DYNAMIC MECHANICAL PROPERTIES OF ARAMID FABRICS IMPREGNATED WITH CARBON NANOTUBE/POLY (VINYL BUTYRAL)/ETHANOL SOLUTION

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Abstract

In this study six samples of polyurethane/*p*-aramid multiaxial fabric forms (Colon fabrics) were coated with 10 wt.% poly (vinyl butyral) (PVB)/ethanol solution with the addition of multiwalled carbon nanotubes (MWCNT). The solution was impregnated on both sides of each of the fabrics. All composite samples consisted of four layers of the impregnated fabrics. The MWCNT/PVB content was 0, 0.1 and 1 wt.%. The three samples of the fabrics with different MWCNT/PVB content were coated with γ-aminopropyltriethoxysilane (AMEO silane)/ethanol solution due to the surface modification. The mechanical properties of the prepared composite samples were studied by dynamic mechanical analysis (DMA). The 60% increase in storage modulus was achieved by addition of MWCNT and impregnation of aramid fabrics with AMEO silane. The pristine multiwalled carbon nanotubes (MWCNT) were introduced in order to enhance additionally the mechanical properties of the materials for ballistic protection.

Keywords: p-aramid fabrics, multiwalled carbon nanotubes, AMEO silane, dynamic mechanical analysis

Introduction

Carbon nanotubes (CNT) represent cylindrical carbon molecules constituted of carbon atoms linked in hexagonal shapes (Figure 1) [1]. Their dimensions are nanometer in diameter and several millimeters in length. Carbon nanotubes have different structures, varying in length, thickness, type of helicity and number of layers [2]. In multiwalled carbon nanotubes (MWCNT), multiple rolled graphitic layers make up concentric tubes [1].

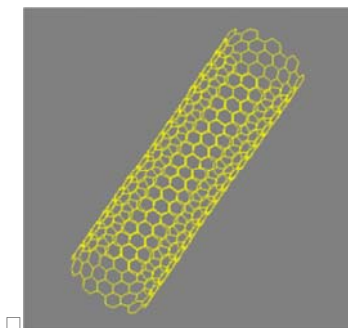* Corresponding author: V. Obradović, vobradovic@tmf.bg.ac.rs

Fig. 1. Carbon nanotube structure

The carbon-carbon connection in graphite represents one of the strongest bonds, making CNTs great candidates for the stiffest construction ever synthesized. It is impressive that the tubes are flexible and do not crack in bending while testing under a transmission electron microscope (TEM) [3]. CNTs exhibit extraordinary mechanical, electronic and magnetic properties. CNTs are probably the strongest material with a tensile strength greater than steel, but only with one sixth of the weight of steel [4]. The graphene layer (in-plane) is as stiff as diamond at low strain [2].

A common purpose for adding fillers into polymers is to increase their modulus or stiffness. Various filler parameters are considered for their good fulfillment in the composite. They include the size of particles, their geometry, orientation, stiffness, dispersion, aspect ratio (high ratio is eligible), and the strength of filler-matrix connections [5, 6]. The interactions between the filler and the polymer matrix are important to enhance the filler dispersion and the adhesion of the polymer matrix to the filler surface, which increases the effective filler volume and creates the load transfer from the matrix to the filler when the material is exposed to mechanical distortion [6]. If the adhesion between the matrix and the CNTs is not strong enough to sustain high loads, the reinforcement with the high tensile strength of CNTs is lost. Surface treatments are always used to improve interfacial bonding if the adhesion between the matrix and the CNTs is not strong enough. The two main ways of improving adhesion and shear strength are: the increase of roughness and reactivity of the outer surface of CNTs [7]. Compatibility with the polymer matrix can be maintained by chemical modification of MWCNTs [8]. CNTs are an excellent choice as fillers in polymer composites because of their high aspect ratio (length/diameter ratio, which can be up to 132000000/1), high strength and stiffness, small size, small mass, low density and high conductivity. When a conducting polymer is used as a matrix, the nanotube fillers improve electrical transfer greatly at low nanotube concentrations [3, 6, 9].

MWCNTs have broad applications, from electronics and space industry to medicine and building industry. They can be used for sensors, lithium ion batteries, fuel cells, atomic force microscope (AFM) tips, technical textiles, drug delivery, etc [2, 8].

In the study, the pristine multiwalled carbon nanotubes (MWCNT) were introduced in order to additionally enhance mechanical properties of materials for ballistic protection. The six samples of polyurethane/*p*-aramid multiaxial fabric forms (Colon fabrics) were coated with MWCNT/poly (vinyl butyral) (PVB) ethanol solution. The surfaces of three samples were coated with γ-aminopropyltriethoxysilane (AMEO

silane)/ethanol solution. The mechanical properties of prepared fabrics were analyzed by the dynamic mechanical analysis (DMA).

Materials

A polymer powder poly (vinyl butyral) (Mowital B60H, Kuraray Specialities Europe) and absolute ethanol (Zorka Pharma, Šabac) were taken for preparing the PVB solution. The MWCNT (Cheap Tubes Inc, USA) were added into the PVB solution. The nanotubes lengths were from 3 μm to 30 μm with their outer diameters from 13 nm to 18 nm. Multiaxial aramid fabrics (Martin Ballistic Mat, Ultratex, Serbia) were used with polyurethane/*p*-aramid fiber type Colon (Heracron, Kolon Industries, Inc, Korea) impregnated with polyurethane (Desmopan, Bayer) [10]. The fabric sample dimensions were 15 cm × 15 cm.

Experimental

The experiments were carried out with the PVB solution in concentration of 10 wt.% where ethanol was used as the solvent. At first, the MWCNTs were added into ethanol with concentration of 0, 0.1 and 1.0 wt.% and ultrasonicated for 30 min separately in order to provide good dispersion of the carbon nanotubes. After the dispersion process, the ethanol-MWCNT mixture was put into the 20 wt.% PVB solution in order to achieve 10 wt.% solution. The solution was then mixed with a magnetic stirrer overnight. Figure 2 displays the difference between the PVB/ethanol solution with MWCNT and the ethanol-MWCNT mixture where after a while the MWCNT formed residue. MWCNTs are well dispersed in the PVB/ethanol solution and the stability of this solution is long term [11].

Fig. 2. MWCNT/PVB/ethanol solution (left) and MWCNT-ethanol mixture with the same content of MWCNT (right)

There were six samples of composites which consisted of four layers of fabrics. The three of them with different MWCNT/PVB content were firstly coated with γ-aminopropyltriethoxysilane (AMEO silane)/ethanol solution due to the surface modification of the fabrics. The modification of these composites was managed by impregnation with 2 wt.% AMEO silane/ethanol solution where 2 g of AMEO silane dissolved in 98 g of 96 wt.% ethanol solution for each sample. The solution was stirred for 10 min with a magnetic stirrer for the hydrolysis of AMEO silane. After the impregnation, the fabrics were left to stay for 24 hours.

Six samples were of the following characteristics:
1. Impregnated with PVB solution (8 g of PVB was dissolved in 72 g of ethanol, and the same content of this solution was used for the next seven samples),
2. Impregnated with PVB and AMEO silane solutions,
3. Impregnated with 0.1 wt. % MWCNT/PVB solution (8 mg of MWCNT was added into the PVB/ethanol solution),
4. Impregnated with 0.1 wt. % MWCNT/PVB and AMEO silane solutions,
5. Impregnated with 1 wt. % MWCNT/PVB solution (80 mg of MWCNT was added into the PVB/ethanol solution),
6. Impregnated with 1 wt. % MWCNT/PVB and AMEO silane solutions.

The samples were obtained by impregnation of both sides of the fabric with the appropriate solutions and then they were left to stand for 24 h for ethanol evaporation. They were processed in the compress machine (N 840 D Hix Digital Press) at a temperature of 170 °C and under the pressure of 3 bars for 30 min. The produced *p*-aramid composites with different content of MWCNT are depicted in Figure 3.
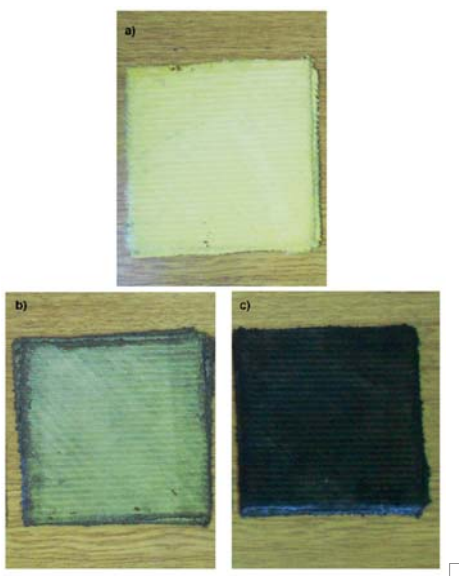

Fig. 3. Samples impregnated with: a) 0, b) 0.1 and c) 1.0 wt.% MWCNT/PVB/ethanol solution

Dynamic mechanical thermal analysis (DMA, Q800 TA Instruments, USA) for the *p*-aramid fabrics was carried out in a dual cantilever mode at a frequency of 1 Hz where the temperature ranged from 40°C to 170 °C with a heating rate of 3 °C/min for the estimation of the storage modulus (E') and damping factor (Tan Delta, tan δ).

Results and discussion

Figure 4a shows that the modulus of Colon/PVB samples increased with the addition of pure multiwalled carbon nanotubes. The storage modulus at the temperature of 40°C for the Colon/PVB and Colon/PVB/1 wt.% MWCNT composites was 1377 MPa and 1669 MPa, respectively (Figure 4a, Table 1).
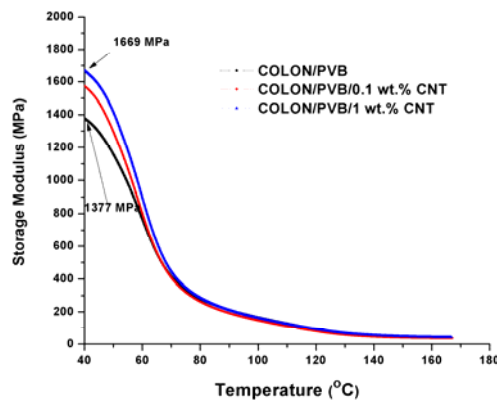
(a)
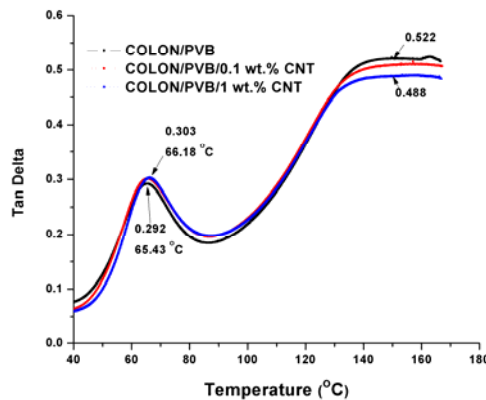
(b)

Fig. 4. Storage modulus (a) and Tan Delta (b) of Colon/PVB fabrics with various content of MWCNT

The high value of Tan Delta of these fabrics (Figure 4b) indicated to the steady motion of polymer macromolecules. The first peak showed the glass transition temperature, T_{g1}, of PVB and the second one, T_{g2}, the glass transition temperature of hard segment of polyurethane in the impregnated Colon fabrics (which was ~150 °C). The T_{g1} value for the Colon/PVB sample was 65.43 °C, and the values for all other

samples with various content of MWCNT were very similar to this one (Figure 4b, Table 1). It is obvious that there was no increase in thermal stability with the addition of MWCNT. Tan Delta of these fabrics showed that the strongest bond between PVB and fabrics was with the Colon/PVB composite (0.292, Figure 4b). Contrary to that fact, tan δ_2 for the same composite had the highest value at the temperature of about 150 °C (0.522, Table 1) which indicated that the bonds were the weakest (Table 1).
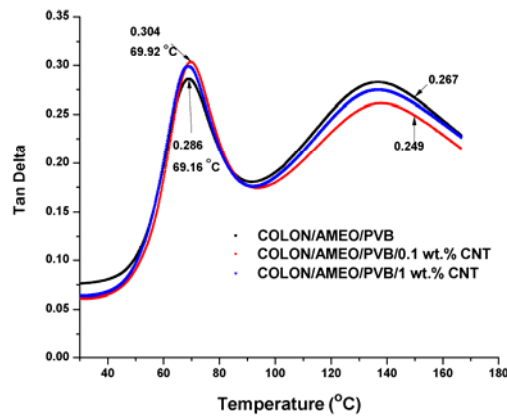
Table 1. DMA results of Colon/PVB fabrics with various content of MWCNT

Composite	E' (MPa, 40°C)	T_{g1} (°C)	tan δ_1 (T_{g1})	tan δ_2 (150 °C)
Colon/PVB	1377	65.43	0.292	0.522
Colon/PVB/ 0.1 wt% MWCNT	1576	65.51	0.301	0.509
Colon/PVB/ 1 wt% MWCNT	1669	66.18	0.303	0.488

Impregnation of Colon fabrics with AMEO silane maximized the storage modulus for all samples due to stronger bonds between CNT and AMEO modified Colon/PVB surface (Figure 5a). The storage modulus value for the Colon/AMEO/PVB and Colon/AMEO/PVB/1.0 wt.% MWCNT composites were 1936 MPa and 2204 MPa, respectively, while they had the same value for the modulus - 812 MPa at the glass transition temperature of PVB (Figure 5a, Table 2). The glass transition temperature of all the AMEO modified composites was increased compared to the unmodified ones, which provided thermal stability in all cases (Figure 5b, Table 2). For example, the T_{g1} value for Colon/PVB/0.1 wt% MWCNT composite was 65.51 °C while the same value for AMEO modified counterpart composite was 69.92 °C.
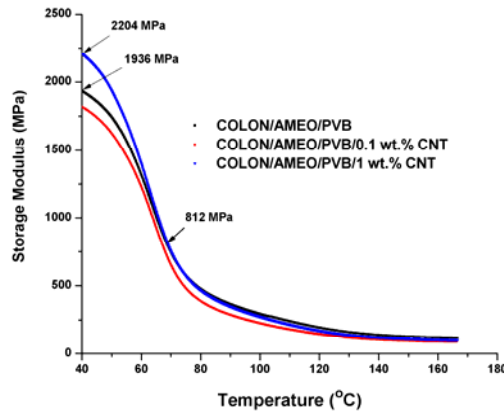
(a)

(b)

Fig. 5. Storage modulus (a) and Tan Delta (b) of Colon/AMEO/PVB fabrics with various content of MWCNT

With the glass transition temperature of polyurethane (~ 150 °C), all the AMEO modified composites had the decreased values of the damping factor (Figure 5b, Table 2).

Table 2. DMA results of Colon/AMEO/PVB fabrics with various content of MWCNT

Composite	E' (MPa, 40°C)	T_{g1} (°C)	tan δ_1 (T_{g1})	tan δ_2 (150 °C)
Colon/AMEO/PVB	1936	69.16	0.286	0.267
Colon/AMEO/PVB/ 0.1 wt% MWCNT	1818	69.92	0.304	0.249
Colon/AMEO/PVB/ 1 wt% MWCNT	2204	68.85	0.299	0.261

Conclusion

The mechanical properties of the prepared composites were studied by DMA. The increase of storage modulus was achieved by addition of MWCNT and impregnation of aramid fabrics with AMEO silane. In that way, the chemical modification of aramid fabrics was accomplished and stronger bonds between CNT and AMEO modified Colon/PVB surface of fabrics enhanced the mechanical properties of the composites as well as the higher content of MWCNT. The storage modulus value of Colon/AMEO/PVB/ 1 wt% MWCNT sample was 60% greater compared to the value of Colon/PVB sample.

Acknowledgements

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