Synthesis of Siloxanes Containing Reactive Side Chains


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The synthesis and characterization of siloxanes containing methacrylate, epoxy, and amino side chains are described. Direct hydrosilylation of unsaturated methacrylate or epoxy compounds with methyl hydrogen siloxanes resulted in the attachment of methacrylate or epoxy groups as side chains on the siloxane in good yields. Amino side chains on siloxanes were formed by acidic hydrolysis of the ketenimine side chains, obtained by hydrosilylation of unsaturated ketenimines with methyl hydrogen siloxanes. Details of the preparation and characterization of such unsaturated ketenimines are reported.

KEY WORDS: Siloxane; hydrosilylation; synthesis; reactive groups.

INTRODUCTION

Organofunctional silane coupling agents have been successfully used for many years on glass surfaces to improve the performance of polymer composites and to promote retention of composite mechanical performance, particularly in the presence of moisture [1–4]. The bonding mode of these silanes at the solid–resin interface is complex but now well understood [1, 5, 6]. It is generally thought that the silanes cross-link to form a siloxane network, which covers the surface and also provides an array of functional groups which bond to the resin. To date, the bonding of functionalized siloxanes to glass surfaces, for use in polymeric composites, has not been seriously characterized or evaluated. The synthesis of such func-
tionalized siloxanes is not straightforward and needed to be addressed before their subsequent bonding to surfaces could be evaluated.

Highly functionalised silicone derivatives possess excellent material properties yet retain reactivity toward other monomers during polymerization [7, 9]. For example, aminosiloxanes have been employed in wire coatings [10, 30], epoxy resins [11, 31], fabric conditioners [12–16], mold release agents [17–19], and hair conditioners [20–24] and in the preparation of polyimide siloxanes [32–34] and acrylic siloxanes [35–40]. Amino-terminated siloxanes are generally prepared by reacting hydroxyl-terminated siloxanes with aminosilane coupling agents [41–44]. Increasing the amine functionality of siloxanes by preparing pendant aminosiloxanes has proved more difficult. Pendant primary aminosiloxanes have been prepared by hydrolysis of aminomethylsilanes [33, 45] or by the cohydrolysis and condensation of silanol terminated siloxanes with aminosilanes [44]. The resulting siloxanes have a broad molecular weight distribution (high polydispersity), relatively high molecular weights, and a tendency for considerable variation between batches in processing.

Piperazine side chains have been attached onto siloxanes by reacting piperazine with the reaction product from the hydrosilylation of allyl glycidyl ether with poly(dimethylsiloxane-co-methylhydrogensiloxanes) of the form Me₃SiO-[Me(H)SiO]ₙ[Me₂SiO]ₘSiMe₃ [46]. Such secondary-amine siloxanes have proved very useful in modifying epoxy resin systems. Unfortunately, these secondary amine siloxanes are difficult to prepare. A large excess of piperazine is needed to avoid polymer formation, and for industrial purposes the subsequent removal of excess piperazine proves cumbersome. The method, of course, also requires prior preparation of the epoxy-functional siloxane.

Riffle et al. [46] synthesized their epoxy siloxanes by hydrosilylating dimethylchlorosilane with allyl glycidyl ether followed by hydrolysis to produce a disiloxane. This was subsequently equilibrated with octamethylcyclotetrasiloxane using a siloxanolate catalyst, to generate epoxy-terminated siloxanes (Scheme I). This procedure represented a significant improvement over earlier work [49–51], where epoxy silicon compounds were prepared by either epoxidation of olefinic organosilicon compounds or hydrosilylation of hydridosilanes with unsaturated epoxy compounds followed by polymerization. Early work by Bayer [52] did attempt direct hydrosilylation of unsaturated epoxy compounds on poly(methylhydrogensiloxanes), but the exotherms produced caused partial gelation, resulting in low yields.

Siloxanes containing functional methacrylate groups have recently gained importance [53–58], because they may be cured by UV irradiation rather than by thermal initiation, so increasing their usefulness in a variety