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Functionalized inorganic/organic nanocomposites as new basic raw materials for adhesives and sealants Part 2[☆]

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Abstract

A high content of nano-sized silica, alumina and titania was embedded in epoxy Novolac adhesives. By grafting a glycidyloxypropyl functionalized trialkoxysilane on different nanoparticles polymerization-active fillers were prepared. ^{29}Si NMR and MALDI-TOF mass spectrometry revealed oligomeric siloxane structures present on the surface of coated nanoparticles. In heat-induced polymerization reactions these surface-modified nanoparticles form covalent crosslinks to the epoxy resin, thus efficiently modifying the viscoelastic properties. The reinforced nanocomposites revealed shifts of the glass transition temperatures of about 20 K pointing to the improved thermal stability.

Keywords: Adhesives; Sealants; Hot-melt adhesives; Nanocomposites

1. Introduction

Advanced adhesives must often meet competing requirements, for instance, they have not only to guarantee a firm bond but also must cushion stress situation by improved toughness. To bring such contradictory material properties into harmony with each other, the incorporation of nanoparticles, having average particles sizes between 5–50 nm, in a variety of matrix resins enabled the development of a rather new class of materials (nanocomposites) which are challenges for adhesive raw materials manufacturers. Heat-curing epoxies and numerous acrylates curable by ultraviolet radiation or beams of electrons can be used as the base resin.

Due to their small size and large surface area nanoparticles are unique fillers yielding totally different effects and improved physical properties compared to conventional fillers with sizes in the μm range. Of particular importance, nanoparticles present in the polymer must be well distributed in order to change the polymer structures. However, physical mixing of inorganic nanopowders and organic resins may lead via particle aggregation to high viscosity even at low filler content. This particular complication can be prevented with the aid of organosilanes which change the hydrophilic nature of the oxide surfaces into a hydrophobic one. Surface modification by trialkoxysilanes is commonly used and extensively described in the literature [1,2]. With the aid of these coupling agents the dispersibility of the inorganic filler in organic media is improved and, hence, the suitability for many applications.

In addition, modification of nanoparticles by acrylic, vinyl or epoxy functionalities enables the formation of chemical bonds between both components, which is expected to guarantee a durable interconnection between the two incompatible phases. Polymerization-active nanoparticles are expected to be centers of crosslinking reactions

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intensifying the stiffness of nanocomposites as well as improving the viscoelastic properties of nanoadhesives. For example, studies of organic and inorganic nanopowders revealed modification effects like glass temperature shifts of about 10 K and mechanical reinforcement [3–5].

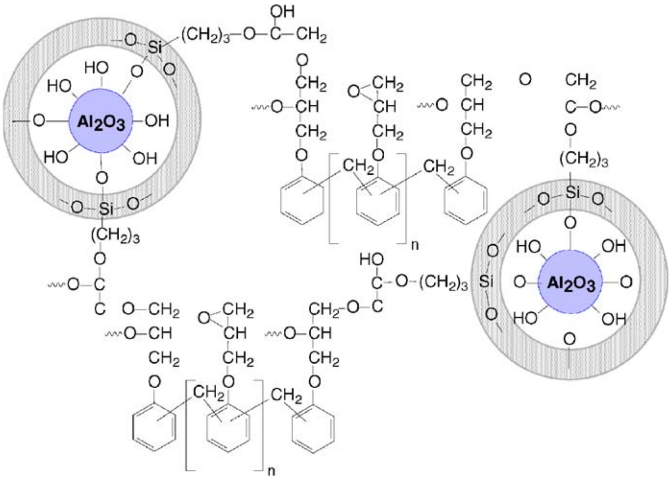
In previous studies, application of modified silica nanoparticles in radiation curable acrylate formulations has shown to result in nanocomposite films with improved scratch and abrasion resistance [6] and reinforced nanoadhesives with improved glass transition temperature of about 50 K [7]. In this paper, the modification of silica, alumina, and titania nanoparticles by trialkoxysilanes as well as the reinforcement of epoxy adhesives will be described.

2. Experimental

The grafting procedure of trialkoxysilanes, e.g. glycidyloxypropyltrimethoxysilane (GLYMO), methacryloxypropyltrimethoxysilane (MEMO), and propyltrimethoxysilane (PTMO), onto the surface of oxide nanoparticles, e.g. silica (AEROSIL OX50), alumina (Aluminiumoxid C), and titania (P25, all available from Degussa), was described in detail earlier [8,12]. The coated nanoparticles were characterized by temperature-programmed oxidation (TPO), ^{29}Si NMR, IR and MALDI TOF mass spectrometry. Embedding of surface-modified fillers led to reinforced epoxy adhesives, based Epoxy Novolac DEN 425 (Dow), with a high fill ratio of oxide nanoparticles of about 30 wt%. These nanoadhesives were heat cured at 160 °C with about 3 wt% hardener component (ANCAMINE 2014AS, Huntsman).

3. Results

Surface modification by trialkoxysilanes implies both hydrolysis of alkoxysilanes to silanols and condensation of silanols formed with terminal OH groups present on the particle surface. For silanes provided with olefinic or epoxy functionalities, e.g. methacryloxypropyltrimethoxysilane (MEMO), vinyltrimethoxysilane (VTMO), and glycidyloxypropyltrimethoxysilane (GLYMO), a polymerization-active siloxane shell is formed around the nanoparticles which results in crosslinking reactions with the acrylate network as depicted in Scheme 1.



Scheme 1. Embedding of polymerization-active nanoparticles, formed by grafting of GLYMO onto the surface of alumina, into epoxy Novolac resins.

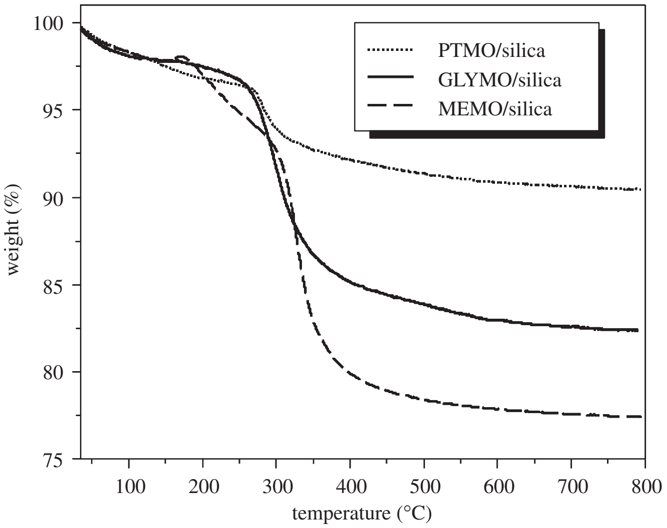


Fig. 1. TPO profile of silica nanoparticles grafted by PTMO, GLYMO, and MEMO.

4. Characterization of grafted nanoparticles

After modification the silane coverage of silica nanoparticles modified by GLYMO, MEMO, and PTMO has been determined by TPO (Fig. 1). For all silanized samples, the overall loss of weight as a function of the temperature revealed burning at about 300 °C. The maximum weight loss of MEMO, GLYMO, and PTMO modification was observed to be 24, 16, and 9 wt% respectively. Assuming a schematic grafting via a tridentate silane structure, a monomolecular surface coverage should be obtained already by about 4.3 wt% GLYMO. The observed organic content of silica modified by MEMO and PTMO is likewise higher than the expected content due to monomolecular silane coverage. The translation of the content of organics into molecular surface coverage is 5.5, 3.7, and 5.6 molecules/nm^2 for MEMO, GLYMO, and PTMO modification, respectively. Compared to 2–3 OH groups per nm^2 on nanosized silica [9] the observed coverage is higher than a monomolecular one and can be taken to suggest grafting of precondensed silane structures.

To characterize silanized oxide surfaces ^{29}Si NMR spectroscopy was proven to be the standard method [10]. With respect to condensed or grafted organosilanes, signals are typically observed in the $-45\ldots-50$ ppm, $-55\ldots-60$ ppm and $-65\ldots-70$ ppm regions and are assigned to mono(T^1)-, bi(T^2)-, and tri(T^3)-fold Si–O-linked silicones, respectively.