VERA OBRADOVIĆ, DUŠICA B. STOJANOVIĆ
IRENA ŽIVKOVIĆ, PETAR S. USKOKOVIĆ,
RADOSLAV ALEKSIĆ

Scientific paper
UDC:620.193.7:66.095.115

Dynamic mechanical properties of aramid fabrics impregnated with multiwalled carbon nanotubes

Carbon nanotubes (CNT) represent allotropes of carbon with a cylindrical nanostructure. In multiwalled carbon nanotubes (MWCNT), graphitic layers make up concentric tubes. The multiwalled nanotubes length in our research is from 3 μm to 30 μm and their outer diameter is from 13 nm to 18 nm. Their purity is greater than 99 wt.%. The carbon nanotubes possess extraordinary physical properties, great electrical and thermal conductivity. The addition of carbon nanotubes as the reinforcement in polymer composites can significantly improve the composite mechanical properties.

In the study, the pristine multiwalled carbon nanotubes (MWCNT) were introduced in order to additionally enhance mechanical properties of materials for ballistic protection.

***Keywords:** multiwalled carbon nanotubes, p-aramid fabrics, AMEO silane, mechanical properties*

INTRODUCTION

Carbon nanotubes (CNT) represent cylindrical carbon molecules composed of carbon atoms linked in hexagonal shapes (Figure 1). In multi walled carbon nanotubes (MWCNT), multiple rolled graphitic layers make up concentric tubes [1].

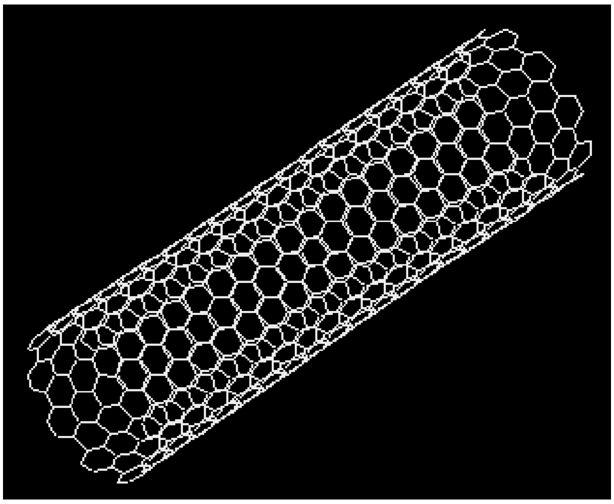

Figure 1- Carbon nanotube structure

The carbon-carbon bond in graphite is one of the strongest in constitution, thus CNTs are great candidates to be the stiffest structure ever synthesized. It is remarkable that the tubes are flexible and do not crack in bending while examining them under a transmission electron microscope (TEM) [2].

Author's address: Faculty of technology and metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

Paper received: 21. 01. 2013.

Carbon nanotubes expose extraordinary mechanical, electronic and magnetic properties. CNTs are probably the strongest composition with a tensile strength greater than steel, but only with one sixth of the weight of steel [3].

A common goal for adding fillers into polymers is to increase the modulus or stiffness. Various filler parameters are taken into account for their good performance in the composite. They include the size of particles, geometry, orientation, stiffness, aspect ratio (high ratio is eligible) and the strength of filler-matrix interactions [4, 5].

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 stress transfer from the matrix to the filler when the material is exposed to mechanical distortion. Novel nano-sized particles are good candidates in reinforcing the polymeric materials especially when they can meet certain reinforce demands at low filler loadings [5].

CNTs are perfect choice as fillers in polymer composites because of their high aspect ratio (length/ diameter ratio, which can be up to 132000000/1), small size, strength, stiffness, low density and high conductivity. When a conducting polymer is used as a matrix, the nanotube fillers greatly increase electrical transfer at low nanotube concentrations [2, 6].

Compatibility with the polymer matrix can be provided by chemical modification of MWCNTs. Carbon MWCNTs exhibit very high hardness and corrosion resistance. Their high adsorption capacity is due to their large surface area. They highly adsorb hydrogen sulfide, sulfur dioxide, disulfides, chlorine, fluorine, ammonia, etc. Addition of MWCNTs into polymers improves their strength characteristics. MWCNTs have widespread applications, from electronics and space industry to medicine and building industry. They can be used for sensors, lithium ion batteries, fuel cells, medical implants, drug delivery, etc [7].

In the study, the pristine multiwalled carbon nanotubes (MWCNT) were introduced in order to additionally enhance mechanical properties of materials for ballistic protection. The polyurethane *p*-aramid multiaxial fabric forms (Colon fabrics) were coated with MWCNT/poly (vinyl butyral) (PVB) ethanol solution. The surface of one sample of the fabrics was coated with γ-aminopropyltriethoxysilane (AMEO silane)/ethanol solution. The mechanical properties of prepared fabrics were studied by dynamic mechanical analysis (DMA).

MATERIALS

A polymer powder poly (vinyl butyral) (Mowital B60H, Kuraray Specialities Europe) and absolute ethanol (Zorka Pharma, Šabac) were used for preparing the PVB solution (10 wt.%). The multiwalled carbon nanotubes (Cheap Tubes Inc, USA) were introduced into the PVB solution. The nanotubes length was from 3 μm to 30 μm and their outer diameter from 13 nm to 18 nm. Multiaxial aramid fabrics (Martin Ballistic Mat, Ultratex, Serbia) were used with *p*-aramid fiber type Colon (Heracron, Kolon Industries, Inc, Korea) impregnated with polyurethane (Desmopan, Bayer) [8]. The fabric sample dimensions were 15 cm × 15 cm.

EXPERIMENTAL PART

The experiments were carried out with the PVB solution in concentration of 10 wt.% where ethanol was used as the solvent. The MWCNTs were added into the solution with concentration of 0.1, 0.5 and 1.0 wt.%. Each of these solutions was ultrasonicated for 15 minutes in order to provide good dispersion of the carbon nanotubes and the stability of the solution for one month (Figure 3).

There were five samples of composites which consisted of four pieces of fabrics:

1) The first one was produced by impregnation of both sides of the fabric with 10 wt.% PVB solution in ethanol (6 g of PVB was dissolved in 54 g of ethanol, and the same content of this solution was used for the next four composites);

2) The second composite was obtained by impregnation of both sides of the fabric with 0.1 wt. % MWCNT/PVB/ethanol solution (6 mg of MWCNT was added into the PVB/ethanol solution);

3) The third composite was produced by impregnation of both sides of the fabric with 0.5 wt. % MWCNT/PVB/ethanol solution (30 mg of MWCNT was added into the PVB/ethanol solution);

4) The fourth composite was obtained by impregnation of both sides of the fabric with 1.0 wt. % MWCNT/PVB/ethanol solution (60 mg of MWCNT was added into the PVB/ethanol solution);

5) Surface modification of the fifth composite was led by impregnation with 2 wt.% AMEO silane/ ethanol solution (the solution which contained 2 g of AMEO silane dissolved in 98 g of ethanol and stirred for ten minutes on a magnetic stirrer for the hydrolysis of AMEO silane). Then, the composite was produced by impregnation of both sides of the fabric with 1.0 wt. % MWCNT/PVB/ethanol solution.

The samples were coated with the appropriate solutions and left to stand for 24 hours for ethanol evaporation (Figure 4 and Figure 5). They were processed in the compress machine at a temperature of 170 °C and under a pressure of 3 bars for 30 minutes.

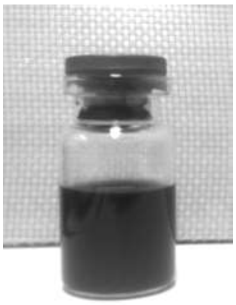

Figure 2 - 1.0 wt.% MWCNT/PVB/ethanol solution after the ultrasonication

Figure 3 - Neat Colon fabric

Figure 4- Colon fabric impregnated with 1.0 wt.% MWCNT/PVB/ethanol solution

Dynamic mechanical thermal analysis (DMA, Q800 TA Instruments, USA) for the *p*-aramid fabrics was conducted in a dual cantilever mode at a frequency of 1 Hz. The temperature ranged from 30 °C - 40 °C to 170 °C with a heating rate of 3 °C/min for the evaluation of the storage modulus (E') and damping factor (Tan Delta, tan δ).

RESULTS AND DISCUSSION

The storage modulus and Tan Delta are determined as functions of temperature for all types of the composites.

The plot depicted in Figure 5 shows that the modulus of Colon/PVB samples is decreasing with the addition of unmodified multiwalled carbon nanotubes. The storage modulus value for Colon/PVB and Colon/PVB/0.1 wt.% MWCNT is 2747 MPa at a temperature of 40 °C. It is evident that with the addition of MWCNT there is no increase in the modulus. For the Colon/PVB/0.1 wt.% MWCNT composite the storage modulus is 2031 MPa.

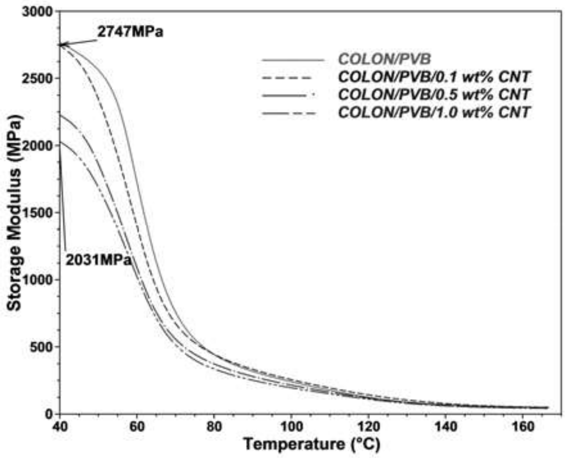

Figure 5- Storage modulus of Colon/PVB fabrics with various contents of MWCNT

The high value of Tan Delta of these fabrics indicates to the steady motion of polymer macromolecules. The first peak shows the glass transition temperature, T_{g1}, of PVB and the second one, T_{g2}, the glass transition of hard segment of polyurethane in the impregnated Colon fabrics. The T_{g1} value of the Colon/PVB sample is 67.09 °C, while this value of Colon/PVB/1.0 wt.% MWCNT is 64.85 °C (Figure 6, Table 1). Thus, there is no increase in thermal stability with the addition of MWCNT.

Tan Delta of these fabrics shows that the strongest bond between PVB and MWCNT is with the highest concentration of MWCNT (1.0 wt.%, figure 7). At the temperature of 64.85 °C the tan δ_1 value of Colon/PVB/1.0 wt.% MWCNT is 0.3132 (at the temperature of about 150 °C tan δ_2 is 0.5249) and is less than the value of Colon/PVB which is 0.3144 (67.09 °C). Tan δ_2 for the same composite is 0.5759 at the temperature ~150 °C, figure 6, table 2).

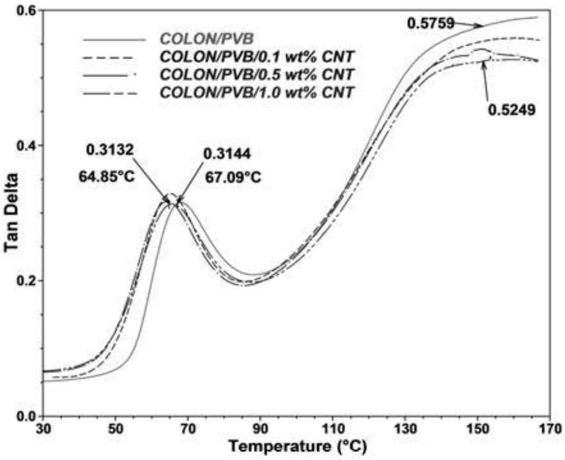

Figure 6- Tan Delta of Colon/PVB fabrics with various contents of MWCNT

Table 1 - DMA results of Colon/PVB and Colon/PVB/ /1.0 wt% CNT composites

Composite	E' (MPa, 40°C)	T_g (°C)
Colon/PVB	2747	67.09
Colon/PVB/ 1.0 wt% MWCNT	2031	64.85

Table 2 - Tan Delta of Colon/PVB and Colon/PVB/ 1.0 wt% CNT composites

Composite	tan δ_1	tan δ_2
Colon/PVB	0.3144	0.5759
Colon/PVB/ 1.0 wt% MWCNT	0.3132	0.5249

Impregnation of Colon fabrics with AMEO silane maximized the storage modulus of the Colon/ PVB/1.0 wt% CNT composite due to stronger bonds between CNT and AMEO modified Colon/PVB surface (Figure 7 and Figure 8). The storage modulus value of the Colon/AMEO/PVB/1.0 wt.% MWCNT composite is 1135 MPa, while it is 737.6 MPa for the Colon/PVB sample at the temperature of ~70 °C, which is close to the glass transition temperature of PVB.

The glass transition temperature of the AMEO modified composite is 71.16 °C, which provides thermal stability of this composite (figure 8, table 3).

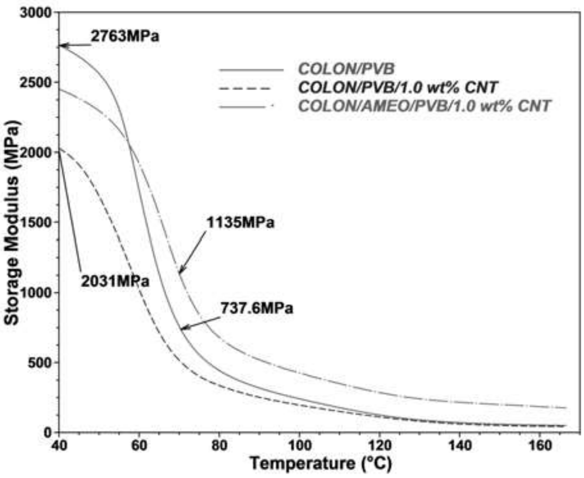

Figure 7 - Storage modulus of Colon/PVB/1.0 wt.% MWCNT fabrics with and without AMEO silane surface modification

Table 3 - DMA results of Colon/PVB and Colon/ AMEO/PVB/1.0 wt% CNT composites

Composite	E' (MPa,	T_g (°C)
Colon/PVB	737.6	67.09
Colon/AMEO/PVB/ 1.0 wt% MWCNT	1135	71.16

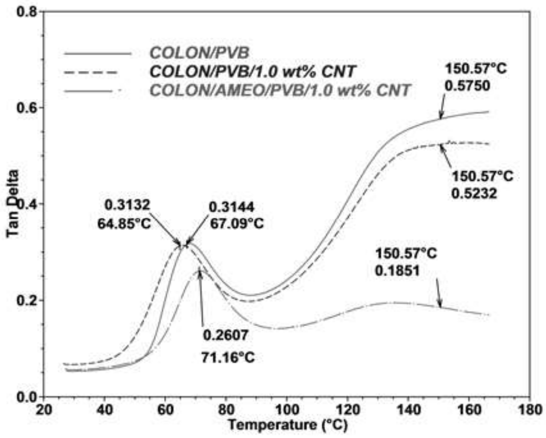

Figure 8- Tan Delta of Colon/PVB/1.0 wt.% MWCNT fabrics with and without AMEO silane surface modification

Tan δ_1 of Colon/AMEO/PVB/1.0 wt.% is decreased to 0.2607, compared to the value of 0.3144 for Colon/PVB composite. With the glass transition temperature of polyurethane (~ 150 °C), the AMEO modified composite has the decreased value of the damping factor - tan δ_2 = 0.1851 (Figure 8, Table 4).

Table 4 - Tan Delta of Colon/PVB and Colon/AMEO/ PVB/1.0 wt% CNT composites

Composite	tan δ_1 (70 °C)	tan δ_2 (150 °C)
Colon/PVB	0.3144	0.5750
Colon/AMEO/PVB/ 1.0 wt% MWCNT	0.2607	0.1851

CONCLUSION

The mechanical properties of prepared composites were studied by dynamic mechanical analysis (DMA). It was determined that the Colon/PVB/1.0 wt.% MWCNT composite had the lower storage modulus value of 2031 MPa compared to the value of the Colon/PVB composite which was equal to 2747 MPa at a temperature of 40 °C. The values of the storage moduli for the Colon/AMEO/PVB/1.0 wt.% MWCNT and Colon/PVB composites were 1135 MPa and 737.6 MPa, respectively. The increase of storage modulus was achieved by impregnation of aramid fabrics with AMEO silane. Thus, the chemical modification of aramid fabrics was accomplished and the covalent bond between polymers and fabrics was created which contributed to reduced motion of polymer macromolecules (PVB, polyurethane), and decreased values for damping factor of Colon/ AMEO/PVB/1.0 wt.% MWCNT. The composite Colon/PVB/1.0 wt.% MWCNT had lower values of damping factor, storage modulus and glass transition temperature compared to the Colon/PVB composite. Also, the AMEO modified composite had higher value of storage modulus above 55 °C and greater glass temperature than both the polymers with 1.0 wt.% MWCNT.

Acknowledgements

This research was financially supported through the Projects No. III 45019 and TR 34011, Ministry of Science and Education – Republic of Serbia.

REFERENCES

[1] Peter J. F. Harris, Carbon nanotube and related structures, Cambridge University Press, 1999.

[2] M. Terrones, Science and technology of the twenty-first century: Synthesis, Properties and Applications of Carbon Nanotubes, Annual Review of Materials Research, 33 (2003), 419–501.

[3] A. Fakhru'l-Razi, M.A. Atieh, N. Girun, T.G.Chuah,M. El-Sadig, D.R.A. Biak, Effect of multi-wall carbon nanotubes on the mechanical properties of natural rubber, Composite Structures 75 (2006), 496–500.

[4] L. Bokobza, Multiwall carbon nanotube-filled natural rubber: Electrical and mechanical properties, eXPRESS Polymer Letters, 6 (2012), 213–223.

[5] L. D. Perez, M. A. Zuluaga, T. Kyu, J. E. Mark, B. L. Lopez, Preparation, Characterization, and Physical Properties of Multiwall Carbon Nanotube/Elastomer Composites, Polymer Engineering and Science, (2009), 866-874.

[6] http://www.cambridgecnt.org/2010/08/carbon-nanotubes-overview.

[7] M. M. Tomishko, O. V. Demicheva, A. M. Alekseev, A. G. Tomishko, L. L. Klinova, O. E. Fetisova, Multiwall carbon nanotubes and their applications, Russian Journal of General Chemistry, 79 (2009), 1982–1986.

[8] A. M. Torki, D. B. Stojanović, I. D. Živković, A. Marinković, S. D. Škapin, P. S. Uskoković, R. R. Aleksić, The viscoelastic properties of modified thermoplastic impregnated multiaxial aramid fabrics, Polymer Composites, 33 (2012), 158-168.

IZVOD

DINAMIČKO MEHANIČKA SVOJSTVA ARAMIDNIH LAMINA IMPREGNISANIH SA VIŠESLOJNIM UGLJENIČNIM NANOCEVIMA

Ugljenične nanocevi (carbon nanotubes, CNT) predstavljaju alotropsku modifikaciju ugljenika cilindrične nanostrukture. Kod višeslojnih ugljeničnih nanocevi (multiwalled carbon nanotubes, MWCNT), grafitni slojevi obrazuju koncentrične cevi. U našem istraživanju dužina višeslojnih nanocevi iznosi od 3 µm do 30 µm i njihov spoljašnji prečnik je od 13 nm do 18 nm. Njihova čistoća je veća od 99 mas.%. Ugljenične nanocevi imaju izvanredna fizička svojstva, veliku električnu i toplotnu provodljivost. Njihovim dodatkom u vidu ojačanja u polimernim kompozitima se mogu značajno poboljšati mehanička svojstva kompozita.

U ovom radu su čiste višeslojne ugljenične nanocevi bile korišćene sa ciljem da se poboljšaju mehanička svojstva materijala za zaštitu u balistici.

Ključne reči: *višeslojne ugljenične nanocevi, p-aramidne lamine, AMEO silan, mehanička svojstva*

Rad primljen: 21.01.2013.
Originalni naučni rad