

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 (T_g), low surface tension and surface energy, low volatility, 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 Patrica, and Elamma 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, acrylic 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

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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 Ultrashield™, Bruker G. E.) spectra, using CDCl₃ as solvent.

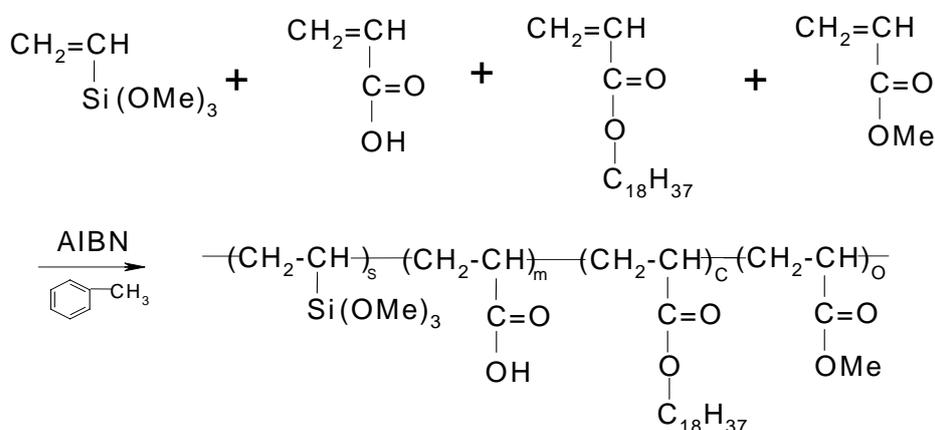
2.4 Determination of reactive ability of co-polymer

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 dichloromethane.

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.



Scheme 1 Processes for the reaction of co-polymer

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}.^{12, 13}

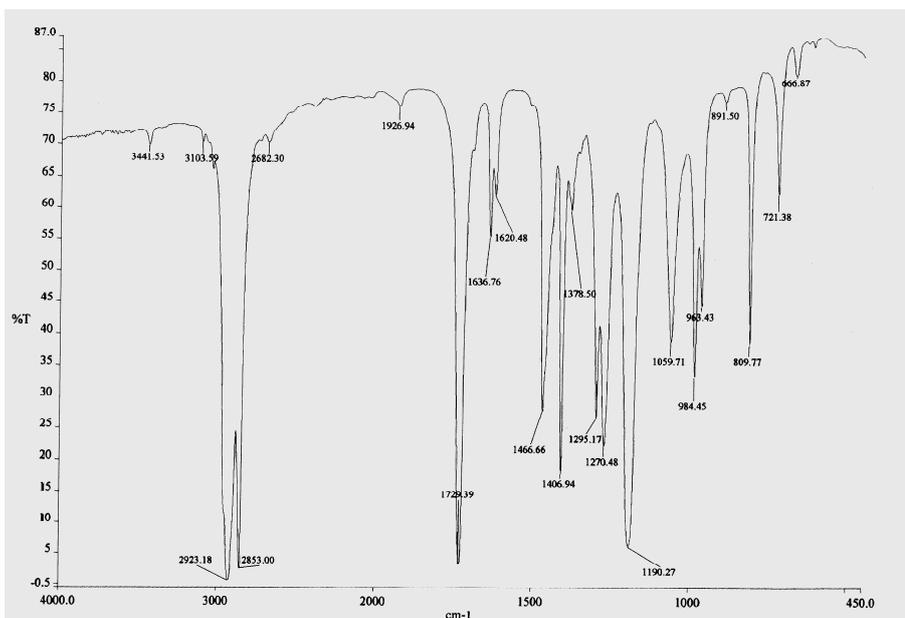


Fig.1 The IR spectrum of stearyl acrylate

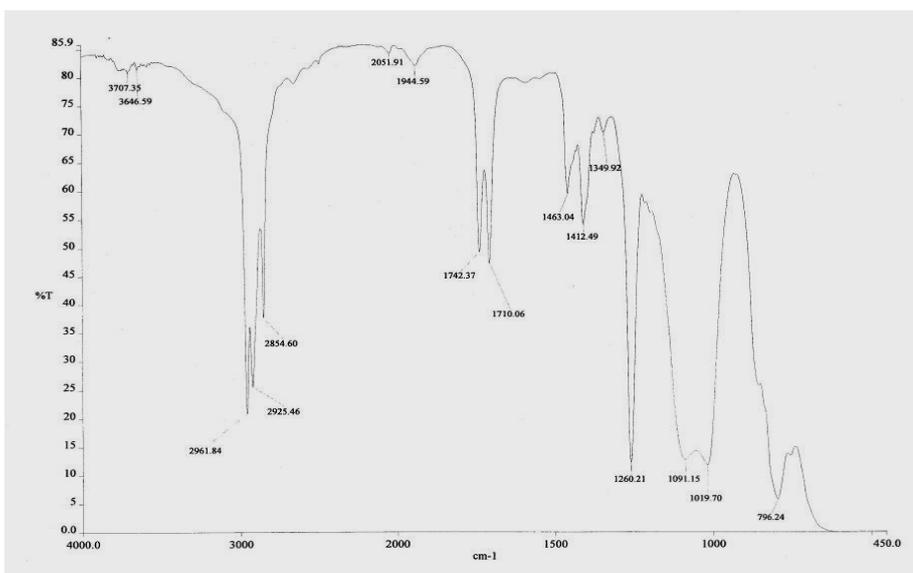


Fig.2 The IR spectrum of co-polymer

In Figure 2, the $\nu_{C=O}$ of unsaturated ester at about 1729 cm⁻¹ and $\nu_{C=C}$ absorption at about 1640 cm⁻¹ almost disappeared, but the $\nu_{C=O}$ of saturated ester at about 1742 cm⁻¹ and the $\nu_{C=O}$ 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 ¹H-NMR Analysis of S AMV

The ¹H-NMR spectra of SA and co-polymer, both of which were dissolved in CDCl₃, are shown in

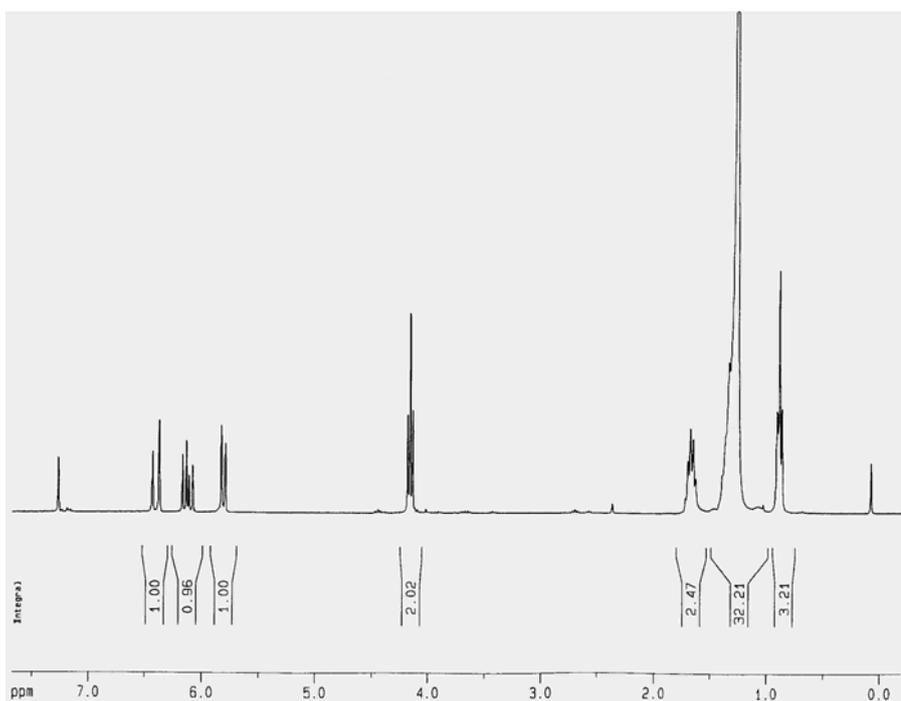


Fig.3 The ^1H -NMR spectrum of stearyl acrylate

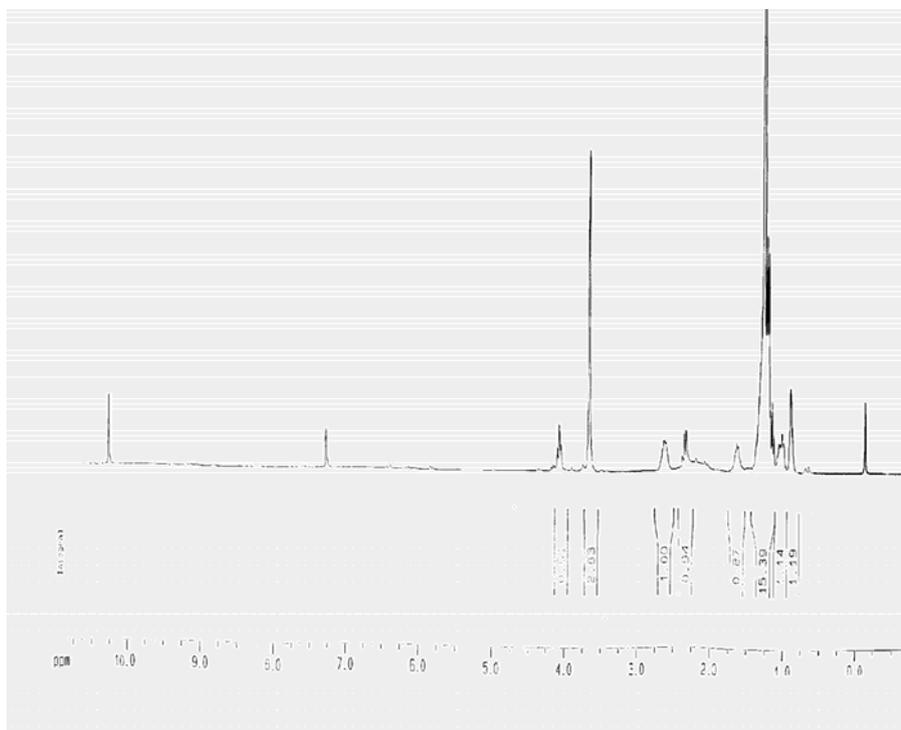


Fig.4 The ^1H -NMR spectrum of co-polymer

Figures 3 and 4, respectively. The ^1H -NMR spectrum of SA in Figure 3 displayed three Chemical shifts at 5.8, 6.2, and 6.4 ppm ($\text{CH}_2=\text{CH}_2$, m, 3) for the three alkene protons, respectively. In Figure 4, three chemical shifts at 5.8, 6.2, and 6.4 ppm ($\text{CH}_2=\text{CH}_2$, 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-CH₂-CH₂-, m, 2) confirmed that the unsaturated carbon atom is attached to SAMV, a strong peak at 3.7 ppm (-OCH₃, 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.

Tab.1 The water and volatile content of leather treated with emulsion

Different emulsion	Content of water and volatile (%)
Polysiloxane	23.82
SA	27.87
Co-polymer emulsion	21.46

Tab.2 The extractive amount from leather treated with varied emulsion

Different emulsion	Extractive amount (%)
Co-polymer emulsion	5.75
SA	80.85
Polysiloxane	86.44

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.

Acknowledgements

We gratefully acknowledge the financial support of the Education Department of Heilongjiang Province.

References

- [1] Lin Zuchen, Schulz Jr., William James, et al. Elastomeric silicone terpolymer. U. S. Pat. 6200581, 2001
- [2] Adams Gerald, Khoshdel Ezat, Moretta Anthony, et al. Polysiloxane block copolymers in topical cosmetic and personal care compositions. U. S. Pat. 6365672, 2002
- [3] Cheng-Liang Chang, Howard Shih-Jen Lee, Cheng-Kwo Chen. Nucleophilic Cleavage of Crosslinked Polysiloxanes to Cyclic Siloxane Monomers: Mild Catalysis by a Designed Polar Solvent System. *Journal of Polymer Research*, 2005,12(6):433-438
- [4] Ciolino, A. E.; Pieroni, O. I.; Vuano, B. M. *J Polym Sci Part A: Polym Chem* 2004, 42, 2920.
- [5] Uozumi, T.; Tian, G.; Ahn, C. *J Polym Sci Part A: Polym Chem* 2000, 38, 1844.
- [6]. Yao, T. P.; Lin, D. Y.; Tao, L. W. *Chem World* 2006, 8, 491.
- [7] Zhuang, B. L. *Text Aux* 2006, 23, 37.
- [8] Shu, X. W.; Mao, S. H.; Ruan, J. S. *Polyurethane Ind* 2005, 20, 24.
- [9] Zhu, H. J.; Liao, H. L.; Li, F. Y. *Fine Chem* 2006, 23, 50.
- [10] An, Q. F.; Li, L. S.; Huang, L. X. *China Leather* 2003, 32, 18.
- [11] Song, Z. Z.; Jiang, Q. Z.; Ge, J. J. *J Xi'an Pet Inst (Nat Sci Ed)* 2002, 17, 50.
- [12] Ciolino, A. E.; Failla, M. D.; Valle's, E. M. *J Appl Polm Sci* 2004, 92, 2303.
- [13] Song, M. Z.; Zhang, T. Y.; Zhang, H. J. *Chem Res Appl* 2003, 15, 879.
- [14] Nation standard of P. R. China: GB/4689.12-84, 1984, 6
- [15] Nation standard of P. R. China: GB/4689.13-84, 1984, 7