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Correlation of epoxy material properties with the toughening effect of fullerene-like WS_2 nanoparticles

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ABSTRACT

This work deals with the toughening effect of inorganic, fullerene-like WS_2 (IF-WS_2) nanoparticles (NPs) on epoxy. It has been hypothesized that this toughening effect depends on the epoxy's cross-link density, its molecular defect fraction or its reference fracture toughness K_{Ic}. Seven different epoxy systems were filled with 0.5% laboratory-made IF-WS_2 NPs by mass and investigated in order to analyze which material properties are determining the toughening effect. These NPs were similar to commercially available IF-WS_2 NPs, but their agglomerates could not be broken up as successfully and they yielded less toughening effect. The cross-link density of the epoxies measured via dynamic-mechanical thermal analysis agreed reasonably well qualitatively with the theoretical estimation. The glass-transition temperature and the compressive yield stress were not affected significantly by the IF-WS_2 NPs. The toughening effect of IF-WS_2 depended entirely on the curing agent type and quantity. Polyetheramine-cured epoxies behaved differently from the others in their yielding behavior, but also in the IF-WS_2 NPs' toughening effect: While some of the investigated material properties correlate strongly with the toughening effect for polyetheramine-cured epoxies, the correlation for all investigated epoxies is rather low. Thus, none of the mentioned hypotheses could be clearly confirmed.

1. Introduction

Epoxy is a thermosetting polymer that is frequently used for high-performance applications like in fiber-reinforced polymers thanks to its good mechanical and chemical properties and its good processability. However, its applications are often limited by its low fracture toughness K_{Ic}. This is why epoxy is usually toughened by toughening additives like elastomeric or rigid particles. Recently, nanoparticle (NP) fillers have attracted much attention as already small quantities showed considerable toughening effects.

Inorganic, fullerene-like WS_2 (IF-WS_2) is a novel class of NPs that is known mostly for their outstanding tribologic properties [1–3]. When used as an additive in epoxy, IF-WS_2 can considerably improve not only its friction and wear behavior [4,5], but also its fracture toughness [6,7]. The reported relative toughness increases are impressive (up to +69% in the critical strain-energy release rate G_{Ic}), considering how little IF-WS_2 was usually added (less than 0.1% by volume) [6].

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However, a recent investigation [8] showed that significant fracture toughness improvements were only possible for certain epoxy systems. In particular, sub-stoichiometric epoxy systems increased in their K_{Ic} when IF-WS_2 was added, while stoichiometric epoxy tended to embrittle. It was consequently hypothesized that the effect of IF-WS_2 on the epoxys K_{Ic} depended on its cross-link density or on its molecular defect fraction, that is to say, the fraction of the epoxy molecule that is not part of the molecular network [8]. Indeed, it was frequently assumed that the molecular network morphology, in particular the cross-link density, is an important factor determining the effectiveness of NP toughening agents [8–10]. Nevertheless, it is unclear whether a high cross-link density is beneficial [10] or detrimental [8,9] for the toughening effect.

Likewise, some models predict that the epoxys yield stress [9,11], its strain at break [9] or its modulus [11] are determining for the toughening effect of NP additives. Finally, it is possible that the toughening effect depends simply on the K_{Ic} of the neat epoxy reference system [8,9]. Indeed, combinations of these parameters could explain the mentioned dependency of the toughening effect on the curing agent concentration [8].

The aim of the present work is to separate these factors from each other by investigating several different epoxy systems. IF-WS_2 is dispersed within an epoxy resin that is then cured with various different curing agents, both stoichiometric and sub-stoichiometric. The resulting materials hence cover a wide range of cross-link densities and K_{Ic}'s, but they also exhibit different mechanical properties, molecular defect fractions, etc. The inter-correlation between these factors is much lower than when only the stoichiometry is varied, which facilitates drawing conclusions.

Most published works on IF-WS_2 in epoxy may be somewhat biased by the fact that the used IF-WS_2 was often from the same commercial source (*Nanomaterials Ltd.*, Israel, formerly known as *ApNano*) [6–8,12,13]. Thus, it is possible that some of the reported effects are specific for NPs from this particular source rather than for IF-WS_2 in general. The present work uses laboratory-made IF-WS_2 from a different source in order to compare it with the earlier results from the commercial product and to allow more general statements on the effect of IF-WS_2 on epoxy properties.

2. Experimental

2.1. Materials

The used IF-WS_2 NPs were synthesized following a recently applied patent [14] via a solid-gas-phase reaction using quasi-spherical WO_3 NPs as precursors and H_2S/H_2 as reactive gases. The synthesis was carried out at 800 °C using a home-made quartz-class set up, which was designed to support a continuous production of WS_2 IF-NPs.

The epoxy resin was a diglycidyl ether of bisphenol A (DGEBA, trade name *EpiKote 828 LVEL* from *Momentive*) with a mass per amount of epoxide groups M_{EP} (also known as *epoxide equivalent weight, EEW*) of 186 g/mol as determined by titration according to ISO 3001 [15].

The methyl-tetrahydrophthalic anhydride (MTHPA, trade name *EpiKure 3601* from *Momentive*) had an *anhydride equivalent weight* M_{anh} of approx. 165 g/mol and was always used in combination with the tertiary amine catalyst 1-methyl imidazole (1MI, trade name *EpiKure Catalyst 201* from *Momentive*).

The diethylenetriamine (DETA) was delivered by *Sigma Aldrich* and had a purity of 99% (molecular mass $M_{DETA} = 103.2$ g/mol.

The polyetheramine (PEA) curing agents were the bifunctional D230 (trade name *Jeffamine D-230* from *Huntsman*) and the trifunctional T403 (trade name *Jeffamine T-403* from *Huntsman*), with *amine-hydrogen equivalent weights* (*AHEW*) of approx. 59 g/mol and 80 g/mol, respectively, as determined by acid-base titration with 10 mmol/l HCl. The structure formulas of the DGEBA and the curing agents are given in the Supplementary content.

2.2. Processing

The DGEBA was mixed with MTHPA in an approximately stoichiometric ratio and with the three different amine curing agents in an approximately stoichiometric or in an approximately 10% sub-stoichiometric ratio (i.e., with approx. 10% lower amount of curing agent). Table 1 shows a list of the seven investigated epoxy systems with their respective type of curing

Table 1
Investigated epoxy systems. The relative mass *W* of curing agent added is given in mass parts per hundred mass parts of DGEBA resin (phr). T_{post} stands for the post-curing temperature. At least two IF-WS_2-filled materials and two neat-epoxy references were produced for each material type.

Denomination	Curing agent	*W*/phr	T_{post} (°C)
EP/MTHPA–89	MTHPA, 1MI	89.2, 2.00	160
EP/DETA–10	DETA	10.0	160
EP/DETA–11	DETA	11.1	160
EP/T403–40	T403	40.0	125
EP/T403–44	T403	44.0	125
EP/D230–29	D230	29.0	125
EP/D230–32	D230	32.0	125