the heterogeneities in the final polymeric network is high photopolymerization reactions rate [6–8]. In spite of these enormous sophisticated matters can be present in this field, using this approach as a coating application technique has attracted a lot of attention in different coating usages for instance automotive industry, coil coating process, functionalized coatings so on. In recent years, many attempts have been focused on the characterization of the mechanical properties photopolymeric coatings to find useful structure-property relationships [9–11]. Recently, Kannurpatti et al. [12] found that the photopolymerizable systems contain two dynamically extreme regions namely "microgel domain" and "a pool of unreacted components". Previously, we demonstrated that the photopolymeric coatings possess some microgel domains as the hard segments self-dispersed in a soft matrix with more large-range molecular relaxations [13]. In our previous work [14], we proposed a theoretical description on the basis of the "trumpet model" proposed by de-Gennes's [15] to explain the physics of the adhesion of the photopolymeric coatings to the elastic surfaces. We were able for the first time to predict the adhesion energy of the photopolymeric coatings as a function of the dynamic and structural heterogeneity. We revealed that the dependency of the adhesion energy on the dynamic heterogeneity is itself dependent on the relaxation time of the photopolymeric network. If the relaxation time is small, the lower dynamic heterogeneity improves the adhesion properties.

In this study, we aimed to study the effect of the surface acidity of the hydrophobic nanosilica filler on the adhesion performance of the final nanocoating. The mechanical dissipation nature and the morphological evolutions as a function of the nanosilica content were studied. The impact of the nanosilica particles on the

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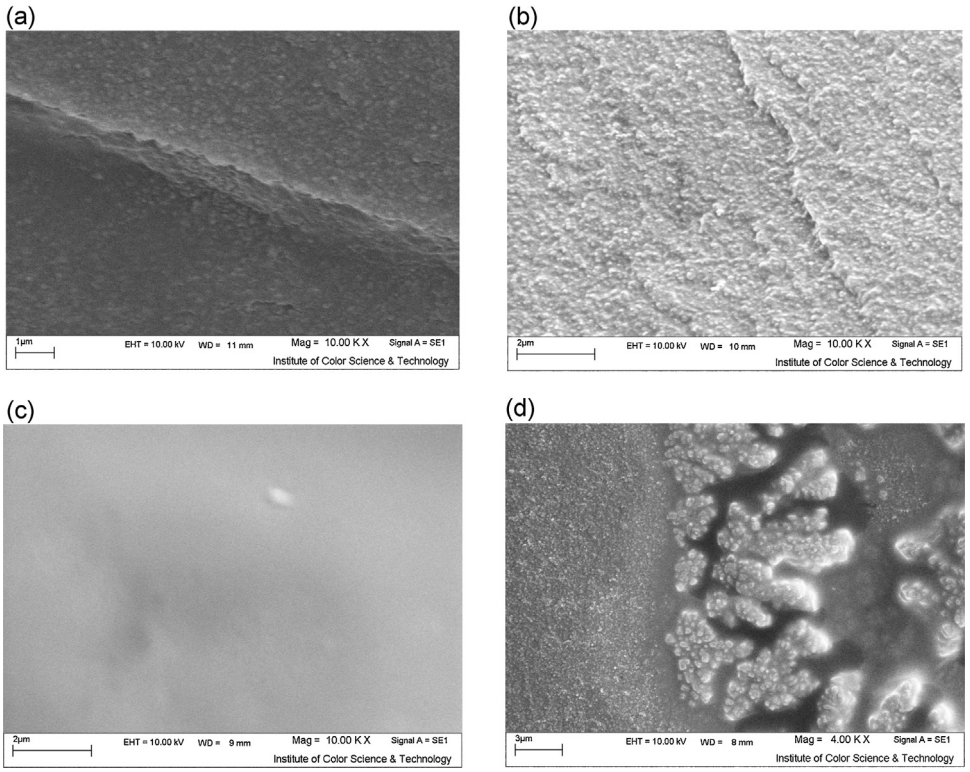

Fig. 1. The SEM micrographs obtained for the nanocoatings with various nanosilica contents: (a) blank coating, (b) 1 wt%, (c) 2 wt% and (d) 3 wt%.

Table 1
Some characteristics corresponding to the nanosilica.

nanoparticle	Primary particle size (nm)	BET surface area (m^2/g)	pH value	Surface groups
Aerosil R 972	16	110 ± 10	3.6–5.5	methyl

structural heterogeneity and the microgelation process in different nanosilica concentrations was evaluated.

2. Experimental

A urethane acrylate pre-polymer with aliphatic structure was purchased from Eternal Company. The weigh averaged molecular weight and the glass transition temperature of this pre-polymer reported by supplier about 2000 g/mol and 35 °C, respectively. Hexandioldiacrylate (HDDA) as a di-functional monomer was used to add into the flexible urethane acrylate pre-polymer for preparing the photo-polymeric sample.

Liquid benzophenone was employed as an H-abstraction photo-initiator. This photo-initiator was supplied from Insight Company without any purification. Using *N*-methyl di-ethanol amine as an amine synergist was necessary in photo-polymerization process. This material was delivered from Rahn Company. The percentage of the photo-initiator system in the photo-curable mixtures was five. A photo-curable mixture containing 1 part monomer and 3 parts pre-polymer in weight percentage was prepared.

A hydrophobic grade of nano-SiO_2 filler (Aerosil R 972) was purchased from Evonic Co. to prepare photo-cured nanocoatings. Some characteristics of this grade of nanosilica are listed in Table 1.

Four concentrations of nanosilica filler including 1, 2, 3 and 5 wt% in order to preparation of the nanocoating samples were used. A three-roll mill (Exakt, China) for about thirty minutes was utilized to disperse nanosilica particles in the photo-curable formulation.

A home-made UV curing oven was exploited to solidify the liquid photo-curable casted films of two thicknesses of 1 mm and 30 μm. These films were exposed to a 33 W/cm UV lamp which has a distinct peak at 365 nm for about 60 s at room temperature. The used curing oven is formed from two different parts namely the illuminator and the sample holder box. To prohibit ageing process of the samples, the mechanical and morphological tests were immediately conducted after sample preparation.

Some rectangular blocks of 1 mm thickness were utilized as the samples used for the dynamic mechanical measurements. A dynamic mechanical analyzer (Tritec 2000, America) was used at a scan rate of 5 °C/min at 1 Hz as the applied frequency. An initial strain of 0.2% was used for the start-up of the oscillation process.

A LEO 1455VP scanning electron microscope at an acceleration voltage of 10 kV was utilized to characterize the structural heterogeneity features of the samples and the presence of the microgel domains (if any).

A Deflesko pull-tester (England) was employed to measure the adhesion energy of the coatings with 30 μm of thickness to the metallic substrates (st-37). A stress rate of 1 MPa/s was used to pull the specimens and the adhesion strength was measured as the final data.

3. Results and discussion

3.1. Morphological and mechanical dissipation measurements

The SEM micrographs obtained for the photo-cured nanocoatings with various concentrations of nanosilica are displayed in Fig. 1.

The dependency of the morphological features of the samples on the nanosilica content is completely clear. It is observed that when just 1 wt% of nanosilica is added to the coating, the fractured surface becomes strangely smoother and there no exist special heterogeneities or aggregated domains throughout the film. This reveals

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