Progress in Organic Coatings 97 (2016) 288–300

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Acrylate hybrid nanocomposite coatings based on SiO_2 nanoparticles by *in-situ* batch emulsion polymerization

Angel Romo-Uribe[a,*], Jose Antonio Arcos-Casarrubias[b], M Lizbeth Hernandez-Vargas[a], Adriana Reyes-Mayer[a], Manuel Aguilar-Franco[c], Jamil Bagdhachi[d]

[a] *Laboratorio de Nanopolimeros y Coloides, Cuernavaca, Morelos 62230, Mexico*
[b] *División de Ingeniería Química y Bioquímica, Tecnológico de Estudios Superiores de Ecatepec, Av. Tecnológico s/n esq. Av. Hank González, Ecatepec, Estado de México 55210, Mexico*
[c] *Lab. Central de Microscopia, IFUNAM, Mexico DF 04510, Mexico*
[d] *Coatings Research Institute, Eastern Michigan University, Ypsilanti, MI 48197, USA*

ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form 12 April 2016
Accepted 16 April 2016

Keywords:
Acrylates
Nanocomposites
Coatings
Nanosilica
Polymerization

ABSTRACT

Waterborne acrylate/SiO_2 nanocomposites were synthesized by *in situ* emulsion polymerization using batch process. Polymethyl methacrylate (PMMA), acrylic acid (AA) and butyl acrylate (BA) were copolymerized in the presence of nanosilica particles of 7 nm size. Nanosilica was added up to 3% g/g and the emulsions thus obtained were stable for at least 6 months in storage at room temperature. The results showed that when the concentration of nanosilica was increased, the degree of conversion decreased, and the percent of coagulum slightly increased. Interestingly, in the presence of nanosilica the latex particle size continually decreased as the polymerization reaction progressed until reaching a nearly constant value of ~150 nm. Conversely, the neat acrylic latex particles exhibited the typical continuous increase of particle size as polymerization time increased. Steady shear rheology showed that the viscosity of the nanostructured emulsions was shear thinning, exhibiting a power-law behavior. As cast coatings were optically transparent and no evidence of aggregation was detected by SEM and AFM, and EDS analysis confirmed the presence of silica throughout the coatings. The nanosilica induced significantly higher thermal stability, as decomposition temperatures, T_{dec}, of the nanostructured acrylics increased by as much as 40 °C relative to the neat acrylic. The glass transition temperature T_g was increased up to 10 °C at only 1 wt% SiO_2 nanoparticle concentration, but at higher concentrations it was slightly reduced. As cast films exhibited higher shear modulus and shift of maximum of tan δ denoting a modification of macromolecular dynamics by the SiO_2 nanoparticles. The results are contrasted with those obtained on acrylate-SiO_2 coatings with equal formulation but polymerized by semi-batch process (Romo-Uribe et al., 2016).

1. Introduction

The use of waterborne acrylate latex coatings is widespread due to their excellent durability, toughness, optical clarity, UV stability, color retention and environmental friendliness, especially in view of current worldwide restrictions on solvent-based coatings which favor low volatile organic compounds (VOC) coatings [1,2]. The most popular areas of application of acrylic coatings are architectural, metal protection, wood, decorative and business machines [3].

Hybrid polymer nanocomposites consist of an organic polymeric matrix and inorganic fillers with dimensions at the nanometer scale [4–8]. It has been reported that small percentage (<5 wt%) of nanoparticles embedded in a polymer matrix can exhibit significant improvement in material properties. For instance, mechanical properties (e.g., hardness, tensile modulus), thermal stability, flame retardancy, and gas barrier properties improve relative to the neat polymer, thus opening opportunities in high performance applications like automotive, electronics, and aerospace [9]. It has also been established that key properties in polymer nanocomposites are the dimension (e.g., aspect ratio) and degree of dispersion of the nanofillers in the polymer matrix [10]. Therefore, different approaches are being investigated for the production of nanocomposites, either chemical which involves in-situ

---

* Corresponding author. Present address: Advanced Science & Technologies Division, JJVC, Johnson & Johnson, USA.
E-mail address: aromouribe@gmail.com (A. Romo-Uribe).

http://dx.doi.org/10.1016/j.porgcoat.2016.04.013
0300-9440/

Nomenclature

AA	Acrylic acid
AFM	Atomic force microscopy
APS	Ammonium persulfate
BA	Butyl acrylate
DSC	Differential scanning calorimetry
EDS	Energy dispersive spectroscopy
FTIR	Fourier-transformed infrared spectroscopy
G'	Elastic shear modulus
G''	Viscous shear modulus
MMA	Methyl methacryate
SEM	Scanning electron microscopy
$\tan\delta$	Mechanical damping [=G”/G’]
T_{dec}	Decomposition temperature
T_g	Glass transition temperature
TGA	Thermogravimetric analysis

polymerization or physical which involve blending of components in solution or molten state [11].

The efficient dispersion of nanoparticles in a polymer matrix is difficult due to its tendency to aggregate in micrometer-scale clusters giving rise to traditional polymer composites. In-situ polymerization, which involves the grow of polymer chains in the presence of nanoparticles, is an attractive approach as dispersion of nanoparticles can be initially attained by use of appropriate conditions (e.g., solvents, surfactants). Suspension, mini- and emulsion polymerization are the most attractive synthetic routes [11,12], with emulsion polymerization being the most favored [13].

The number of inorganic nano-particles added to polymeric coatings has increased over the years including but not limited to nanoclays [14,15], nano-oxides [16–21], carbon nanotubes [22], and polyhedral oligomeric silsesquioxanes (POSS) [4,6,8,23].

Inorganic SiO_2 nanoparticles are commonly used reinforcers in polymeric coatings, especially acrylic coatings. The interest has grown thanks to their effectiveness to improve the physical properties of neat acrylates. For instance, Khalina et al. [24] reported up to 200% increase in storage shear modulus and up to 300% increase in tack resistance adding only up to 4 wt% nanosilica. On the other hand, Pishvaei and Tabrizi [25] reported an increase of thermal decomposition temperatures of 8 °C adding only 5 wt% nanosilica [25]. Zhang et al. [26] reported for acrylate-SiO_2 nanocomposites a reduction of conversion and increase of coagulum as concentration of nanosilica increased up to 15 wt%. Furthermore, water absorption of as-cast coatings first reached a minimum at 5 wt% nanosilica and then more than double at 10 and 15 wt% indicating that about 5 wt% was the optimum concentration to produce low water absorption coatings. Asua and coworkers reported acrylate latexes filled with SiO_2 at 20% solids and adding 20% nano-SiO_2 using mini-emulsion polymerization. Those authors reported an increase of glass transition temperature and a three-fold increase in hardness [27]. In this regard, the synthesis of nanostructured acrylates-SiO_2 coatings has also been investigated in our Group utilizing 3-(trimethoxysilyl) propyl methacrylate, MPS as compatibilizing agent, and seeded batch emulsion polymerization [28]. The results showed a five-fold increase in mechanical modulus of film coatings.

Surface modification of nanoparticles however is usually tedious, energy-consuming and conveys additional costs, which are a hurdle to large-scale production and commercialization. Therefore, the synthesis conditions for acrylates based on methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA) in presence of inorganic nanoparticles (alumina, silica, clay and TiO_2) with no surface treatment have been a main focus of investigation in this Laboratory. Furthermore, the syntheses routes to obtain nanostructured acrylate coatings have been researched utilizing seeded batch [29–31] and semi-batch emulsion polymerization [32]. The aim is to contrast the polymerization method with latex characteristics (e.g., conversion, coagulum, particle size) and physical properties (e.g., emulsion viscosity, thermal stability, mechanical modulus). For the sake of comparisons, the acrylate composition and solids content have been kept constant.

Polymerizations utilizing batch and semi-batch techniques have been applied to the *same* system. This approach was proved valuable to get insight into the efficiency of grafting of styrene onto polybutadiene lattices [33], significant differences in degree of grafting were obtained by following these two routes. This approach was also used to determine the influence of polymerization route on the final morphology of acrylonitrile-styrene-acrylate latexes [34], core-shell versus raspberry morphologies were obtained. Moreover, batch and semi-batch syntheses were utilized to determine copolymer composition control in acrylamides [35], and to determine modelling parameters of emulsion polymerization using kinetics data from the batch process to simulate the semi-batch process [36,37]. As those reports have shown, it is difficult *a priori* to determine the efficiency and outcome of one polymerization process versus another.

It is reported that semi-batch emulsion polymerization enables better control of molecular weight, particle size and polymerization rate [2,3]. Indeed, our previous report is in agreement [32]. Thus, relative to the semi-batch process where SiO_2 nanoparticles and monomers (BA, MMA, AA) were gradually added to the reactor, it would be expected that the utilization of batch polymerization would reduce conversion and increase coagulum due to hindrances afforded by the presence of nanosilica particles. For the same reasons, it is also likely to have less control on molecular weight. However, it is unclear what the physical properties of coating films would be when using batch process.

Therefore, this research focused in the synthesis of acrylate emulsions using *untreated* SiO_2 nanoparticles and seeded batch emulsion polymerization. The influence of nanoparticle concentration on conversion, latex particle size, coagulum, viscosity of the emulsion and morphology and thermo-mechanical properties of films cast from the emulsions has been investigated. These results are contrasted with those obtained from the same system but polymerized by semi-batch process [32]. We are not aware that this approach has been utilized in nanostructured acrylate emulsions at high solids content.

2. Experimental

2.1. Materials

Fumed SiO_2 nanoparticles with an average diameter of around 7 nm were purchased from Aldrich Chemical Co. Butyl acrylate, BA [$CH_2=CHCOO(CH_2)_3CH_3$, with 10–60 ppm monomethyl ether hydroquinone, MEHQ inhibitor], methyl methacrylate, MMA [$CH_2=C(CH_3)COOCH_3$, with $\leq$30 ppm MEHQ inhibitor] and acrylic acid, AA [$CH_2=CHCOOH$, with 180–200 ppm MEHQ inhibitor] monomers were acquired from Aldrich Chemical Co. The monomers were purified using an inhibitor remover for MEHQ prior to polymerization using a prepacked column for removing hydroquinone and monomethyl ether hydroquinone acquired from Sigma Aldrich Co. The initiator, ammonium persulfate (APS) [ULTRAPURE BIOREAGENT, (NH4)2S2O8] was acquired from J.T. Baker. The surfactant ethoxylated nonylphenol sulfate ammonium salt (trademark Surfacpol 9010-S, 30% solid content in water) was purchased from Polaquimia, S.A. de C.V. (Mexico D.F., Mexico) Ammonium hydroxide was used as neutralization agent. Deion-