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Nano Congress 2017 Preparation of acrylic silicon dioxide nanoparticles as a binder for leather finishing- Ola A Mohamed National Research Center Ola A Mohamed

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Polyacrylic resin, methyl methacrylate and 2-ethyl hexylacrylate, was prepared via microemulsion polymerization with ratio 2:1, and then modified with silicon dioxide nanoparticles (SiO2) prepared by sol–gel process. Different ratios of these nanoparticles combined with acrylic resins were then coated on leather surface. The physical, chemical, and mechanical properties of coated leather were evaluated through various instrumental analysis as nuclear magnetic resonance, Fourier transmission infrared, dynamic light scattering, thermal gravimetric analysis, energy-dispersive X-ray spectroscopy, and transmission electron microscope. Water vapor permeability was improved with increase in the percentage of the nanoparticles. Tensile, tear strength, and elongation percentage were increased up to 3% of SiO2 nanoparticles followed by decreasing behavior. The acrylate water-based SiO2 nanoparticles exhibited good eco-friendly leather finishing system.

Introduction

Leather industry is one of the greatest pollutant industries in the world. It produces different types of pollutants especially in the finishing step which uses organic hazard solvents.1-3 Water-based recipes were proposed for leather finishing for the minimization of hazard solvents. Finishing aimed to enhance the leather properties, in general, to correct the greater damages of hide, and to protect it from wetting and soiling. Leather finishing uses solution or suspension of synthetic or natural polymers which may incorporate dyes, pigments, or other additives. Due to the quick development of nanoscience and nanotechnology, nanocomposites have been widely used in several applications such as coating adhesions, plastics, and fibers. Nanocomposites exhibit many unusual properties in leather finishing.10-13 The method of sol–gel has attracted significant research consideration.14-16 Preparation of modified acrylic resin by SiO2 as a binder and application in leather were investigated by Ma.11 It showed that the physical–mechanical property of the film from SiO2–acrylic resin coating agent composite increased. Also, air and water vapor permeability was enhanced by 15.4% and 11.5%, respectively. Also, Ma et al13 discussed the preparations of modified acrylic resin SiO2 via sol–gel method for leather finishing. T g temperature of modified acrylic latex SiO2 was elevated than that of unmodified. Dynamic light scattering (DLS) showed that the average diameter of the modified silica latex particles (177 nm) was larger than that of the unmodified latex particles (105.3 nm).

MATERIALS AND METHODS

This work is partly presented at 19th Nano Congress for Next Generation August 31-01, 2017 Brussels, Belgium

Materials

Crust bovine leather was supplied by Hafez-Abaas Medium Tannery (Misr-Elkadima, Cairo, Egypt). MMA, 2-EHA, and tetraethoxysilane (TEOS) were provided by Sigma-Aldrich (Germany) and redistilled before use. Potassium persulfate (KPS) was supplied by Modern Laboratory Co. Sodium bicarbonate (NaHCO3), ethanol, and ammonium hydroxide were supplied by Fine-Chem Ltd. Sodium dodecyl sulfate (SDS) was obtained from Merck-Schuchardt, Germany.

Emulsion polymerization

Microemulsion polymerization was carried out in a 250-ml three-necked flask with a reflux condenser: Water, the emulsifier SDS, NaHCO3, and the monomer (MMA:2-EHA) were added. After that, the monomers–water mixture is then agitated in homogenizer (VELP Scientifica) for 30 min to form a stable homogenized solution. Finally, the initiator, KPS was dissolved in a small amount of water and added to the reactor under a nitrogen atmosphere. The reactions were run with mechanical stirrer at 800 rpm for 4 hr at 70°C.1

Coating process

The leather coating proceeds using Elcometer 3620 Baker film applicator made in Belgium. Every leather piece was coated three times by prepared polymers with film thickness of 90 µm and left to dry.

Synthesis of silicon dioxide nanoparticles.

Silicon dioxide nanoparticles were synthesized by sol–gel method, using tetraethylorthosilicate (TEOS), ethanol, and de-ionized water in the presence of ammonia as catalyst at room temperature.12 It is a simple step based on hydrolysis and condensation process of TEOS in ethanol and water mixture in alkaline condition at room temperature. An experiment was carried out by taking 20 ml of ethanol in 50-ml beaker, followed by 2 ml of TEOS, 25 ml de-ionized water, and 4 ml of concentrated ammonia solution. The mixture was stirred for 30 min, and at the end of which a milky white solution obtained then was centrifuged. The resulting material was dried and kept for further analysis.

Modification of binder resin leather coating agent with SiO2

The binder acrylic resin coating agent was modified by mixing with the SiO2 sol. A fixed quantity of acrylic binder resin was weighted, and the SiO2 sol was added into a three-necked reactor with different molar ratios 1%–5% stirred for 30 min at 60°C. Then, the mixture was disposed into a supersonic wave cell disruption machine for a period of time.

Application of silicon dioxide nanoparticles for leather finishing

After coating processes, the performance of leather properties was evaluated. Nanoparticle, dispersing agent, and water were premixed and sonicated for 30 min, and it was added to the coating mixture formulation, that is, with water and acrylic binder. The final mixture was sonicated for 30 min. Coated cow upper crust leather from Egyptian origin with thickness of 1.6/1.8 mm was taken for evaluation.

CONCLUSIONS

This work deals with the preparation of modified acrylic binder, MMA:2-EHA copolymers (2:1) with different monomer molar ratios through microemulsion polymerization with different ratios of silicon dioxide nanoparticles (SiO2) (1%–5%). This modified latex was applied as a binder for leather finishing. Nuclear magnetic resonance analysis of the prepared binders showed the absence of the vinyl part *CH=CH2 signals of both monomers confirming that complete copolymer reaction and formation of MMA:2-EHA copolymers. FTIR spectra of leather treated by copolymer and with or without SiO2 showed the presence of the functional groups of SiO2 combined with the copolymers onto leather surface. TEM of SiO2 and acrylic binder modified with 3% SiO2 exhibited that particle size of SiO2 and modified acrylic binder ranges from 10 to 70 nm and 20 to 80 nm, respectively. Water vapor permeability of the coated leather modified with silicon dioxide nanoparticles showed improvement of water vapor permeability. SEM micrographs of the leather coated with MMA:2-EHA (2:1) modified with different ratios of SiO2 showed good covering, smooth, and homogenous texture of collagen fibers of the leather coated with acrylic binder containing different percentages of SiO2 (1%–5%) than the uncoated one. EDX spectrum of the treated leather with SiO2 confirmed that the presence of Si and oxygen elements. TGA of the coated leather modified with SiO2 showed enhancement in the thermal stability. Mechanical properties of the coated leather with MMA:2-EHA (2:1) modified with different ratio of SiO2 showed an increasing of the tensile strength, tear strength, and elongation % at break with an increasing of SiO2 concentration up to 3%, above that, it starts again to decrease. This promising study succeeded in preparation of eco-friendly water-based binders modified with nanoparticles materials and its application in the leather finishing.

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