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Preparation and investigation of silica nanoparticles on the lap shear strength of reactive hot melt polyurethane adhesive

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Abstract

A reactive hot melt moisture curable polyurethane adhesive was synthesized and investigated some of its physical and mechanical properties. Nano-silica was used as additive. With the addition of the nano-silica (0.4 w%) the mechanical properties of lap shear strength were improved (from 4.17 MPa at 5.08 MPa).

Keywords: RHMPUA, lap shear strength, NCO/OH ratio, nano-silica, moisture-curing.

Introduction

Reactive polyurethane hot melt adhesives (RHMPUA), which are obtained from the reaction of isocyanates with polyols, do not need a drying process, eliminating environmental pollution and toxicity problems caused by solvents. They react with moisture in the air to form a strong bond that increases adhesion and improves chemical properties. Some RHMPUA can form strong initial bonds in as little as 15 minutes, and most require 24 hours to several days to fully cure. RHMPUA are used in various industries, including footwear, packaging, wood processing, and automobiles, due to their easy and solvent-free processing [1]. The properties of the RHMPUA can be tailored simply with varying the NCO/OH molar ratio and the molecular weight of the polyol. The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO groups and those containing OH groups. According to the literature, for preparing of RHMPUA, it is preferable to use the NCO/OH ratio of the diisocyanate and polyol of about 1.05 to 8. Many studies have been carried out to investigate the effect of the NCO/OH ratio on the properties of polyurethane [2,3]. Traditional polymer composites have high levels of filler loadings, up to 60% by volume. Polymer nanocomposites are being developed with very low loadings of well-dispersed nanofillers, less than 5% by volume. Many studies have been done on polyurethane/nano-silica composites. Adding a small amount (around 5 w%) of nano-silica was found to increase the lap shear strength, abrasion resistance, and tensile properties of the polymer films. However, these mechanical properties worsened at higher of the nano-silica contents [4,5].

Material

Polypropylene glycol (M_n= 1000 g.mol^{-1}), 1,4-butanediol (99%), glycerol (98%) and toluene diisocyanate (TDI, 98%) from Yantai Wanhua Polyurethanes Co., Ltd, China. dimorpholinodiethyl ether (96%) from Baomanbio Co., Ltd, China. Nano-silica (Aerosil200) from Evonik Co., Ltd, Germany.

Experimental

In a typical polymerization, polypropylene glycol (0.575 g, 1 equiv.), 1,4-butanediol (0.220 g, 0.5 equiv.), and glycerol (0.150 g, 0.5 equiv.) were added to a 250 ml reactor with a round bottom, were mixed and dried under reduced pressure (110-120 °C for 2-3 h). The isocyanate calculated for the index [NCO]/[OH]=1.05 (toluene diisocyanate 1.760 g, 2.10 equiv.) along with the dimorpholinodiethyl ether (0.5-1 w%) was added and reacted (for 3-4 h) at a temperature of 60-70 °C under a nitrogen atmosphere until all the calculated isocyanates were consumed, which were measured using ATR-FTIR device. After completing the steps to form the film, the final solution was transferred into a teflon mold and hept in an oven (50-60 °C for 12-18 h). To prepare reactive polyurethane hot melt adhesive containing silica nanoparticles, a certain amount of silica nanoparticles (0, 0.2, 0.4, and 0.6 w%) was added to the mixture of polyols and stirred (for 12 h). The compound was sonicated (5 times and each time for 5 minutes) to homogenize.

Results and discussion

The RHMPUA was synthesized via polycondensation of polypropylene glycol, 1,4-butanediol, glycerol, and toluene diisocyanate. The reaction was observed and analyzed using a technique called attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. This method allows for the monitoring and study of the reaction as it progresses. The disappearance of the isocyanate signal at 2275 cm^{-1} and a new strong carbonyl absorption peak at 1732 cm^{-1} and a new weak N-H absorption peak at 3290 cm^{-1} indicated the formation of the urethane unit (Fig. 1). Adhesion properties of the RHMPUA were assessed through a lap shear test. Initially, stainless steel was used as the typical adhesion substrate. The substrates and adhesive film were secured together using paper clips (Fig. 2). The RHMPUA film was cut into rectangle shapes (25 mm × 12.5 mm) and then placed between the two identical substrates (100 mm × 25 mm × 2 mm) with an overlap area (25 mm × 12.5 mm). Subsequently, two paper clips held the film and the two substrates together. The thermal treatment was performed in an oven at (150 °C for 30 min).

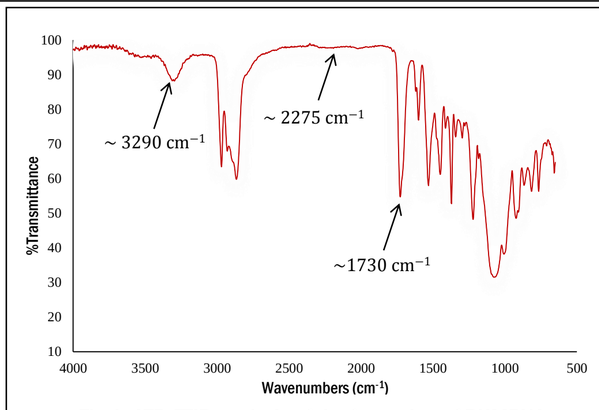

Fig 1. ATR-FTIR analysis of the formation of RHMPUA.

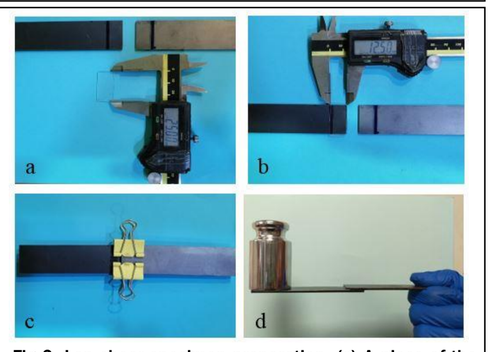

Fig 2. Lap shear specimen preparation. (a) A piece of the cured RHMPUA. (b, c) Paper clips hold together stainless steel and the RHMPUA. (d) After thermal treatment in an oven (at 150 °C for 30 min), the two stainless-steel pieces were bonded together and supported with a 500-g weight.

Prior to study, the specimens were cooled down to room temperature and cured for predetermined times (15 min, 2 h, 3, 7, 10, 14 days). The lap shear strengths were measured at a deflection rate of 5 mm.min^{-1} (Fig. 3). After determining the complete curing time of the adhesive film (7-10 days), samples containing the silica nanoparticles were also studied in the same way. The improvement was obtained in the RHMPUA-0.4 formulations. Lap shear strength of adhesive containing the silica nanoparticle, was almost retained constant owing to a good interaction between the nan-silica and the RHMPUA and indicate a proper dispersion of the nanoparticles in the matrix (Fig. 4).

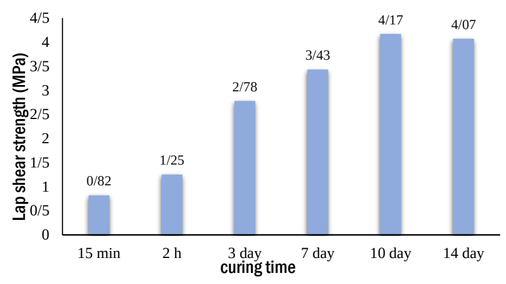

Fig 3. Lap shear strength of HMPUA to the plate of stainless steel under different curing times at room temperature.

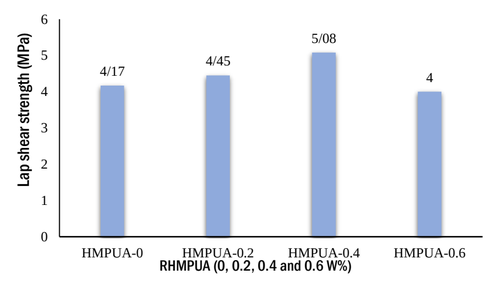

Fig 4. RHMPUA lap shear strength contains the silica nanoparticles (0, 0.2, 0.4, 0.6 w%) after complete curing time (10 days).

Conclusion

A reactive hot melt polyurethane adhesive was synthesized and analyzed using ATR-FTIR. The analysis revealed the presence of urethane groups and the structure of the synthesized adhesive. The synthesized adhesive is fully cured after 7-10 days and its lap shear strength is 4.17 MPa, which increases to 5.08 by adding 0.4 w% of the nano-silica.

Acknowledgements

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