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Comb-shaped silicone-alkyd resins with high solid content

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ABSTRACT

An unique com-shaped silicone-alkyd resins (SiAR) were synthesized with high solid content (65 wt%) prepared from an alkyd resin (AR) and a varying weight% (5, 10, 15, 20) of silicone moiety (Z-6018) by etherification reaction. The viscosity and the hydroxyl value (OHV) of the SiAR were found to be higher than those of the AR. The formation of the SiAR was confirmed by infrared spectroscopy and mass spectrometry analysis. The glass transition temperature (T_g), thermal stability, and molecular weight of the SiAR, increased with increasing the silicone content and compared with those of the AR. The results of chemical resistance showed that the SiAR exhibited a better resistance than AR against 0.1 M sodium hydroxide (NaOH) solution.

1. Introduction

Alkyd resins have been employed in the coating industry extensively because; these materials have good gloss, flexibility and adhesion properties [1]. They have been usually prepared with high content of volatile organic compounds (VOCs) [2]. VOCs produce photochemical smog and enhance the production of tropospheric ozone, which is toxic to plants, animals and humans [3]. For reducing VOCs content several alternative has been employed in order to obtain ARs with long oil length [4], waterborne ARs [5] and hyperbranched AR [6,7]. So far the properties have not been the best, since coatings based on unmodified alkyd resins show chalking, fading and loss of gloss, due to intense UV radiation, thermal fluctuations, high humidity and wind driven salt spray [8]. Actually, researchers are exploring with others synthetic methods of ARs with improved properties.

ARs have been modified with acrylic [9], silicone [10,11] melamine-formaldehyde [12] and phenol [13]. In these studies a synergy in the properties of these materials has been obtained.

Silicone containing polymer are attractive because they exhibit low surface tension, excellent electrical properties, good weatherproofing ability, non-flammability, high gas permeability, good thermal and chemistry stability [14]. All these properties can be acquired by ARs for obtaining materials with better properties than unmodified ARs. Kanai et al. [15], developed a novel silicone-acrylate soya AR by combining soya AR and varying wt% of silicone acrylate monomer (10, 20 30 and 40 wt%). Silicone-acrylate monomer was prepared from Z-6018 silicone and hydroxyethyl methacrylate (HEMA). The silicone acrylate–soya alkyd resin exhibited more hardness than soya AR [15]. Furthermore the gloss value increased with the proportion of silicone acrylate [15]. Hyperbranched AR were modified with a Z-6018 silicone (10, 20, 30 and 40%). The grafting of Z-6018 silicone on hyperbranched AR increased the number average molecular mass, the thermal stability, gloss and the hydrolytic stability [10,11].

Usually, ARs have been synthesized with linear structural morphology, but so far, the study of the alkyd resins with comb type structural morphology has not been explored. Therefore, according to critic review of the literature, it is apparent that there is no report on SiAR. The aim of this work, therefore, is to synthesize these materials and evaluate the effect of the content of Z-6018 silicone on the structural, thermal, rheological and film properties of the materials. The properties of a previously synthesized AR will also be compared [16] with those of the SiAR.

2. Experimental part

2.1. Materials

The AR was previously prepared in our laboratory by a reaction between a styrene-hydroxyethyl acrylate copolymer and macromonomer prepared from dimethylol propionic acid and tall

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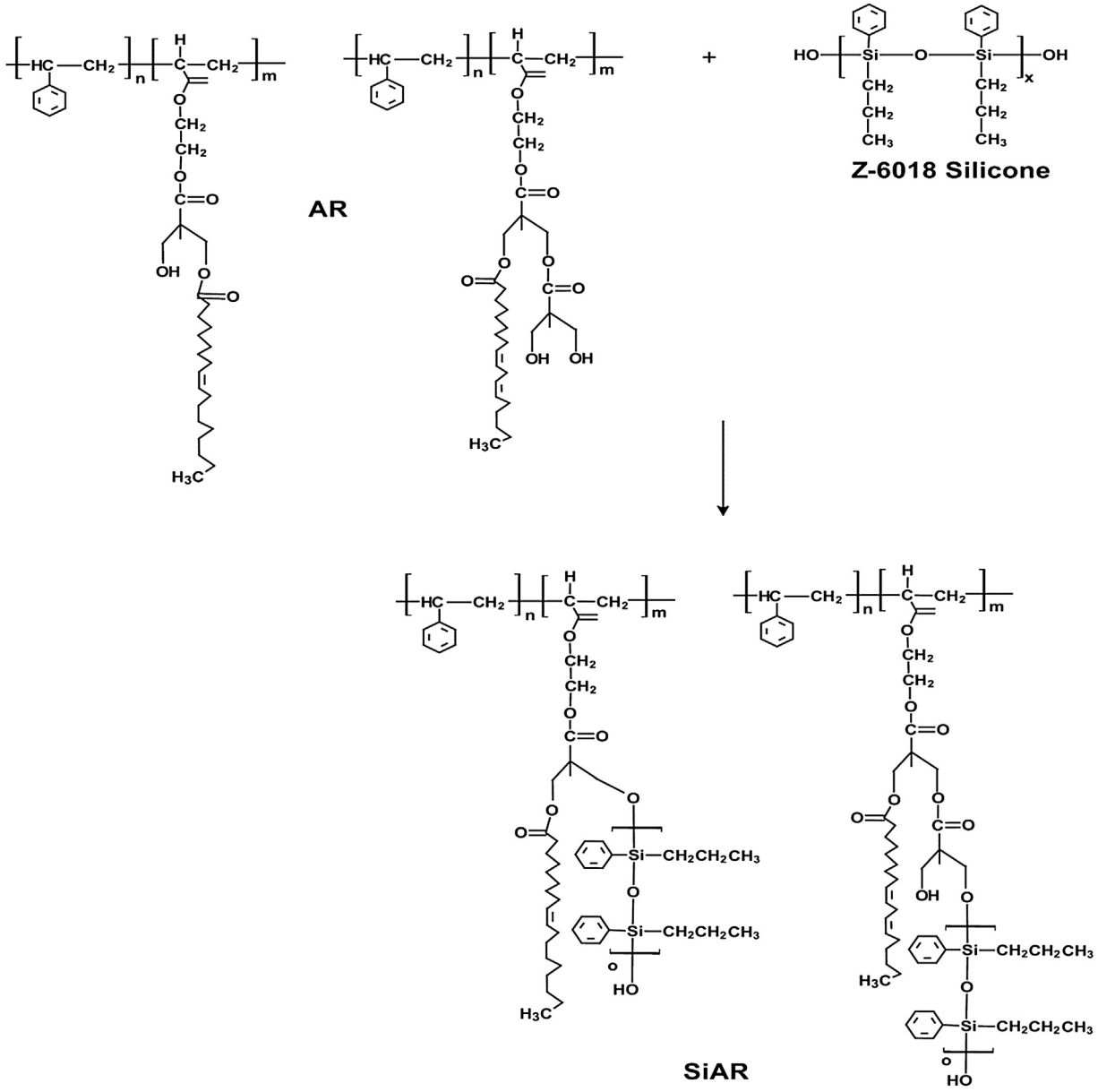

Fig. 1. Schematic representation of the synthesis of a SiAR.

oil fatty acids (TOFA) [16]. The structural, thermal, morphological and films properties were already reported in a previous study [16]. Z-6018 silicone was supplied by Dow corning, *p*-toluenesulfonic acid, xylene, ethanol, potassium hydroxide, NaOH, sodium chloride (NaCl), pyridine and acetic anhydride were supplied by Sigma Aldrich.

2.2. Preparation of the SiAR

In order to prepare the SIAR the respective amount of the AR and Z-6018 silicone (Table 1) were carried out in the reactor and kept at 100 °C under nitrogen atmosphere with a stirring rate of 200 rpm, then 0.1 wt% of *p*-toluenesulfonic acid was added. The reaction time was 30 min, once finished the reaction was added to the respective proportion of xylene to obtain a solid content of 65 wt%. Fig. 1 shows a schematic representation between two structures present in the AR trough which reacted AR with the Z-6018 silicone.

Table 1
Proportions of AR and Z-6018 silicone employed in the synthesis.

Samples	AR (g)	Z-6018 silicone (wt%)	Z-6018 silicone (g)
SiAR1	55.27	5	2.91
SiAR2	55.81	10	6.20
SiAR3	57.35	15	10.12
SiAR4	56.33	20	14.08

2.3. Characterization

2.3.1. Hydroxyl value (OHV)

OHV analysis was performed according to methodology reported in a previous study [17]. The analysis was done in duplicate.

2.3.2. Infrared (IR) analysis

This analysis was realized with an equipment Perkin Elmer Spectrum one, a film of the AR and SiAR on a zinc selenide cell was