CHEMICALLY GRAFTED "KEVLAR" FIBRES AND THEIR SURFACE CHARACTERISATION

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ABSTRACT

A number of functional groups have been successfully grafted onto the surface of "Kevlar" fibres. This grafting has been accomplished via an anhydrous solution reaction route involving dimethyl sulfoxide and dimethyl-sulfanyl carbanion chemistry. The groups grafted include propane-diol, alkyl, epoxy and trimethyl silane.

Modified and un-modified fibres have been examined by both X-ray photoelectron spectroscopy and via fibre wettability experiments. Both techniques confirm changes in the fibre surface chemistry. In the case of the alkyl grafted fibres, wetting measurements indicated that these fibres were more hydrophobic than untreated "Kevlar" fibres whilst diol grafted fibres were found to be more hydrophilic. The surface fibre energetics and the surface composition of the fibres are discussed.

INTRODUCTION

Aramid fibres, such as "Kevlar" which is composed of high orientated polyphenylene terephthalamide (PPTA) polymer chains, are an important class of fibres for composite reinforcement. The poor performance of aramid fibre reinforced composites under loading conditions off axis to the orientation of the fibres is primarily attributed to poor adhesion between the fibres and the polymer matrix. It is generally accepted that the adhesion between the reinforcing phase and the matrix phase in a composite material is dependent on the interfacial chemistry. Thus, a number of workers have modified the surface of aramid fibres such as "Kevlar" via the use of chemical plasmas and by solution reaction techniques in an attempt to improve the interfacial adhesion. Although a number of these fibre modifications have resulted in changes in the properties of the composite materials manufactured from these modified fibres, the surface chemical properties of the fibres, as characterised by wettability, sometimes remain unchanged. Consequently it is not clear whether the changes in the mechanical properties of the composite are due to changes in the chemical adhesion between the fibre and the matrix, or some other phenomenon.

ARAMID FIBRE SURFACES

Surface Modifications

A number of research workers have reported chemical methods for modifying the functional surface chemistry of aramid fibres. Allred et al. [1] have employed gas phase O₂ plasmas for the oxidation of "Kevlar 49" fibres whilst a wide range of plasma treatments was used by Wertheimer and Schreiber [2] to modify "Kevlar 29" fibres. These included non-polymerisable vapours such as Ar, N₂, NH₃ and air, as well as the plasma activated polymerisation of vapours such as propane, epoxy and hexamethyl siloxane. The mechanical performance of these materials was found to be strongly dependent on the lapsed time between...
plasma reaction and sample fabrication. A detailed study of the use of ammonia plasmas to
aminate "Kevlar" fabrics has been undertaken by Allred [3]. Amine group surface
concentrations on "Kevlar" fibres were successfully monitored using dye adsorption studies
following exposure of the fabric to ammonia plasmas. However contact angle measurements
showed no differences between the modified and unmodified fibres. Recently Penn et al. [4]
have examined the effect of amine plasmas on "Kevlar" fibre adhesion and wettability. The
same workers [4] have also reported on the modification of aramid fibres by an isocyanate
solution graft reaction. However, specific chemical tests for covalent bond formation between
the terminal amine of the pendant group and the epoxy molecules showed that covalent bonding
did not occur. Keller et al. [5] have studied a solution reaction scheme for "Kevlar" fibres
based on the aqueous hydrolysis of the amide linkages with strong aqueous acidic and basic
solutions. Following hydrolysis, a bifunctional epoxy monomer was reacted with the amine
groups released by the hydrolysis reaction. Whilst this reaction was successful, the hydrolysis
step led to a 20 % decrease in the fibre tensile strength.

Recent work has shown that normal substituted PPTA polymers, such as N-alkylated,
N-arylated and N-carboxymethylated can be synthesised (Takayanagi and Katayose [6]). It
was previously found that NaH and dimethyl sulphoxide (DMSO) react to form sodium methyl
sulphinylcarbanion which can ionise the proton of the amide group of aramid molecules
resulting in homogeneous dissolution in DMSO. Following the metallation of the PPTA
polymer, a nucleophilic substitution reaction allowed N-substitution to be accomplished.
Metallated PPTA fibre surfaces were reacted with alkyl halides and epoxy compounds so that
N substituted epoxy and alkyl groups were grafted onto the fibre surface (Takayanagi et al.
[7]).

Surface Energetics

Using acid-base concepts, Fowkes and Maruchi [8] have proposed that the work of
adhesion, $W$, consists of two components. The first component is a measure of the dispersive
interactions, $W^d$, and a second component describes the more specific acid-base interactions,
$W^{a-b}$ (see Equation 1). Equation 2 relates to the work of adhesion, $W_{A-B}$ between phases A
and B, with $\gamma^d$ the dispersive component of the solids surface tension. Using Equation 2,
these authors were able to estimate the acid-base components of $W_{A-B}$ for a number of
polymer-liquid pairs from experimental wettability data.

\[ W = W^d + W^{a-b} \]  
\[ W_{A-B} = 2\sqrt{\gamma^d_{A} \gamma^d_{B}} + W^{a-b} \]  

Equation 2 allows the specific chemical interfacial interactions to be estimated from appropriate
wettability experiments.

The two primary theories likely to account for increased adhesion in aramid fibre
composites are the adsorption and the chemical bonding adhesion theories. Increased adhesion
between the fibre and the matrix phase would also be expected to result in changes in the
surface energetics of the fibre. In the case of the adsorption theory, improvements in adhesion
should directly relate to the fibre surface energy. For the chemical bonding theory, it would be
anticipated that the potential for covalent bonding at the fibre-matrix interface would also be