Journal of Industrial and Engineering Chemistry 20 (2014) 1623–1632

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Nano-SiO_2/fluorinated waterborne polyurethane nanocomposite adhesive for laminated films

Heqing Fu *, Caibin Yan, Wei Zhou, Hong Huang

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 4 May 2013
Received in revised form 26 June 2013
Accepted 5 August 2013
Available online 1 September 2013

Keywords:
Empirical model
Waterborne polyurethane
Nanocomposite adhesive
Laminated films
Adhesion strength

ABSTRACT

High performance nanocomposite adhesives used for the laminated films were synthesized. The effects of nano-SiO_2 and HFBMA contents on the properties of SiO_2/FWPU nanocomposite adhesive were investigated by the static contact angle measurement, X-ray photoelectron spectroscopy, atomic force microscopy, thermogravimetric analysis and tensile test machine. It proved that the wetting behavior, water resistance and thermal stability of nanocomposite adhesive had effect on the adhesion of the nanocomposite adhesive for low surface energy materials. And an empirical equation, $T = e^{32.04} \times \gamma_L^{-8.08} \times \gamma_S^{0.45}$, revealing the relationship among adhesion strength (T), surface tension of adhesive (γ_L)and the surface energy of adhered substrate (γ_S)was obtained.

1. Introduction

Nonpolar polyolefin films, such as polyethylene (PE), biaxially oriented polypropylene (BOPP) and cast polypropylene (CPP), are widely used in the soft package of food, medicine, household and so on. In order to fit the need of soft packages, these films should be adhered together by adhesive [1]. However, they are difficult to bond due to their nonpolarity and low surface free energy. Therefore, the surface polarity of polyolefin films need to be improved. Some methods, such as plasma, corona discharge, electronic radiation, acid etching and so on, appear to improve the surface polarity of polyolefin films [2–7]. Particularly the corona discharge method appears to be the most convenient approaches. When polyolefin films were treated by the corona discharge, the carbonyl groups and carboxyl groups were generated on the surface of polyolefin films, their surface polarity can be improved and their surface energy can be enhanced to 38–40 mN/m [8].

The solvent-borne polyurethane (PU) adhesive is widely used due to the excellent adhesive strength, water resistance and thermal stability. However, its use in the laminated soft package industry is restricted for emission of volatile organic compound (VOC) causing problems like toxicity, flammability and pollution. Waterborne polyurethane (WPU) adhesive overcomes these problems, and thus takes the place of the solvent-borne PU adhesive in the laminated soft package industry [9,10]. However, the poor wettability, heat resistance, and inferior water resistance of the WPU, it needs to be modified to ensure its application in the soft package.

Nano-SiO_2 is often used in polymer composites [11–14]. For this purpose, its compatibility with the polymer matrix should be modified. Different surface modifiers such as coupling agents, surfactants, aliphatic acids, and so on, have been used in surface modification of nano-SiO_2 [15–18]. Among them, the silane coupling agents are one of the best due to the alkoxy groups of silane coupling agent are able to react with the surface silanol groups of nano-SiO_2, and the organic functional groups which contained amino, epoxy and acrylic functionality, can react with the –NCO groups in the PU chains. The formation of stable chemical linkages between the nano-SiO_2 and the polymer improve the heat resistance, radiation resistance and mechanical properties of WPU.

On the other hand, fluorine acrylic has relatively low surface energy due to the low polarizability and the strong electronegativity of fluorine atom [19–21]. Fluorine acrylic is widely used in the fluorinate waterborne polyurethane (FWPU) hybrid emulsion via emulsion polymerization. Compared to the conventionally prepared WPU dispersion, the FWPU hybrid emulsion exhibits good wettability to the low surface energy substrates. In addition, the surface properties of the FWPU films can also be significantly improved with the incorporation of fluorinate acrylic.

Theoretically, multiple approaches have been given to explain the complex adhesion mechanism, including the absorption

* Corresponding author. Tel.: +86 20 87114919; fax: +86 20 87112047.
E-mail address: fuhq@scut.edu.cn (H. Fu).

1226-086X/$ – see front matter © 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jiec.2013.08.009

theory, the electrostatic theory, the diffusion theory, the mechanical bonding theory, the chemical bonding theory, the coordination bond theory, and so on [22–25]. Unfortunately, none of them could completely explain all of the existed adhesion phenomenons due to their limited applying conditions and the complexity of theoretical models. And the adhesion mechanism in the adhesion process is still no clear currently.

Hence, in this work a series of nano-SiO_2/fluorinated waterborne polyurethane (SiO_2/FWPU) nanocomposite emulsions with core–shell particle structure modified by nano-SiO_2 (treated by 3-aminopropyltriethoxysilane) and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA) were synthesized. A high performance nanocomposite adhesive was made through the SiO_2/FWPU nanocomposite emulsion. The influences of wettability, water resistance and thermal stability of nanocomposite adhesive on the adhesion strength were examined.

Although there are some reports about the WPU modified by either fluorinated acrylic or modified nano-SiO_2, there is no report about preparing and characterizing nano-SiO_2/fluorinated waterborne polyurethane (SiO_2/FWPU) nanocomposite adhesive modified by nano-SiO_2 and fluorinated acrylic at the same time. Moreover, the SiO_2/WPU hybrid dispersions were used as seed emulsion and internal reactive macromolecule emulsifier instead of adding traditional emulsifier. As a result, the bad effect of traditional emulsifier defect on the properties of nanocomposites has got rid of.

On the other hand, it proves that the adhesion process of the adhesive to the adhered substrates is a complex physicochemical process, and the adhesion strength depends strongly on the interface interaction between the adhesive and the adhered substrates [26–28]. In relation to these observations, we developed an empirical model that incorporated the adhesion strength, the surface tension of nanocomposite adhesive and the surface energy of adhered substrate together. And a new empirical equation was obtained via multiple linear regressions to present a possible correlation among these three parameters. There is no report about this research.

2. Experimental

2.1. Materials

Nano-SiO_2 (supplied by Degussa, Germany) was modified by 3-aminopropyltriethoxysilane (APTES) through surface chemical modification in situ [15]; isophorone diisocyanate (IPDI), 1,4-butylene adipate glycol (PBA, Mn = 2000), acetone (supplied by Donghao Resine Co. Ltd., China), dimethylol propionic acid (DMPA) (supplied by Perstop, Sweden), ethanol, *n*-methyl pyrrolidone (NMP) and triethylamine (TEA) (supplied by Shanghai Fine Chemical Agent Factory, China), dibutyltin dilaurate (DBTDL) (supplied by Shanghai Lingfeng Chemical Agent Co. Ltd, China), 2-hydroxyethyl acrylate (HEA) and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA) (supplied by Harbin Xeogia Fluorine-Silicon Chemical Co., Ltd.), sodium bicarbonate ($NaHCO_3$) and ammonium persulfate (APS) (supplied by Shanghai Chemical Reagent Co., Ltd.).

2.2. Preparation of the SiO_2/WPU hybrid dispersion

The SiO_2/WPU hybrid dispersions were prepared by prepolymer process, as shown in Fig. 1. A dry 1000 mL four-necked glass reaction kettle equipped with a mechanical stirrer, thermometer, condenser and a nitrogen inlet was placed in a water bath. The stoichiometric PBA was dried at 110 °C for 1.5 h in a vacuum oven, IPDI and the catalyst DBTDL were added into the reactor under N_2 atmosphere, and the reaction was carried out at 80 °C for 2 h. After that, DMPA dissolved in NMP was added into the kettle where the reaction temperature was 75 °C. Then, modified nano-SiO_2 (in weight fraction of 0, 0.5, 1, 1.5, 2 wt%) was added into the reactor to react for 2 h. The reaction proceeded until the residual NCO reached the expected content (determined by the standard dibutylamine back-titration method [29]). After the prepolymer was cooled to 50 °C, HEA was added to end-cap the prepolymer and the reaction continued for 2 h. The carboxylic acid in the prepolymer was neutralized by TEA solution for 30 min at 40 °C to obtain ionomer (before the neutralization, a little amount of acetone was added to adjust the viscosity of the prepolymer). The ionomer was dispersed into the stoichiometric amount of deionized water with vigorous stirring. The SiO_2/WPU hybrid dispersion with a solid content of 30 wt% was finally obtained after removing the acetone by vacuum distillation.

2.3. Synthesis of the SiO_2/FWPU nanocomposite emulsions

The SiO_2/FWPU nanocomposite emulsions were synthesized via seed emulsion polymerization process by using SiO_2/WPU hybrid dispersion as seed emulsion and macromonomer, fluorinated acrylic HFBMA, as presented in Fig. 2. The SiO_2/WPU hybrid dispersion and deionized water were added into a reaction kettle under high speed stirring to obtain a stable emulsion. The pH value of the emulsion was adjusted to 8 by adding $NaHCO_3$. Then, HFBMA was added into the mixture solution with vigorous stirring for 30 min, and the temperature is up to 80 °C. Then the $(NH_4)_2S_2O_4$ dissolved in water with mass concentration of 0.5 wt% was dropped into the reactor in 3 h. After heating for another 2 h, the emulsions were cooled down to 40 °C and the SiO_2/FWPU nanocomposite emulsions were finally obtained. The compositions of SiO_2/FWPU nanocomposite emulsions were shown in Table 1. The nanocomposite adhesives were ultimately obtained by adding predetermined amount of assistants into the nanocomposite emulsions.

2.4. Film preparation

The nanocomposite films were prepared by casting the nanocomposite emulsion on a PTFE mould dried at room temperature for 7 days. Then the films were placed in a vacuum oven at 60 °C for 24 h before characterization.

2.5. Characterization

Differential scanning calorimetry (DSC) analysis was measured by a TA Instruments Q20 DSC analyzer over the range from −60 to 150 °C at a heating rate of 10 °C/min under N_2 atmosphere.

The surface tension of nanocomposite emulsions was measured with the pendant drop apparatus affiliated to the contact angle goniometer (JC2000C1 Powereach®, Shangai Zhongchen) using the pendant-drop method at 25 °C. Samples for surface tension measurement were the polymer solutions in deionized water with different polyurethane content. The reported results were the average of three measurements. While the contact angles were measured by the JC2000C1 using the sessile-drop method at 25 °C. The reported values were the average of three replicates.

The water swelling of nanocomposite films was measured by immersing the nanocomposite films in deionized water, and the degree of swelling was calculated by the following formula:

$$Swelling\% = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m_1 are the mass of dry film and the wet film which immersed in water for 24 h, respectively.