Epoxy/Anhydride Networks Modified by Epoxy/Anhydride Oligomers Containing SiOH Groups

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ABSTRACT: Epoxy/anhydride oligomers containing variable amounts of trialkoxysilane groups were synthesized from phenyl glycidyl ether (PGE), 3-glycidoxypropyl trimethoxysilane (GPMS), and methyl tetrahydrophthalic anhydride (MTHPA), using benzyldimethylamine (BDMA) as an initiator. They were hydrolyzed and partially condensed using diluted formic as a catalyst, with the last step carried out in a solution of diglycidyl ether of bisphenol A (DGEBA). By curing with a stoichiometric amount of MTHPA, in the presence of BDMA, plasticized epoxy/anhydride networks were obtained without any evidence of phase separation. These materials showed a better abrasion resistance than that of the neat matrix. The presence of free SiOH groups can be used to improve the adhesion to glass surfaces. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1365–1370, 2000

Key words: epoxy/anhydride networks; SiOH-modified epoxy/anhydride oligomers; plasticized epoxies; abrasion resistance

INTRODUCTION

In the search of epoxy coatings with improved abrasion resistance and adhesion to glass surfaces, we investigated the effect of adding epoxy/anhydride oligomers functionalized with free SiOH groups. The following route was used to generate the SiOH-functionalized additives: First, epoxy/anhydride oligomers containing trialkoxysilane groups were synthesized. They were then hydrolyzed and partially condensed using diluted formic as a catalyst, with the last step carried out in a solution of diglycidyl ether of bisphenol A (DGEBA). By curing with a stoichiometric amount of an anhydride and a tertiary amine as an initiator, a plasticized polymer network was obtained without any evidence of phase separation. Several properties of the modified networks were determined and compared with those of the neat epoxy matrix.

EXPERIMENTAL

Materials

The structures of the different chemical reagents are shown in Figure 1. The selected monoepoxides were phenyl glycidyl ether (PGE, Aldrich, Milwaukee, WI) and 3-glycidoxypropyl trimethoxysilane (GPMS, Sigma, St. Louis, MO). The diepoxide was DGEBA (MY 790, Ciba-Geigy, with an average *n* value equal to 0.03). It was carefully dehydrated before use. The epoxides were polymerized with methyl tetrahydrophthalic anhydride (MTHPA, HY 918, Ciba-Geigy), using benzyldimethylamine (BDMA, Sigma), as an initiator, in an amount of 0.04 mol per mol of epoxy groups.

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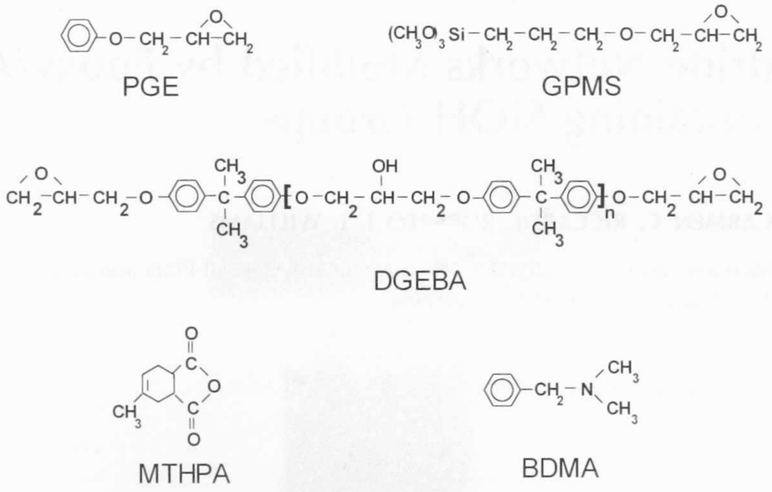

Figure 1 Chemical reagents.

Characterization

Molar-mass distributions were determined by size-exclusion chromatography (SEC), with a Waters 510 GPC provided with ultraStyragel columns 100 (×2), 500, and 1000, using a refractive index detector. Tetrahydrofuran (THF), at 1 mL/min, was used as a carrier. Fourier-transformed infrared spectroscopy was used to follow the polymerization and the hydrolytic condensation (FTIR, Bruker IFS 25 on NaCl windows).

Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC, DuPont 990 TA, onset value at 10°C/min under N_2) or by thermal mechanical analysis (TMA, Mettler TA 3000, onset value at 10°C/min using both static and dynamic forces). DSC (Mettler TA 3000) was also used to obtain the heat of reaction of the epoxy/anhydride polymerization.

Minicylindrical compression-test specimens with a diameter $D = 4$ mm and $L/D = 1.5$ were machined and deformed under an uniaxial compression mode in a Shimadzu Autograph S55-C universal testing machine. The crosshead displacement was measured using an LVDT placed very close to the specimen. The elastic modulus and the compressive yield stress, σ_{yc}, were determined from the experimental curves.

The microhardness was measured using a Wilson Tukon 300 device with a Vickers indenter, applying a 5 kg force for 15 s. The abrasion resistance was determined with a dry sand/rubber wheel apparatus (ASTM G65, 91, Procedure D).

RESULTS AND DISCUSSION

Synthesis of Epoxy/Anhydride Oligomers Containing Trialkoxysilane Groups

The copolymerization of epoxides with cyclic anhydrides in the presence of tertiary amines proceeds through an anionic chainwise mechanism comprising initiation, propagation, and chain-transfer steps. Propagation involves the alternating addition of epoxy and anhydride groups to the growing chain. But as the alkoxide at a chain end reacts at a faster rate than does the carboxilate,[1,2] the (almost) simultaneous addition of an epoxy–anhydride couple to the growing chain takes place. A chain-transfer step that regenerates the active species must be present to account for the experimental values of the gel conversion.[3] Figure 2 shows a fragment of a linear chain formed in the PGE/GPMS/MTHPA reaction.

The PGE/MTHPA copolymerization in stoichiometric amounts was first analyzed. Figure 3

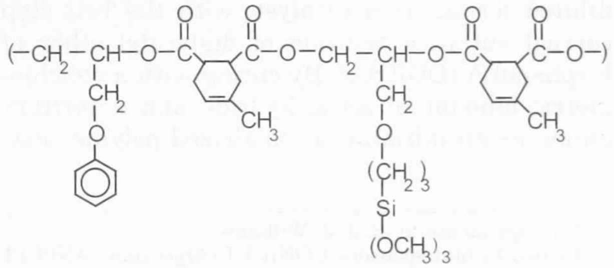

Figure 2 Fragment of a linear chain formed during the polymerization of PGE, GPMS, and MTHPA.