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QUANTITATIVE INTERPHASE STUDY OF COMPOSITE MATERIALS

Interphase Engineering: A Scientific Way of Tailoring the Mechanophysical Properties of Composite Materials

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The projects covering July, 1988 - December, 1991 were concerned with the application of a new technique, NMR imaging, to interface studies; preparation of composites with special innerlayers; and systematic surface treatment of carbon fibers and characterization of surfaces. We have studied all proposed areas and obtained several major breakthroughs as summarized in the formal Final Report.

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Final Report for the Project No. N00014-88R-0330

The projects covering July 1988 - December 1991 were concerned with the application of a new technique, NMR imaging, to interface studies; preparation of composites with special innerlayers; and systematic surface treatment of carbon fibers and characterization of surfaces. We have studied all proposed areas and obtained several major breakthroughs as summarized below.

A. Application of NMR Relaxation and NMR Imaging to Composite Interphase Studies.

Solid-state ^{13}C NMR relaxation technique is effective in monitoring molecular mobility of polymer chains. We have applied this technique to model materials which simulate the composition of silane coupling agent/epoxy interphase in a glass fiber reinforced epoxy composite. T_{1r} measurement of the component was used to study the molecular miscibility as a function of silane/epoxy composition. Alkyl-functional silane coupling agents were used to vary systematically the chain length of the alkyl group in order to evaluate the effect of compatibility to the interpenetration of silane/epoxy system. In addition to the ^{13}C NMR analysis, ^{29}Si was also used to study the structure of silane on a high surface area silica.

NMR imaging allows water diffusion to be studied nondestructively. The silane/epoxy copolymers were varied in their composition and exposed to hot water. The diffusion of water depended strongly on the composition, thus on the network structure of the interpenetrating system. This technique has emerged to become a very sensitive tool to detect the difference in water sorption as a function of polymer network structure.

B. Preparation of Composites with Special Innerlayers.

A carbon fiber reinforced polyimide composite was used for the study. The polyimide used was the so-called PMR-15 (polymerization of monomeric reactants), a norbornene end-capped polyimide of methylene dianiline and benzophenone dianhydride. The composite under study is known to be thermally stable with typical use temperature of 300 °C over 1000 hours. However, the brittleness of the composite limits the usefulness of the system. We constructed a special fiber coating device to coat individual carbon fibers with elastomeric innerlayers. The base system is polydimethylsiloxane elastomer, but is specially formulated to be stable at elevated temperatures. Introduction of elastomeric innerlayers to high temperature composite has never been attempted due to the limited availability of high temperature elastomers. In our system, the use of iron octoate as an agent to counter enbrittlement due to excessive cross-linking of polydimethylsiloxane chain allowed the silicone elastomer to be used at the use temperature of the polyimide. In some instances, the impact strength was improved as much as 300% while the other samples showed marginal improvements. The degree of polyimide cure on the effectiveness of the innerlayer has been studied. The results will be reported as a technical report in the middle of fall, 1991.

While deliberately introducing an elastomeric innerlayer was effective in improving the impact strength of composites, there are other types of innerlayers. A transcrystalline layer around a reinforcing fiber is one such example that might be termed as <u>*in-situ* formation of innerlayers.</u> The transcrystalline morphology is formed by massive nucleation of the matrix polymer on a reinforcing fiber having crystal growth direction only normal to the fiber direction. The transcrystal morphology is believed to improve interfacial adhesion of a semicrystalline polymer matrix (4,5). We have developed a new quantitative way to determine the interfacial energy difference function, Ds,which is needed to estimate the ability of a given fiber/matrix combination to form the transcrystal morphology (6,7). The heterogeneous nucleation theory which is used to determine the Ds suffers from the inability to determine the nucleation rate on materials such as carbon fibers where identification and counting of nuclei is nearly impossible. Our proposed "induction time" approach circumvents counting the number of individual nuclei but relies on the crystal growth measurement which can easily be achieved. We have further defined a term "Advantage A" with which we can determine if a system is predisposed to form either the transcrystal or spherulitic morphology. The Advantage A is defined as the ratio between the interfacial energy difference

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function of the pure matrix, Ds', and composite, Ds, systems. The calculated Advantage A has properly predicted the reported interfacial morphologies. This breakthrough now allows us to evaluate the possibility of the fiber/matrix pair to form transcrystal in a quantitative fashion, an ability seldom reported in the literature.

C. Systematic Surface Treatment of Carbon Fibers and Its Characterization.

We have completed the installation of both electrochemical and plasma surface treatment devices. The electrochemical surface treatment device is similar to what industrial operation can achieve in order to simulate practical application examples. On the other hand, the plasma device has a special low power feature. The surface treatment by plasma has been done in the past in the 20 - 200 W range. While this power range was effective in aggressive treatment, the surface morphology is also altered. As a result, the improved adhesion cannot be simple-mindedly attributed to the change of surface energetic and surface functionality. Topological change of the surface can change the degree of mechanical interlocking. In order to avoid this complication, we have decided to use very low power plasma on the order of 1 - 5 W in addition to the traditional power range (8).

Carbon fiber surface was treated by a plasma of inert gas, the plasma was stopped, and then a polymerizable gas was introduced. The activated surface still has remnant free radical which can initiate the reaction of the polymerizable gas. Since only free radicals remain on the surface, the polymerization initiated by this method is clean and well controlled. ESCA results indicate that indeed polymer layers are introduced on the surface.

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The project resulted in 14 publications in three-year period and the brief description of each paper is described in the following section.

Technical Report No. CWRU/DMS/TR-30

"Monitoring of Composite Processing Using Magnetic Resonance Imaging"

Nuclear magnetic resonance imaging was used to study the internal defects in composites which were processed under different conditions. Void contents were observed by exposing the composites to water and imaging the water in the composites. Tubular voids that followed the direction of the fibers in the composites were mapped.

Technical Report No. CWRU/DMS/TR-31

"Surface Characterization of Graphitized Carbon Fibers by Attenuated Total Reflection Fou9rier Transform Infrared Spectroscopy"

A pitch-based graphitized carbon fiber has been oxidized and its surface has been studied by Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR). The spectra of the samples oxidized for different times are compared and the bands at 1720cm^{-1} and 1580 cm^{-1}, arising from the oxidative treatment, followed as a function oxidation time. A curve fitting program has been used to separate the contribution of different functional groups to the relatively broad, composite peaks arising from the oxidation treatment. Tentative assignments are presented here. After oxidation, we detect the presence of carboxylic acid (1705 cm^{-1}), ester (1730 cm^{-1}), lactone (1750 cm^{-1}), enol (1640 cm^{-1}), and quinone structure (1583-1570 cm^{-1}) moieties as well as a product due to the nitration of the aromatic ring (1545 cm^{-1}). Some of the assignment of the chemical functionalities present on the fibers have also been verified by designning and performing approapriate specific derivatization reactions on these functional groups. The results of such reactions with aniline, epichlorohydrin, lithium aluminum hydride, sodium hydroxide and epoxy resin coating are reported.

Technical Report No. CWRU/DMS/TR-32

"Carbon-13 and Silicon-29 NMR of the Silane Coupling Agent/Matrix Resin Interface"

Solid-state ^{13}C NMR and ^{29}Si NMR are used to study the change in mobility due to the hydrolysis of silane in a gradient model of the silane coupling agent/matrix resin interface. ^{13}C NMR is used to compare carbon spin-lattice relaxation times, T_1, for the reactive mixtures of γ-aminopropyltriethoxysilane (APS) and epoxy resin. When the silane is first hydrolyzed before reacting with the epoxy, the carbon T_1 values are increased as compared to the mixtures containing unhydroliyzed silane. ^{29}Si NMR is used to measure the relaxation of the silane network itself in the APS/epoxy resin model systems. The T_{SiH} values are shorter for the hydrolyzed mixtures of APS/epoxy resin than for the unhydrolyzed mixtures of APS/epoxy resin, reflecting a more rigid system. The feasibility of using ^{29}Si NMR in the study of composite interfaces is demonstrated.

Technical Report No. CWRU/DMS/TR-33

"Enhancement of the Absorptions of Surface Species Present on Graphitized Carbon Fibers: A Theopretical Approach"

An oxidized carbon fiber has been modeled as a thin polymeric film, representing the surface species, coated with a graphite overlayer. Optical theory has been utilized to calculate the variations in the electric field intensities, occurring when the graphite layer is overlayed on a film or PVAc (Polyvinylacetate). The increase of the $<E_z^2>$ component has been observed. Spectral simulations based on Hansen's formulas, clearly show the enhancement or the infrared absorbances. The entity of the enhancement result to be dependent from the air gap thickness, existing between the germanium element and the polymeric film and the nature of the substrates.

Technical Report No. CWRU/DMS/TR-34

"Influence of the Surface Treatment of Graphitized Carbon Fibers on the Curing of an Amine Catalyzed Epoxy-Anhydride System"

The surface of graphitized carbon fibers is oxidatively treated by nitric acid. Fourier transrorm infrared attenuated total reflection spectroscopy has been utilized to monitor the influence of the surface species on the curing of an epoxy system. A curve fitting program is used to deconvolve the overlapped infrared bands. The integrated intensitites of the ester, anhydride, epoxy, and carboxylic acid, plotted against the curing time, clearly show the dependence of the crosslinking process on the concentration of the surface species. The surface groups themselves act as a catalyst: there exists an optimal concentration, a retardation of the curing process has been detected.

Technical Report No. CWRU/DMS/TR-35

"Surface Induced Crystallization in Ultra-High Modulus Polyethylene Fiber Reinforced Polyethylene Composite"

Surface induced crystallization of a high density polyethylene matrix on a gel spun, ultrahigh modulus polyethylene fiber has been investigated both qualitatively and quantitatively. Under the microscope, the fiber exhibits a very good nucleation ability as seen from a uniform transcrystalline zone. The free energy difference function $\Delta\sigma$, as it appears in the classical nucleation theory, is also calculated. Because of the very high nucleation rate which prevent the direct observation of individual spherulites at the interface, a new approach based on induction time is used to obtain an estimate of the free energy difference function $\Delta\sigma$ which is calculated to be $\Delta\sigma = 0.32$ erg/cm^2. This very low value may he explained considering the similar lattice parameters and surface energy of this polymer/substrate system. Crystallization by melt epitaxy rather than transcrystallization may be observed.

Technical Report No. CWRU/DMS/TR-36

"Effect of Fuming Nitric Acid Surface Treatment of Ultra-High Modulus Polyethylene Fibers on the Mechanical Properties of Their Composites"

The effect of hol fuming nitric acid (FNA) treatment on the adhesion of ultrahigh modulus polyethylene fabrics to an epoxy resin has been investigated. Mechanical and molecular characterization of the interface has been attempted. Fourier transform infrared diffuse transmittance spectroscopy has been used to monitor the chemical changes introduced by the FNA treatment as well as the nature of the interface between the fibers and the epoxy resin on the morphological consequences of the FNA treatment. Flexural and interlaminar shear properties of the composites have been measured as a function of the extent of surface treatment. Esterification of the FNA treated polyethylene fibers is used to examine the role of surface functionality to the mechanical performance.

Technical Report No. CWRU/DMS/TR-37

"Surface Characterization of Carbon Fibers and Interphase Phenomena in Epoxy-Reinforced Composites"

A new Fourier transform infrared spectroscopic method to study the surface of carbon fibers using the attenuated total reflection technique are described. The surface species as a function of nitric acid oxidation time is quantitatively measured. The influence of oxidized carbon fiber surface on the interphase structure of epoxy primer is also measured as a function of the concentration of the surface polar groups.

Technical Report No. CWRU/DMS/TR-38

"An Induction Time Approach to Surface Induced Crystallization in Polyethylene/Poly(ε-Caprolactone) Melt"

The surface induced crystallization of poly(ε-caprolactone)(PCL) on an ultra-high modulus polyethylene (PE) fiber was investigated using a new approach based on the induction time t_i. This approach allows to estimate the value of the free energy difference function $\Delta\sigma$ as it appears in the theory of heterogeneous nucleation. The classical approach based on the rate of heterogeneous nucleation I is not applicable to transcrystallization because the nucleation density at the fiber surface cannot be measured. A relationship between I and t_i is proposed and a theoritical justification is presented. Good agreement between the two approaches is obtained for a verification case where both I and t_i can be determined. A transcrystalline growth rate study yields an estimate of parameter for PCL of 680 erg^2/cm^4. The maximum growth rate g* is also obtained. The results obtained allow to clarify the influence of certain parameters in the appearance of transcrystallinity. It is also shown how the interfacial morphology can be controlled by the knowledge of the variations of the induction time with temperature.

Technical Report No. CWRU/DMS/TR-39

"Properties of Anhydride-Cured Epoxy Filled with Silica Treated with Silane Blends of Amino and Alkyl End Groups"

Cylinders made of a benzyldimethylamine (BDMA)-catalyzed, nadic methyl anhydride (NMA) cured diglycidyl ether of bishphenol-A (BDGE) were filled with 30 weight % of silica. The silica had previously been treated by silane blends of varying composition, of either γ-aminopropyltriethoxysilane (APS) and butyltriethoxysilane (BTS) or APS and ethyltriethoxysilane (ETS). A variety of techniques were utilized in order to compare the effects of BTS versus ETS and the concentration of amine in the silane blend. These techniques include cross polarization magic angle spinning (CP-MAS) ^{29}Si solid state nuclear magnetic resonance (NMR), photoacoustic (PAS)-Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), compression strength, scanning electron microscopy (SEM) of fracture surfaces, ^{1}H NMR imaging, and gravimetric analysis of water sorption. The results indicate the importance of structure and composition of the silane interphase on the properties of composite materials.

Technical Report No. CWRU/DMS/TR-40

"An Infrared Analysis of the Effect of Composition of Silane Blends of Amino and Alkyl Silane Blends in Tertiary Amine-Catalyzed Anhydride-Cured Epoxy Mixtures"

The property enhancement caused by silane coupling agents in glass-reinforced epoxy matrices is a function of the structure and composition of the silane. The effect of hydrolyzed and nonhydrolyzed of various compositions of silane coupling agent blends of γ-aminopropyltriethoxysilane (APS) and either butyltriethoxysilane (BTS) or ethyltriethoxysilane (ETS) on the cure of a benzyldimethylamine (BDMA)-catalyzed, nadic methyl anhydride (NMA) cured diglycidyl ether of bisphenol-A type epoxy were investigated by Fourier transform infrared spectroscopy (FTIR). The presence of the amine group perturbs the alternating copolymerization of the anhydride and epoxy groups by initiating and catalyzing the reaction. Hydrolysis also promoted the reaction rate. Samples containing ETS cured more rapidly than those containing BTS at the same composition. Imide formation was not significant in the presence of the alkyl-ended silanes. A very simple mathematical simulation was invoked to justify assumptions made during data analysis.

Technical Report No. CWRU/DMS/TR-41

"An Infrared Analysis of the Effect of Composition of n-Buthyltriethoxysilane and γ-Aminopropyltriethoxysilane Blends on Tertiary Amine-Catalyzed Anhydride-Cured Epoxy Mixtures"

The enhancement in mechanical properties observed for silane-treated glass-reinforced epoxy materials is highly dependent on the structure of the coupling agent at the interphase. The effect of varying composition of nonhydrolyzed silane coupling agent blends of γ-aminopropyltriethoxysilane (APS) and butyltriethoxysilane (BTS) on the cure of benzyldimethylamine (BDMA)-catalyzed, nadic methyl anhydride (NMA)-cured diglycidyl ether of bisphenol-A epoxy (BDGE) was studied by Fourier transform infrared spectroscopy (FTIR). The silane blends perturbed the kinetics of the alternating anhydride-epoxy copylmerization reaction, with the perturbation being a nonlinear function of the relative amine concentration in the system .

Technical Report No. CWRU/DMS/TR-42

29Si Solid State NMR Studies of the Effect of Composition of Amine and Alkyl Silane Blends in Tertiary Amine-Catalyzed Anhydride-Cured Epoxy Mixtures"

Silane coupling agent blends of γ-aminopropyltriethoxysilane (APS) and butyltriethoxysilane (BTS) of varying composition were added to an epoxy matrix made of a benzyldimethylamine (BDMA)-catalyzed, nadic methyl anhydride (NMA)-cured diglycidyl ether of bishpenol-A (BDGE) epoxy. ^{29}Si nuclear magnetic resonance (NMR) was utilized in order to deterrnine the effect of composition of the silane coupling agent blend on the mobility of the various portions of the siloxane network. It was found that hydrolysis caused an increase in the rigidity of the highly condensed structures, but decreased the rigidity of the silicon atoms bonded to only one or two oxygen atoms. This phase separation could possibly lead to stress concentration within the network structure. Increasing amine concentration caused only slight increases in rigidity. Although ETS gave consistently lower rigidity values than BTS, these values were not statistically significant.

Technical Report No. CWRU/DMS/TR-43

"Surface Induced Crystallization in Fiber Reinforced Semicrystalline Thermoplastics Composites"

This paper reviews the parameters influencing the appearance of a transcrystalline zone and the experimental techniques which have been used in the study of transcrystallization. A significant example is given for each characterization technique. The influence of transcrystallinity on the mechanical properties of the composite is then examined. Lastly, a theoretical approach based on the theory of heterogeneous nucleation and on the inducation time is presented, which allows to control the extent of the transcrystalline morphology. Little has been published on the mechanical aspect of transcrystallinity but this is an important aspect because this will ultimately determine if it is desireable to induce transcrystallization in semicrystalline thermoplastic composites. Although the main application of transcrystallization seems to be in fiber reinforced composites, results of studies with films as a substrate are directly applicable to fiber reinforced composites and have also been included in this paper.