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Synthesis of a novel siloxane-based crosslink agent

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Introduction

Polydimethyl siloxane (PDMS) is an extremely used silicon compound to improve other materials properties due to its unique characteristics such as high flexibility, good thermal stability, low surface energy and biocompatibility [1]. Application of crosslink agents in polymers structure can improve their chemical stability as well as enhance abrasion resistance and thermal stability [2]. In the present study a novel siloxane-based crosslinker was synthesized using oligomeric hydroxyl terminated PDMS and maleic anhydride which characterized by FT IR and ^{1}H NMR methods.

Experimental

Materials

An oligomeric hydroxyl terminated polydimethyl siloxane (HO-PDMS-OH, Mn: ~550, viscosity: ~25 cSt) purchased from Sigma Aldrich, St. Louis, MO, USA. Maleic anhydride, sodium hydride (NaH) and tetrahydrofuran(THF) all attained from Merck, Germany.

Synthesis of siloxane-based crosslink agent

In a round bottom flask, HO-PDMS-OH (44 g, 0.08 mol) was dissolved in THF (150 mL). Reaction was carried out under agitation and in an atmosphere of Ar gas in an ice bath. Sodium hydride (3.84 g, 0.16 mol) was slowly added to the reaction mixture. After completion of the sodium hydride addition, temperature was reached to ambient temperature and maleic anhydride (15.69 g, 0.16 mol) was added gradually in to the reaction mixture and condition was kept for about 3 h. Reaction progress was monitored using thin layer chromatography (TLC). At the end of the reaction, the mixture was transferred to a petri-dish to evaporate the solvent and the product was washed several times using THF and dried at room temperature [3].

Result and Discussion

HO-PDMS-OH used as main material to synthesize the siloxane-based crosslinker. After absorption of both protons of HO-PDMS-OH by NaH, generated anion attacks the carbonyl carbon of maleic anhydride which ring opening occurs, producing PDMS maleate terminated (M-PDMS-M) (Figure 1).

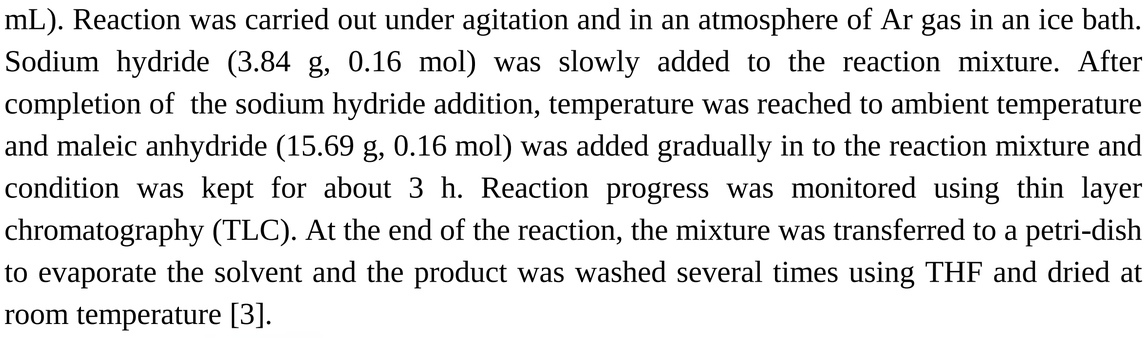

Figure 1. Reaction of dihydroxyl terminated PDMS to maleic anhydride with sodium hydride.

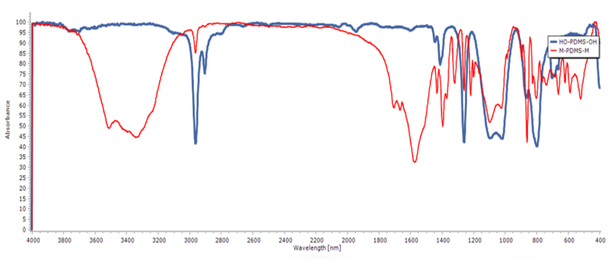

Figure 2. FT-IR spectra of both HO-PDMS-OH and M-PDMS-M.

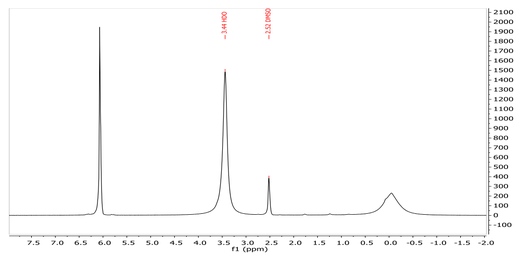

Figure 3. The ^{1}H NMR spectra of M-PDMS-M.

The chemical structure of HO-PDMS-OH and M-PDMS-M were confirmed using FT-IR technique. The results are shown in Fig. 2. Compared with the HO-PDMS-OH, the M-PDMS-M displays the new peaks at about 3400, 3050, 1600 and 1200 cm^{-1}. The broad absorption peak around 3400 cm^{-1} assigned to the stretching vibration of O-H and the weak absorption about 3050 cm^{-1} is attributed to stretching vibration of H-C= bond. Absorption peaks between 1750-1450 cm^{-1} are related to C=C, ester and acid carbonyl groups. However, FT-IR spectra clearly demonstrate successful synthesis of the crosslinker, ^{1}H-NMR spectra of the product (Fig. 3) also confirm the reaction which take placed. The peaks appear at about 0 ppm and 6 ppm attributed to Si-CH_3 and H-C=C, respectively. (the peaks at 2.52 ppm and 3.44 ppm are attributed to solvent and impurity, respectively).

Conclusion

A novel siloxane-based crosslink agent was synthesized using a kind of oligomeric polydimethyl siloxane hydroxyl terminated. Reaction was carried out through two steps. At first, proton elimination of HO-PDMS-OH in basic condition, and then a nucleophilic attack and ring opening of maleic anhydride occurred. The product was characterized using FT-IR and ^{1}H-NMR methods.

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