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Preparation and Application of Polyurethane Polymer Modified by Nano Silica

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Abstract

One kind of nano silica was prepared by KH550 and TEOS via sol-gel method, and this kind of nano silica was then applied for modification of solvent free polyurethane used for Paper/Al laminating. The chemical structure and morphology of the nano silica were characterized by FT-IR, SEM and laser particle size analyzer. The mechanical properties of the polyurethane polymer were well studied by Universal tensile testing machine, shore durometer and thermogravimetric analysis. Results indicated that KH550 was successfully synthesized to the nano silica and the particle size of the silica was within sub-micro. The adding of nano silica enhanced the bonding strength of the polyurethane but increased the hardness of the cuing film. Meanwhile too much nano silica with low density was hard to disperse evenly in the film. The content of nano silica should be controlled within 0.8%wt.

INTRODUCTION

With the rapid development of the economy and enhancement of people's awareness of environmental protection, the paper-plastic packaging materials which are easily to post-processing and recycled emerged accordingly [1-2]. The performance of the flexible packaging not only related to the choice of the packaging material, but also on the quality of the adhesive. Polyurethane with excellent cold resistance, flexibility, adhesion strength and other properties is suitable for bonding a variety of flexible packaging. The food packaging bags which need high-temperature sterilization put forward higher requirements for the polyurethane adhesive.

Polyurethanes which are easily to hydrolysis under high temperature and high humidity reduced the bonding strength of the bonding layer of the flexible packaging material. In order to improve the boiling resistance and heat resistance of the polyurethane, many scholars have done a lot of related research [3-9].

Nano-silica has larger specific surface area and highly reactive hydroxyl, can improve the compatibility and bonding forces of polyurethanes. But nanoparticles are not easily dispersed in the polymer due to the small particle size and its higher surface energy. In this paper, the organically modified nano-silica was prepared by sol-gel method, and then as-prepared nano-silica was used to modify the solvent free polyurethane in order to improve the adhesion strength of paper-plastic/paper-Al composite packaging.

EXPERIMENTAL

Experiment materials

Tetraethyl orthosilicate (TEOS), an analytical reagent, was supplied by Guangdong Guanghua Chemical Plant and Couple Agent KH-550, Dibutyltin dilaurate and Isophorone diisocyanate (IPDI) were supplied by Aladdin. Ethanol and 1, 4 butanediol was provided by Guangzhou Donghong chemical plant. Poly-1,4-butylene adipate glycol(PBA, Mn=1230), Polyoxyalkylene propylene glycol ether (PPG, Mn=1000) and Castor oil were all Chemically Pure and purchased from Guangdong Guanghua Chemical Factory. All the materials and solvents were used without further purification.

Preparation of SiO_2 by Sol-gel Method

5mL TEOS was dissolved in ethanol and H2O, and stirred at room temperature for 20min. 3.37mL NH3H2O (1mol/L) was added slowly dropwise to the solution, stirred at room temperature for another 1 h. Then add 4 mL TEOS and 1.6mL KH550 slowly to the above solution. After stirring for 1 h, the solution was put into the centrifugal separator (13000r/min) to eliminate ethanol and H_2O. The product was then put into the vacuum oven at 80℃ for 5h to obtain Nano-SiO_2 which was pre-treated with couple agent (KH-550)

Preparation of NCO component of the adhesive

Added polyester polyols, polyether polyols and castor oil into four mouth flask equipped with a thermometer and stirrer by a certain ratio. After strring in vacuum at 120℃ for 2h, adding IPDI based on certain ratio, then reacting at the atmosphere of nitrogen at 80℃. the amount of NCO groups during the reaction was examined with dibutylamine titration method. As far as the residual isocyanate ester content closing to the theoretical value, ended the reaction.

Preparation of polyurethane adhesive

Nano SiO_2, 1, 4 butanediol, OH component of castor oil and NCO component of the adhesive was mixed in certain ratio, added dibutyltin dilaurate with trace injection, and then the adhesive was put into the ultrasonic dispersion machine for 30 min. The adhesive was then gelatinized with BOPP film (25mm×180mm) and coated paper (180g/m^2) to make composite membranes according to standard GB/T2791-1995. The BOPP/Paper samples were then cured in the oven at 60□ for 72h, which ensured complete cure of the PUA.

Characterization and Measurements

Structure of the nano SiO_2 was recorded with FT-IR (Spectrum 2000, Perkin Elmer); the morphology and particle size of the SiO_2 were researched by Scanning electron microscope (EVO MA10, ZEISS Co. Ltd.). The bonding properties of the adhesive were tested by T-peel strength test method according to GB/T 2791-1995 using Universal tensile tester (2380 type, U.S. Instron). Thermogravimetric analysis [TGA] measurements were carried out with a TGA Q-500 (TA U.S Co. Ltd.), and the platinum pans containing 5-10mg of PU adhesive film were heated from 40□ to 500□ at a heating rate of 10□/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed with a TA Q-200 (TA U.S Co. Ltd.) at a heating rate of 10°C/min from − 100 to 200°C. The shore hardness was tested according to

GB/T531•1-2008 standard measurement with a Shore A durometer (Wenzhou Jingcheng instrument Co., Ltd.)

RESULT AND DISCUSSION

Modified silica

In this study, FT-IR was used to record the structure of the modified nano SiO_2, shown as Figure 1. In the infrared spectrum, the peak at 463 cm^{-1} reveals bending vibration peak of Si-O-Si; 797cm^{-1} and 951 cm^{-1} were the antisymmetric stretching vibration peak and symmetric stretching vibration peak of Si-O-Si respectively; and the absorption peak of Si-OH was at 947 cm^{-1}. The peaks at 1640 cm^{-1} and 3400 cm^{-1} were the bending vibration peak of H-O-H and the antisymmetric stretching vibration peak of O-H. Besides, after the modification, 2971 cm^{-1} appears the absorption peak of Si $(CH_3)_2$ which proves that the silica was successfully modified by KH550.

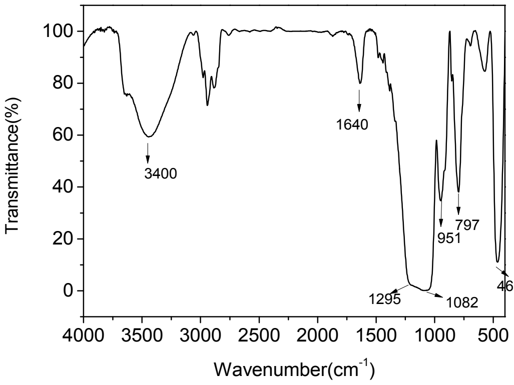

Figure 1. *FT-IR of modified nano SiO_2*

Scanning electron microscope (SEM) system has been applied to identify the morphology and particle size of the nano SiO_2. Specimens were added onto the slide and sputter coated with gold before examining with SEM. As is shown in Figure 2, the particle size distribution of the SiO_2 is between 0.1um to 0.3um, and the microspheres around 0.2 um accounted for 90% of the total. The nano SiO_2 microspheres which were modified via sol-gel method showed good monodispersity with small particle size and uniform distribution. This is because, under alkali catalysis condition, hydroxyl in TEOS initiated nucleophilic reactions and began the hydrolysis reaction; with the removal of alkoxy, electropositive of the silicon atom became more favorable for the nucleophilic attack. The hydrolysis products then condensed from multi-dimensional direction forming spherical particles.

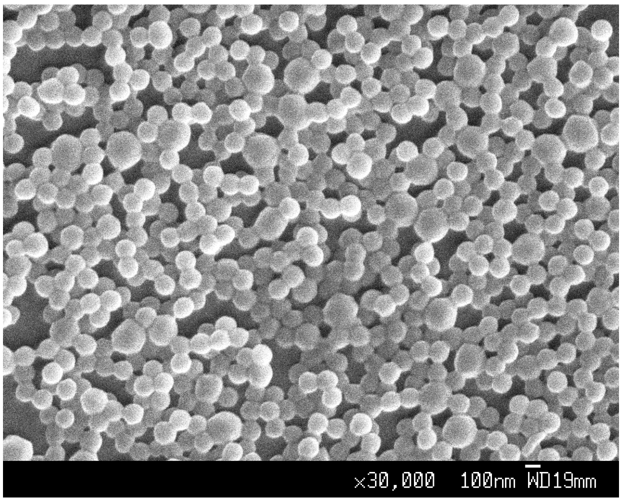

Figure 2. *SEM of modified nano SiO_2*

Characteristics of polyurethane

The study tested the infrared characterization of the adhesive when the addition amount of the modified nano SiO2 was 1.0% wt, shown in Fig.3. In the infrared spectrum of the adhesive, 1735cm-1 and 1458cm-1 were the absorption peaks of NH-COO group. The strong stretching vibration in 1735cm-1 was caused by C=O of ammonia ester bond. The deformation vibration in 1458cm-1 was the characteristic absorption peak of N-H. 3382cm-1 was the stretching vibration of N-H. the asymmetric stretching vibration peak of –NCO in component –NCO at 2260~2280 cm-1 disappeared, which means component OH and NCO reacted successfully and synthesized polyurethane adhesive film.

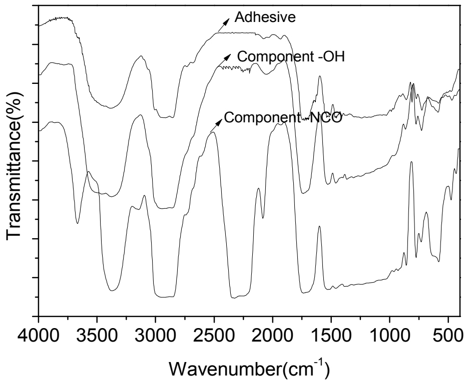

Figure 3. *FT-IR of curing film of the adhesive*

The glass transition temperature of polymerization product could be estimated according to DSC. The polyurethane composed of polyester polyols, polyether polyols, castor oil and IPDI should have been a kind of segmented polyurethane consisting of soft segments and hard segments. The macromolecular chain mainly composed of soft segment should have been segmented by IPDI. The temperature range of the glass transition should have been narrow if the segmentation was well proportioned. In this work, the PUA macromolecule contained silica, which was bonded in the PUA macromolecule.

Figure 4 prove that the temperature range of the glass transition became wider with an increasing amount of the modified silica. This means an asymmetrical distribution of the silica in PUA.

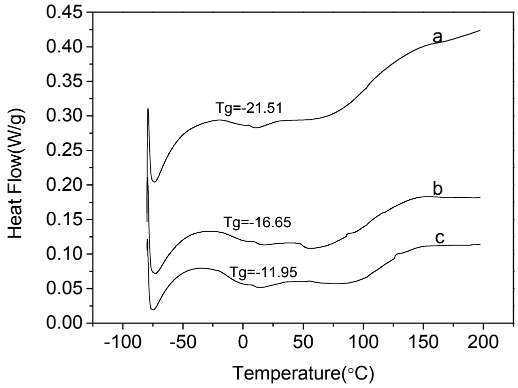

Figure 4. *DSC spectra of PUA with various contents of modified silica: (a) PUA with 0.2%wt silica, (b) PUA with 0.4% wt silica, and (c)PUA with 1%wt silica.*

Mechanical Properties of the nano-SiO2 modified polyurethane adhesive

The study measured the bonding strength, hardness and thermal stability of the adhesive with 0.1%wt silica, 0.2%wt silica, 0.4%wt silica, 0.8%wt silica and 1.0%wt silica, respectively.

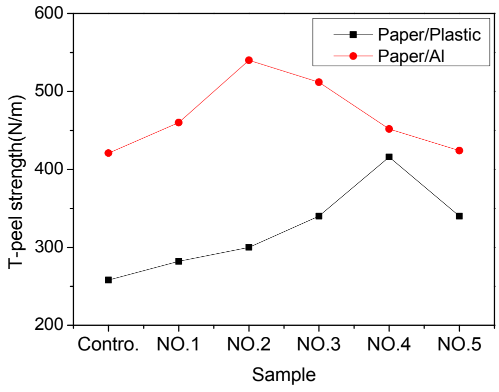

Figure 5. *T-peel strength of the adhesive with various contents of modified silica: (Cortro., NO.1, NO2, NO3, NO4 and NO5 respective the PUA with 0, 0.1%wt, 0.2%wt, 0.4%wt, 0.8% wt and 1.0%wt content of silica)*

Figure 5 presents the T-peel strength of the adhesive with different silica contents used for laminating Paper/Plastic and Paper/Al, respectively. With the addition of modified nano silica, the T-peel strength of the adhesive enhanced accordingly. The modified nano SiO_2 molecular chain contains organic groups $-OC_2H_5$ and inorganic group -Si. When the adhesive was coated on substrates, the -Sitended to the inorganic materials surfaces producing chemical crosslinking and the $-OC_2H_5$ groups approached to the corresponding functional groups of the adhesive causing intermolecular forces. For this reason, the T-peel strength of the adhesive increased after modified with nano SiO_2. But the SiO_2 with low density is difficult to disperse in the adhesive and is easily reunited, so the addition of the SiO_2 must be moderate. The optimum additive of the SiO_2 used for paper-plastic composite and paper-aluminum composite are 0.8wt% and 0.4wt%, respectively.

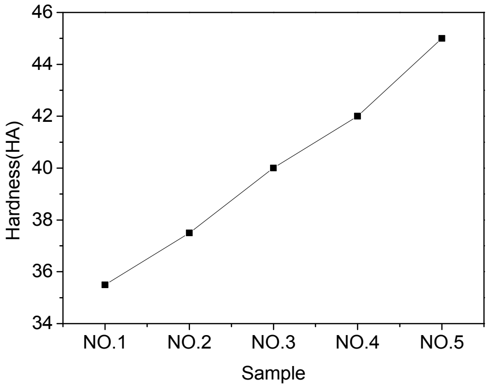

Figure 6. *Hardness of adhesive film modified with SiO_2*

As shown in Figure 6, the hardness of the adhesive films increased with the adding of the SiO_2. From NO.1 to NO.5, the hardness of the adhesive films varies from 35.5 to 45, which means a greater dosage of the modified silica led to a harder surface for the film. Compared with bulk materials, nano SiO2 have many unique properties, such as small size effect, surface and boundary effect, quantum size effect and so on. So they are more easily to spread to the gap of the polymer chain and improved the strength, toughness and ductility of the material greatly. In other word, the rigidity of the molecular chain was enhanced by the hard silica particles chemically bonded in the backbone of PUA, and the mobility of the molecular chain was hindered.

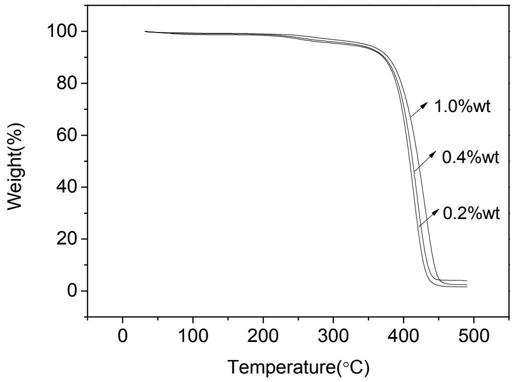

Figure 7. *Influence of modified SiO_2 on adhesive's thermostability*

In addition to the aforementioned effect, the thermostability of the adhesive films, demonstrated in Figure 7, were improved when the concentration of the modified silica was increased.

CONLUSIONS

The nano SiO_2 particles which were modified by KH550 via sol-gel method showed good monodispersity with small particle size and uniform distribution. Chemical bonds were partly formed between KH550 and silica. A kind of PUA adhesive modified with nano silica was obtained. And the rigidity of the molecular chain was enhanced by the hard silica particles. The mechanical properties such as T-peed strength, hardness, thermostability were also improved as the concentration of the modified silica was increased. The optimum additive of the SiO_2 used for paper-plastic composite and paper-aluminum composite are 0.8wt% and 0.4wt%, respectively.

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Qing Wang obtained her masters in Digital printing and green packaging materials at the South China University of Technology in 2014. Now She continued her study in South China University of Technology for her doctor diploma with the focus on the preparation of superhydrophobic printing and packaging materials. The topics include printing and reprography, liquids separation and self-cleaning.