The making and application of a type of multifunctional silicone co-polymer

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Abstract: Acrylic acid (AA) and stearyl acrylate (SA) were co-polymerized with vinyl-ended polysiloxane using AIBN as the catalyst. The polymer has been characterized by FT-IR and 1H-NMR techniques. The co-polymer can be used as retaining agent, which has the ability of fatliquoring and water-proofing for full chrome leather. The results were compared with non-reactive silicone treated leathers on the aspect of reactive ability with mineral-tanned leather. It was found that the synthesized co-polymer has superior permanent anti-water properties when used on full chrome leather.

Key words: vinyl-ended polysiloxane; acrylate; stearyl acrylate; polymerization; retaining agent

1 Introduction

Polysiloxanes, which are usually known as “silicone” or “silicone elastomers,” have received widespread attention as a special family of polymers because of their unique properties, such as low glass transition temperature (Tg), low surface tension and surface energy, low solubility, low dielectric constant, transparency to visible and UV light, high resistance to ozone, and stability against atomic oxygen even oxygen plasmas.1-3

Recently, John and Patricia, and Ela’mma et al. have reported that when the mineral-tanned leather was treated with acrylic resin grafted with additional long alkyl ester group, it could attain excellent water repellency, softness, and strength.4, 5 So, it is of great interest to know whether the resulting product might possess the extra similar properties. At present, monomer silane or siloxane is usually used as raw material for the synthesis and modification of polysiloxane.6-8 Meanwhile, the structure of long alkyl group, which contains eighteen or more than eighteen carbons, is similar to that of body fat. Therefore, it has better compatibility with human skin and could be used in cosmetic or textile as sheeny auxiliary agent, lubricant, etc.9 So, in this paper, stearyl acrylate (SA) was selected to polymerize with acrylic acid and methylmethacrylate (MMA) and vinyl-ended siloxane to obtain a type of co-polymer(SAMV). In practical application, co-polymer has excellent reactivity and adhesiveness, which would have good compatibility with other finishing materials (polyurethane, polyacrylate, etc.) used in leather-making process and could endow leather with good softness, pleasant handle, and preferable elasticity.10 The structure of co-polymer was determined by FTIR and 1H-NMR spectra.

2 Experimental

2.1 Materials

Vinyl-ended siloxane was of industrial grade and supplied by Debang Chemical Company, Hubei, China; SA (C.P., > 99%) was purchased from Beijing Dongfang Chemical Company, Beijing, China; methylmethacrylate, crylic acid, AIBN, and other conventional chemicals, which were purchased from Bodi Chemical Company, Tianjin, China, were of reagent grade and used without further purification.

2.2 Preparation of SAMV co-polymer

The synthesis of SAMV co-polymer was carried out in a four-neck glass reactor equipped with a
mechanical stirrer, a thermometer, and a nitrogen inlet. The co-polymer was synthesized by free radical polymerization according to the Ref. 11, with toluene as solvent. The synthesis conditions were as follows: The concentration of SA was 0.3M, mass ratio of SA to initiator azobisisobutyronitrile (AIBN) 100:1, the reaction temperature 80°C, and the reaction time 7 h. The resulting polymer was purified by washing with trichloromethane and ethanol thoroughly.

2.3 Characterization

2.3.1 FTIR Analysis

Structures of obtained co-polymer products and raw materials were ascertained by FTIR (Nicolet AVATAR370, USA) spectra, using CCL₄ as solvent.

2.3.2 ¹H-NMR Analysis

Structures of obtained co-polymer products and raw materials were ascertained by ¹H-NMR (BRUKER 300 UltrashieldTM, Bruker G. E.) spectra, using CDCl₃ as solvent.

2.4 Determination of reactive ability of co-polymer

The co-polymer was mixed with several different ratios emulsion agent of Tween-80 and Span-80 for using them on mineral-tanned leather. Then the leather was extracted by bichloromethane.

3 Results and discussion

3.1 Synthesis route of co-polymer

The reaction of Vinyl-ended siloxane and stearyl acrylate and methyl methacrylate and acrylic acid will be described in Scheme 1. The co-polymer was synthesized by free radical polymerization according to the Ref. 11, with toluene as solvent.

3.2 FTIR Analysis of SAMV

In the figure 1 and 2, it was showed the IR spectra of SA and co-polymer, respectively, both of which were dissolved in CCl₄. The IR spectrum of SA in Figure 1 should have two characteristic absorption regions at about 1729 cm⁻¹ due to ν C=O of unsaturated ester and at 1640 cm⁻¹ due to ν C=C.

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In Figure 2, the $\nu_{\text{C=O}}$ of unsaturated ester at about 1729 cm$^{-1}$ and $\nu_{\text{C=C}}$ absorption at about 1640 cm$^{-1}$ almost disappeared, but the $\nu_{\text{C=O}}$ of saturated ester at about 1742 cm$^{-1}$ and the $\nu_{\text{C=O}}$ of carboxyl group at about 1710 cm$^{-1}$ appeared. It represented that the vibration of carbonyl of unsaturated ester was greatly weakened and substituted with two peaks at 1742 cm$^{-1}$ and 1710 cm$^{-1}$ of saturated ester and carboxyl group. Meanwhile, there was a broad peak at about 3300 cm$^{-1}$. Both the changes of characteristic peaks clearly revealed the formation of carboxyl group. Therefore, the co-polymer was obtained.

3.3 $^1$H-NMR Analysis of S AMV

The $^1$H-NMR spectra of SA and co-polymer, both of which were dissolved in CDCl$_3$, are shown in
Figures 3 and 4, respectively. The $^1$H-NMR spectrum of SA in Figure 3 displayed three Chemical shifts at 5.8, 6.2, and 6.4 ppm (CH$_2$=CH$_2$, m, 3) for the three alkene protons, respectively. In Figure 4, three chemical shifts at 5.8, 6.2, and 6.4 ppm (CH$_2$=CH$_2$, m, 3) for the three alkene protons disappeared, a new signal at 1.15 ppm (Si-CH$_2$-, m, 2) provided evidence for the introduction of Si-CH$_2$- group. Chemical
shift at 2.35 ppm (Si-CH$_2$-CH$_2$-, m, 2) confirmed that the unsaturated carbon atom is attached to SAMV, a strong peak at 3.7 ppm (-OCH$_3$, s, 3) was attributed to the methyl protons next to oxygen atom, chemical shifts at 10.3 ppm (-COOH, s, 1) confirmed that carboxyl group is attached to SAMV.$^{12,13}$

3.4 Reactive ability analysis of co-polymer

The co-polymer was mixed with several different ratios emulsion agent of Tween-80 and Span-80 for using them on mineral-tanned leather. Then the leather, which was treated by co-polymer emulsion, was treated according to the Ref. 14, and was extracted by bichloromethane according to the Ref. 15. The results were listed in Table 1 and Table 2.

<table>
<thead>
<tr>
<th>Tab.1 The water and volatile content of leather treated with emulsion</th>
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<tbody>
<tr>
<td>Different emulsion</td>
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<tr>
<td>--------------------</td>
</tr>
<tr>
<td>Polysiloxane</td>
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<tr>
<td>SA</td>
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<td>Co-polymer emulsion</td>
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<table>
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<tr>
<th>Tab.2 The extractive amount from leather treated with varied emulsion</th>
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<tr>
<td>Different emulsion</td>
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</tr>
<tr>
<td>Co-polymer emulsion</td>
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<tr>
<td>SA</td>
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<tr>
<td>Polysiloxane</td>
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As shown in Table 1, the water and volatile content of leather treated with co-polymer emulsion was nearly same as them of the other two kinds of emulsion. This is owing to free radical polymerization, whose yield of co-polymer is acceptable, otherwise, the value should be higher more than the other two values, because of the volatile of those little molecules. But in table 2, the extractive amount from leather treated with co-polymer emulsion is least in the table 2. This is caused by the carboxyl group, which can react with mineral-tanned leather.

4 Conclusions

The resulting co-polymer can be synthesized by free radical polymerization using Vinyl-ended siloxane and stearyl acrylate and methyl methacrylate and acrylic acid as monomer, with toluene as solvent. To mineral-tanned leather, the resulting co-polymer is availability, because of the carboxyl group blocked in the co-polymer.

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References