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Improving the mechanical properties of waterborne nitrocellulose coating using nano-silica particles

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ABSTRACT

In this study several nitrocellulose emulsions containing different percentage of nano-silica particles were prepared, and the effect of different content of nano-silica particles on the drop size, morphology and stability of nitrocellulose emulsions as well as optical and mechanical properties of the resultant films was investigated. Incorporation of nano-silica particles up to 2% not only did not adversely affect the properties of nitrocellulose emulsions and appearance of the formed films but also the glass transition temperature (Tg), storage modulus, tensile strength, elongation at break, Young's modulus and pendulum hardness all increased with increasing nano-silica particles content. High content of nano-silica particles (3% and 4%) surprisingly resulted in emulsion phase inversion from oil in water emulsion (O/W) to water in oil emulsion (W/O). Theses phase inversions were attributed to the presence of the nano-silica particles at the oil-water interface which conducted the large variation in the affinity of stabilizers. Formation of multiple drops prior to phase inversion indicated that catastrophic phase inversion was responsible for these inversions. In comparison with bare nitrocellulose film, at 2% nano-silica particles, the Young's modulus increased by 91.1%, the tensile strength increased by 46.6%, elongation at break increased by 12.7%, the Tg increased from −7.3 °C to 6.8 °C, and pendulum hardness increased from 31 to 40. The results demonstrated a homogenous dispersion of nano-silica particles in the nitrocellulose resin matrix and strong interfacial interaction of the nano-silica particles with the nitrocellulose resin matrix which caused improvement in mechanical performance of waterborne nitrocellulose coating.

1. Introduction

As a film former, nitrocellulose (NC) is used widely in different industries such as leather, food packaging, inks and wood coating due to rapid drying, compatibility with other polymers, good mechanical properties and pigment dispersion and its degradability by microorganisms [1,2]. Moreover, regarding to environmental issues in recent years, the biodegradability of nitrocellulose highlights its great potential as an alternative for non-biodegradable polymers [3–8]. Nowadays, however, using nitrocellulose emulsions (waterborne nitrocellulose) has attracted much attention because of restriction on the use of solvents and the implementation of VOC (volatile organic solvent) directive. In addition, emulsions provide several advantages such as independency of viscosity to molecular weight, non-flammable, very low odor, easy application using conventional equipment, ease of clean up, and improved recoatability [9,10]. However, waterborne systems have some drawbacks, such as poor storage stability, poor mechanical properties and high water sensitivity of films, which have restricted its extensive application [11,12].

In recent years, enormous efforts have been made to develop new waterborne coating with better performance. Recent findings have shown that incorporation nano-particles can play a significant role in the modification of waterborne coating [13–18]. Various nano-particles, such as SiO_2, TiO_2, ZnO, Fe_2O_3 and Al_2O_3 are the examples of the nano-particles which have been used in the coatings [18]. It has been found that nano-silica particles can significantly enhance the performance of waterborne coating from the stand point of mechanical strength and durability. Ahmad Dashtizadeh et al. studied the mechanical and optical properties of acrylic based waterborne coatings containing nano-silica particles [19,20]. It was shown that addition of nano-silica particles caused an improvement in the hardness and solvent resistance of acrylic based waterborne coating. Limin Cheng et al. reported that waterborne polyurethane/nanosilica composites exhibited a remarkable improvement in the mechanical strength, thermostability, water resistance, and UV absorbance compared with conventional waterborne polyurethane coatings [21]. Dongmei Wu et al. modified mechanical performance of conventional waterborne polyurethane by adding nano-silica particles [22]. Zhaofeng Wu et al.

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showed that both water resistance and mechanical properties of hybrid films of waterborne polyurethane and fluorinated polymethacrylate were improved significantly in the presence of the nano-silica particles [23]. To the best of our knowledge, there is no systematic research concerning the mechanical properties of waterborne nitrocellulose/silica composites.

In the previous study, stable waterborne nitrocellulose (with nano size drops) was successfully prepared using gel emulsification method [24]. The aim of this work is studying the effects of nano-silica particles on mechanical and optical properties of waterborne nitrocellulose clear coats. In this regard, nanocomposites were prepared using various loadings of nano-silica particles. First, we investigated the effect of nano-silica particles content on the drop size and stability of nitrocellulose emulsions and then morphological and mechanical properties of the resultant films.

2. Materials and methods

2.1. Materials

Nitrocellulose flake containing 11 ± 0.5% of nitrogen provided by Parchin Co. *n*-butyl acetate (products of Merck) was used as the solvent of nitrocellulose. The nonionic surfactant NP-40 (Nonylphenol Polyethylene Glycol Ether 6) used here was chemical grade (product of Kimyagaran Emrooz chemical IND.CO. Iran). Hydrophobic nano-silica particles (Aerosil R 972) having a specific surface area of 90–130 m^2/g and particle diameter of 16 nm were supplied by Degussa Co.

2.2. Preparation of nitrocellulose/silica composites (dispersed phase)

i To prepare nitrocellulose solution, 50 g nitrocellulose was soaked in 115 ml *n*-butyl acetate for 24 h and then they were mixed and stirred thoroughly at speed of 2000 rpm
ii To prepare the pre-dispersed nano-silica particles (dispersed in *n*-butyl acetate solvent), different weight contents (1%, 2%, 3% and 4% w/w nitrocellulose) of hydrophobic nano-silica particles were dispersed in 115 ml *n*-butyl acetate and then homogenized by ultrasonic (Hielscher, UP400S model), operating at 45 kHz, for 20 min
iii The pre-dispersed nano-silica particles (dispersed in *n*-butyl acetate solvent) were added to the nitrocellulose solution and then were mixed by conventional mixer at 2000 rpm for 60 min. This represented dispersed phase.

2.3. Preparation of waterborne nitrocellulose/silica composites

In this study gel emulsification method (as an energy efficient method) was used to prepare waterborne nitrocellulose [24]. This approach encompasses two steps; in the first step, 280 ml of dispersed phase was added to the small fraction of aqueous phase (31 ml water containing NP-40 (6% w/w of the whole water)) under continuous stirring to make concentrated emulsion with high dispersed phase volume fraction ($\Phi = 90$). The concentrate emulsion was then diluted with 89 ml water containing no surfactant in the second step to make target emulsion with $\Phi = 70$. Emulsions were made in 1-lit glass reactor (10 cm in diameter). A mechanical mixer was used to rotate 4-blade impeller, 5 cm in diameter at 2000 rpm during emulsification and the addition rate of dispersed phase to the continuous phase was 5 ml/min. Emulsification was carried out at 25 ± 2 °C. Fig. 1 shows schematic representation of emulsification process.

2.4. Stability and characterization of emulsions

2.4.1. Drop size measurement

Drop size was measured using laser diffraction method by Malvern master sizer 2000 with range of 0.02 μm − 2000 μm. The mean drop size was calculated from the particle size distribution. The specimens were dissolved in a 0.6 wt% SDS (sodium dodecyl sulfate) solution before measurement to reduce drop concentration and stabilize the dilute emulsion. The mean volume-surface diameter, d_{32}, defined as:

$$d_{32} = (\Sigma N_i d_i^3)/(\Sigma N_i d_i^2) \quad (1)$$

where N_i is the number of drops with diameter d_i.

2.4.2. Stability

Final emulsions were poured into measuring cylinders and were stored in oven at 40° C (to accelerate breakdown process). Stability of emulsions was assessed by visual observing samples as a function of time. The release of the oil phase was used as an indicator of the end of the stability. The period of stability (hours or days) was considered as a criterion to measure emulsion stability.

2.4.3. Emulsion type

Emulsion type was determined by the conductivity of the emulsions which was determined using a digital conductivity meter and also by observing what happened when a drop of each emulsion was added to a volume of either pure oil or pure water. Oil in water (O/W) emulsions dispersed in water and remained as drops in oil, while water in oil (W/O) emulsions dispersed in oil and remained as drops in water [25].

2.5. Preparation of nanocomposite films

Portions of formed emulsions were applied onto the surface of Preplex plates. Films were dried under controlled conditions (25 ° C and 50% relative humidity), and dried films were peeled and stored at 25 ° C and 50% relative humidity. The thickness of the free films was randomly measured at three different locations using a micrometer (Mitutoyo, Tokyo,Japan). All films approximately had the same thickness (0.4 ± 0.05 mm).

2.6. Characterization of nanocomposite films

2.6.1. Morphological characterization of the films

The quality of nano-silica dispersion in the nitrocellulose coating matrix was studied by SEM microscope (LEO 1455VP). The fracture surface of the samples was sputter coated by gold prior to analysis.

2.6.2. Thermal characterization of the films

Tg and storage modulus of the nanocomposite films were determined by dynamic mechanical thermal analyzer (Tritec 2000). Samples were made by cutting films into strips about 1.5–2 cm long and 7.5–8 mm wide. Samples were tested in tension while being heated from −20 to 100° C at frequency of 1 Hz and heating rate of 5 ° C/min according to ASTM E1640(2002).

2.6.3. Tensile test

Tensile tests were performed using an Instron dynamometer instrument at 25 ° C and 50% relative humidity according to ASTM D882-02 (2002) on free films, having length and width of 120 mm, 25 mm respectively, at a crosshead speed of 2 mm/min.

2.6.4. Hardness

The hardness of surfaces on the glass plate was tested with a BYK-Gardner GMBH pendulum hardness tester according to ASTM-D 4366 (2002) standard as follows: the panel table was moved to its limit stop. The pendulum deflected through 6◦ and locked in its position. Then it was released and the number of oscillations identifies the damping time of surfaces by changing to the second unit. The damping time required to slow the oscillation down from 6◦ to 3◦ by using the adjusting glass plate, should be 250 ± 10s.