Preparation and Properties of Aramid-Silica Hybrids with Inter-Phase Bonding Through (3-glycidoxypropyl)-trimethoxysilane

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Abstract. Nano-composites from aramid-silica system have been prepared via sol-gel process. Poly (phenyleneterephthalamide) copolymer chains were prepared by reacting a mixture of p- and m-phenylenediamines with terephthaloyl chloride in dimethylacetamide used as solvent. The sol-gel process in the polymer matrix was carried out through hydrolysis and condensation of a mixture of tetraethoxysilane and (3-glycidoxypropyl) trimethoxysilane. The latter was used to develop linkage, on one hand with silica network structure using alkoxy groups and on the other hand with aramid chains at its secondary amine groups through glycidal groups of silane. Mutual interaction between the two disparate phases aramid and silica network was thus created. Thin films of the composites containing different proportions of silica ranging from 5.0 to 25.0-wt% were cast by the solvent elution technique. The \( \alpha \)-relaxation temperature associated with the glass transition was measured by the dynamic mechanical thermal analysis. The results showed an increase in the glass transition temperature from 328°C for the pure aramid to 352°C for the hybrid materials containing 25-wt% silica, an indicative of the increased interfacial interaction between the two phases. Films having relatively low silica content were flexible and transparent, but those with high silica content were opaque and brittle. These films were tested for their tensile strength, modulus and toughness. The mechanical strength of the composites as compared to the pure aramid increased initially but with further addition of silica the strength decreased. The initial increase can be explained due to increased interfacial interaction between the two phases, however agglomeration of silica particles was responsible for decreasing strength at higher silica contents.

Keywords: sol-gel process, aramid-silica hybrids, inter-phase bonding, (3-glycidoxypropyl)trimethoxysilane

1. Introduction

Typical advantages of organic polymers are flexibility, low density, toughness and ease in processability, where as ceramics have excellent mechanical, thermal and optical properties. If these materials can be combined effectively, a new class of high performance organic-inorganic hybrid materials can be achieved [1]. These hybrid materials are currently of great interest within the material community. Among the high temperature polymers, aromatic polyamides play an im-
important role in modern technology based on advanced materials, owing to their high thermal stability, strong intermolecular forces, chain rigidity and inherent stability of the aromatic moiety [2]. The thermal and mechanical properties of these polymers can be improved further if they are effectively combined with ceramic phase such as silica, titania or zirconia [3–5]. The most important chemically based route to achieve this goal is the sol-gel process [6–9] which allows the in-situ generation of ceramic phase in the polymer matrix by the hydrolysis of metal alkoxides, followed by a condensation reaction to produce metal oxides. Over the last several years the sol-gel method has been explored extensively to produce organic-inorganic hybrid materials [10–18]. The properties of the hybrid materials depend on the nature and proportion of the components [19]. Interfacial interactions or interconnectivity between the two phases play an important role in determining the mechanical behavior of the composites [18, 20, 21]. Hybrids, composed of inorganic oxides covalently bonded to organic polymers are of special interest, since they benefit from the lack of interface imperfections. In recent years, we have reported various types of aramid based composite systems with and without inter-phase bonding [3–5, 19–23]. In systems where no covalent linkage was developed between the two phases, no significant increase in the mechanical strength of polymer was observed. The tensile strength of the films was reduced and the properties of such hybrids appeared to be very similar to those of glass bead reinforced plastic [22, 23]. The introduction of silica to the aramid matrix raises the modulus, but the toughness and elongation to break are greatly reduced. However, by chemically linking the two phases, using aminophenyltrimethoxysilane as coupling agent, both the transparency and tensile strength of the films were improved [21]. The present study is a part of our continuous effort to produce novel organic-inorganic hybrids using high temperature polymer matrix and reinforcing it with different ceramic phases using the sol-gel technique. The chains from poly (phenylene terephthalamide) copolymer were prepared. The sol-gel process in the polymer matrix was carried out through hydrolysis and condensation of a mixture of tetraethoxysilane (TEOS) and GPTS. GPTS was used to condense on one side with TEOS and hence with silica network and on other side with secondary amine groups of aramid chain. The hydrid materials thus obtained were characterized for their tensile strength, tensile modulus and toughness and thermal behaviour using dynamic mechanical thermal analysis (DMTA).

2. Experimental

2.1. Chemicals

The monomers 1,4-phenylenediamine (97%), 1,3-phenylenediamine (99%) and terephthaloyl chloride (TPC) (99%) were received from Fluka and were used as received. The solvent dimethylacetamide (DMAc) anhydrous (99%) was obtained from Aldrich and was used as such. Tetraethoxysilane (TEOS) (>98%) was obtained from Merck, the coupling agent (3-glycidoxypropyl) trimethoxysilane (GPTS) (97%) was obtained from Fluka were used as received. The polymerization and subsequent reactions were carried out under complete anhydrous conditions.

2.2. Preparation of Aramid and Aramid-Silica Hybrids

Aramid chain was prepared by poly-condensation of 1,3- and 1,4-phenylenediamine and TPC in DMAc. For this purpose 5.407 g mixture (0.05 mol) of 1,4- and 1,3-phenylenediamine (in a mole ratio of 35:65) was taken in a conical flask. DMAc (130 g) was added to this mixture and stirred vigorously to get a clear solution. The solution was then cooled to a temperature below 0°C and 10.150 g (0.05 mol) of TPC was added. After half an hour of reaction the temperature of reaction mixture was allowed to come to room temperature and the stirring continued for 24 h after to complete the reaction. The polymer solution thus obtained was used for further processing. GPTS and TEOS were mixed in a mol ratio of 0.85:0.15 in DMAc. The solution was stirred