



## Styrene–acrylate/carbon nanotube nanocomposites: mechanical, thermal, and electrical properties

Juris Bitenieks<sup>a\*</sup>, Remo Merijs Meri<sup>a</sup>, Janis Zicans<sup>a</sup>, Roberts Maksimovs<sup>b</sup>, Cornelia Vasile<sup>c</sup>,  
and Valentina Elena Musteata<sup>c</sup>

<sup>a</sup> Institute of Polymer Materials, Riga Technical University, Azenes iela 14/24, Riga, LV-1048, Latvia

<sup>b</sup> Institute of Polymer Mechanics, University of Latvia, Aizkraukles iela 23, Riga, LV-1006, Latvia

<sup>c</sup> “Petru Poni” Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania

Received 7 November 2011, revised 14 March 2012, accepted 4 April 2012, available online 30 August 2012

**Abstract.** Styrene–acrylonitrile copolymer (SAN) and multi-walled carbon nanotube (CNT) nanocomposites were prepared by solution casting from aqueous solution. The composites were prepared with different CNT concentrations. CNTs significantly affected mechanical properties of the obtained materials. The elastic modulus and ultimate strength of the composite films were improved though ultimate elongation reduced by increasing the CNT content. Apart from studying stress–strain characteristics, some calorimetric investigations were carried out to explain the specific deformation behaviour from the structure viewpoint. Dielectric measurements indicated an increase in AC conductivity and dielectric permittivity already at a small CNT addition.

**Key words:** styrene–acrylonitrile copolymer, carbon nanotubes, mechanical properties, electrical properties.

### INTRODUCTION

Nowadays carbon nanotube/polymer nanocomposites have attracted much attention due to their extraordinary properties that make them ideal candidates for various multifunctional material systems. Intense research has focused on various carbon nanotube filler containing composite materials with enhanced mechanical, electrical, and thermal properties. Most significantly, they are considered to be ideal candidates for mechanical reinforcement of polymer materials. Carbon nanotubes (CNTs) are known to have an extremely high Young's modulus of up to 1 TPa and tensile strength approaching 10–200 Gpa [1]. All these properties open up broad possibilities for the use of CNTs as light-weight, highly elastic, and very strong composite fillers. However, the development of CNT/polymer nanocomposites has been largely hindered by the lack of good dispersion of CNTs in the polymer matrix. It has been reported that the enhancement of mechanical properties of the polymer/CNT composites is limited

due to the phase separation of the polymer matrix and CNT. Therefore CNTs are generally considered to be nonuniformly dispersed in the polymer matrix because they have very large surface areas and strong van der Waals interactions, which can lead to the formation of very strongly bound CNT aggregates [2–7]. Multiple approaches are used to improve dispersion of CNTs in a polymer matrix: in situ polymerization [8], ultrasound assisted solvent casting [7,9], latex concept [10,11], compatibilizer containing melt blending [12] a.o. By using these technologies CNTs have been successfully introduced in a broad range of thermoplastic and thermosetting polymer matrices (mainly in polyolefins, polyamides, thermoplastic polyesters, unsaturated polyesters, and epoxies).

Much less research has been done on polymers such as polyvinylacetate, styrene–acrylonitrile copolymer (SAN), and polyvinyl alcohol [13–15]. Generally an increase in mechanical and electrical properties of CNT modified nanocomposites is reported [14,15]. Taking into account these aspects investigations SAN/CNT nanocomposites seem particularly interesting, especially considering broad potential application of these com-

\* Corresponding author, [jurisbitenieks@inbox.lv](mailto:jurisbitenieks@inbox.lv)

posites in coating applications like antistatic coatings and films.

In this paper, we report on a simple method for preparing SAN/CNT composite films. In order to achieve good CNT dispersion in the SAN matrix during composite preparation intensive ultrasound mixing was used. Considerably improved mechanical, electrical, and thermophysical properties of these nanocomposite films were observed as compared to the pure SAN material.

## EXPERIMENTAL

*FINNDISPA 10* SAN dispersion was selected as the matrix material. According to the manufacturer's specifications, it is an unplasticized SAN dispersion stabilized with an anionic emulsifying system.

*Bayer* multi-walled carbon nanotubes *Baytubes C 150 P* were added to the polymer matrix in the amounts from 0.01 to 2 wt%. The nanocomposites were manufactured applying the latex concept. Sodium dodecylsulphate (SDS) was used to stabilize the corresponding SAN/CNT dispersions.

To disperse CNTs in the SAN matrix *Hielscher UIS250V* ultrasound sonication equipment was used. First CNTs were dispensed in 50 mL of distilled water by sonication for about 30 min. To stabilize the solution SDS was added (~1% of the solution). After that the obtained aqueous dispersion of CNTs was combined with the polymer suspension and mixed for 30 min with *Heidolph RZR 2051* mechanical agitator, and then repeatedly sonicated for 30 min. SAN dispersions containing different concentrations of CNTs were cast in *Teflon* forms and dried at ambient temperature for 3–4 days.

Tensile stress–strain characteristics were determined by using a *Zwick/Roell BDO020* universal testing machine (speed of the upper moving clamp 1 mm/min for Young's modulus  $E$  determination and 50 mm/min for measuring stress–strain characteristics at yield and at break ( $\sigma_Y$ ,  $\varepsilon_Y$ ,  $\sigma_B$ , and  $\varepsilon_B$  respectively)).

Differential scanning calorimetry (DSC) measurements were carried out with *Mettler Toledo DSC 1/200W* equipment. Glass transition temperature ( $T_g$ ) was determined within temperature scans from  $-10^\circ\text{C}$  to  $+150^\circ\text{C}$  at heating rate  $10^\circ\text{C}/\text{min}$ .

Measurements for thermogravimetric analysis (TGA) were made using *Mettler Toledo TGA1/SF* equipment. Changes in weight in relation to change in temperature from  $+25^\circ\text{C}$  to  $+800^\circ\text{C}$  were determined at heating rate  $20^\circ\text{C}/\text{min}$ .

Thermal conductivity was determined with a *NETZSCH* model *LFA 447 NanoFlash<sup>TM</sup>* diffusivity apparatus. The measurements were conducted between room temperature and  $80^\circ\text{C}$ . The front and back sides of the sample were coated with graphite.

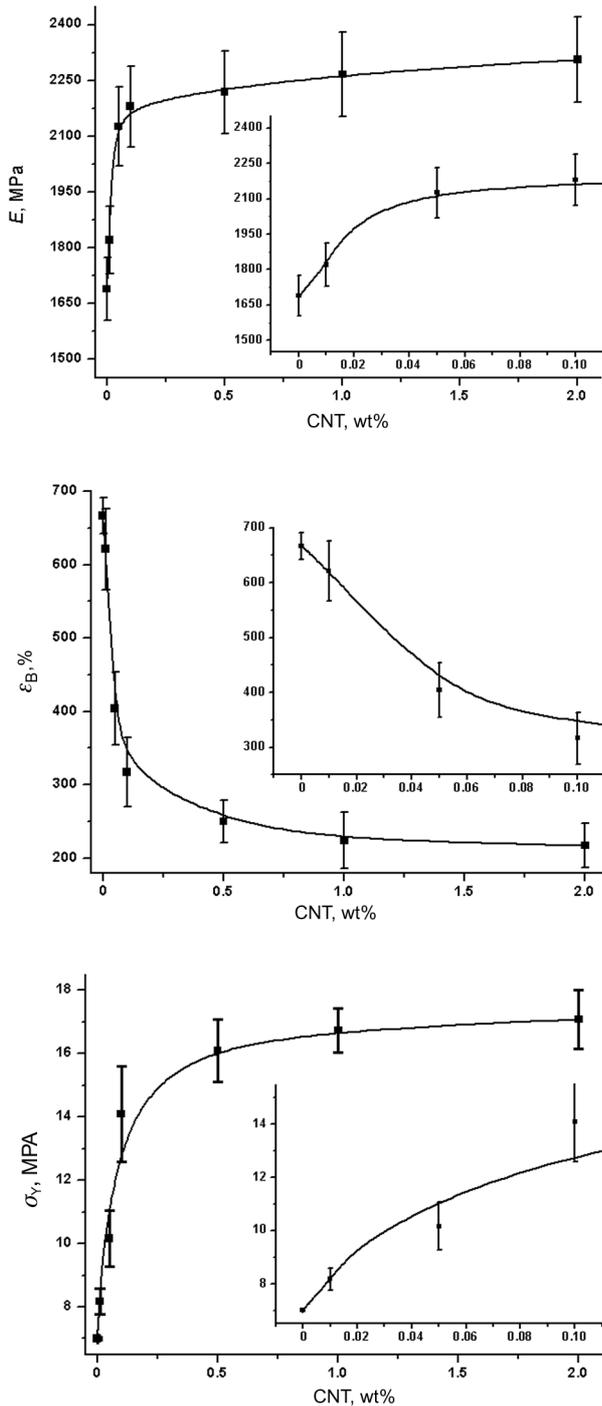
The measurements of dielectric properties of the films were carried out with a *Novocontrol Concept 40* broadband dielectric spectrometer. Dielectric measurements of the selected polymer nanocomposites were performed in a wide frequency region (typically from  $10^{-2}$  to  $10^6$  Hz). Permittivity ( $\varepsilon'$ ) and the real part of AC conductivity ( $\sigma'$ ) were recorded.

## RESULTS AND DISCUSSION

Stress–strain characteristics of SAN/CNT nanocomposites as functions of CNT wt% are presented in Fig. 1. Results indicate that addition of CNTs shifts the stress–strain curves of the nanocomposites towards the higher stress and lower strain regions. Most intensive change of stress–strain characteristics of the nanocomposites is observed at the lowest CNT concentration (below 0.5 wt% of CNT), where the modulus of elasticity  $E$  and yield strength  $\sigma_Y$  increase approximately 1.3 and 2.3 times for SAN/CNT nanocomposites. At CNT concentration above 0.5 wt% the increase in  $E$  and  $\sigma_Y$  starts to slow down. The breaking stress  $\sigma_B$  varies nonmonotonically; however, these changes are not very significant. The effect of CNT content on the ultimate elongation  $\varepsilon_B$  is more pronounced. Thus  $\varepsilon_B$  of the nanocomposite with 2 wt% loading of CNTs is 3 times lower than that of unfilled SAN.

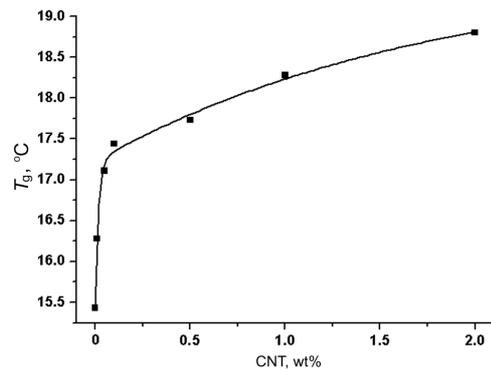
It should be noted that a markedly nonlinear relationship of  $E$  as a function of CNT weight content, characterized by a fast increase of  $E$  at low nanofiller contents (0.5–1%), and followed by a slower increase or even decrease of  $E$  upon introduction of nanotubes at higher weight contents was observed in other studies as well [16,17]. The main reason for the decreased efficiency of reinforcement of the material is the worsening of nanotube dispersion. There is ample evidence from other studies [18,19] that at higher nanofiller contents (usually above 3 to 6 and higher wt%) the composite contains clusters (even entanglements) of nanotubes randomly crimped and aggregated in bound bunches. From the composite theory it is also well known that elastic modulus of a nanocomposite is a function of the theoretical elastic modulus of the filler, aspect ratios of the fillers, and the degree of fibre alignment.

Some calorimetric investigations were carried out to explain the specific deformation behaviour from the structure viewpoint. DSC measurements revealed that glass transition temperature ( $T_g$ ) of the investigated nanocomposites increased from  $\sim 15^\circ\text{C}$  to  $\sim 19^\circ\text{C}$  showing significant dependence on the CNT content (Fig. 2). Increase in  $T_g$  indicates that CNTs greatly limit macromolecular movements of SAN, thus increasing the stiffness and reducing the deformability of the nanocomposites. This is mentioned also in the literature [20]



**Fig. 1.** SAN/CNT nanocomposite stress–strain properties as functions of CNT weight fraction.

where higher  $T_g$  of the nanocomposites is attributed to the thorough dispersion of graphene in the polymethylmetacrylate and the strong chemical bonding between the nanofiller and the polymer matrix. The filler is stated to prevent the motion of polymethylmetacrylate chain segments in the nanocomposites.

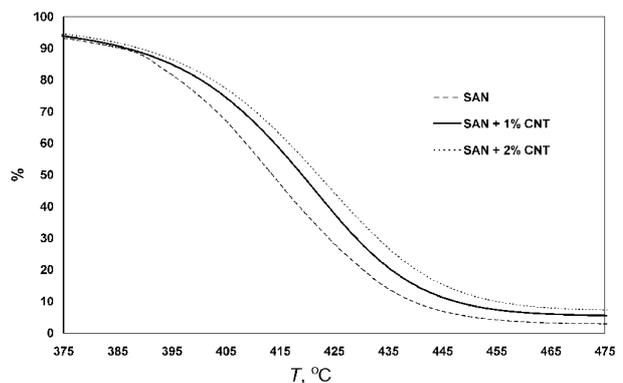


**Fig. 2.** SAN/CNT nanocomposite glass transition temperature as a function of CNT weight fraction.

TGA measurements (Fig. 3) of the investigated SAN/CNT nanocomposites showed that the temperature at which significant weight losses started was shifted to higher values when the CNT content was increased.

These results are most probably due to CNTs' thermal properties: CNTs improve thermal stability of nanocomposites by dissipating the applied heat through the whole sample volume making it more resistant to thermal degradation. These results were explained with thermal conductivity measurements. For example, the increase of the thermal conductivity  $\lambda$  for the SAN nanocomposite with CNT content of 0.5 wt%, as seen in Fig. 4, was about 34% compared to the matrix thermal conductivity.

Dielectric spectroscopy measurements in the frequency range from 0.1 Hz to 1 MHz showed a sharp increase in the real part of AC conductivity  $\sigma'$  (see Fig. 5) already at a small CNT addition (e.g. 0.5% of CNT concentration). Moreover, above 0.5 wt% of CNT loading ( $\sigma' = 10^{-11}$  S/cm) the AC conductivity levelled off ( $\sigma' = 10^{-6}$  S/cm), indicating that the conductivity percolation threshold of the composite was reached and its conductivity was now controlled by the conducting CNTs which had formed a network of CNTs within the



**Fig. 3.** SAN/CNT TGA curves.

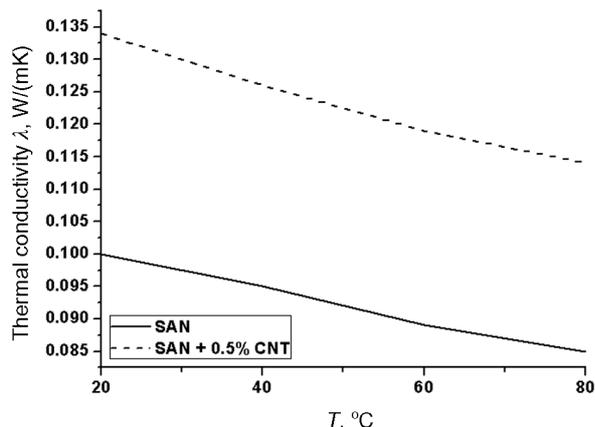


Fig. 4. Thermal properties of SAN and SAN + 0.5% CNT samples.

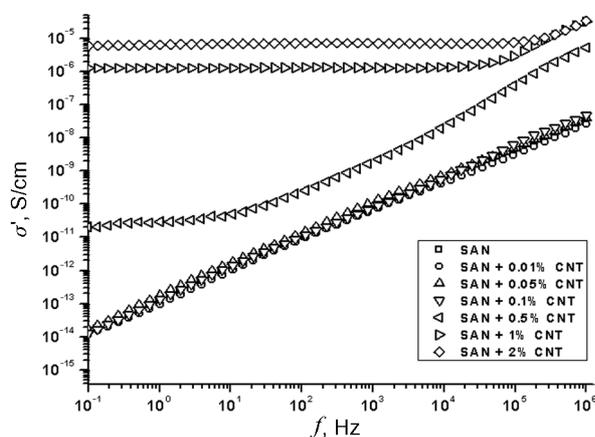


Fig. 5. AC conductivity  $\sigma'$  as a function of frequency for SAN/CNT nanocomposites.

SAN matrix. In other words, below this concentration the nanocomposites were resistant to electrical flow, whereas above this value they were conductive. Similar results are reported with copolyester CNT nanocomposites obtained with melt blending where percolation threshold was observed at much higher CNT concentrations (between 5% and 7% of CNT weight content) by raising  $\sigma'$  from  $10^{-10}$  S/cm up to  $10^{-6}$  S/cm [21]. At the same time a decrease in dielectric permittivity  $\epsilon'$  for SAN/CNT nanocomposites with CNT content increased from 1 to 2 wt% can be observed due to the high conductivity of these samples (see Fig. 6). This decrease in  $\epsilon'$  is due to the mobility decrease in the nanocomposite above the percolation composition as the filler network acts as a hindrance to the dipole orientation. Thus, charge separation is reduced as a result of the decreased polymer segmental mobility, which translates into a decrease in the dielectric constant [21]. However, at the smaller CNT concentration  $\epsilon'$  basically

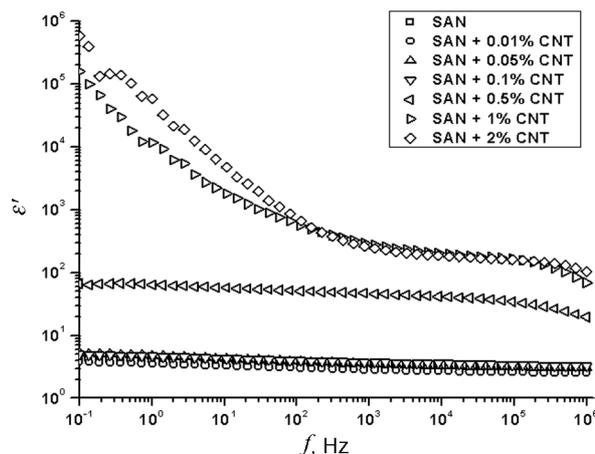


Fig. 6. Dielectric permittivity  $\epsilon'$  as a function of frequency for SAN/CNT nanocomposites.

remained linear in the whole frequency range. This indicates that CNT has superior properties compared to other carbon based fillers, as mentioned also elsewhere [22], where SAN samples filled with nanoscale graphite sheets showed a high permittivity  $\epsilon'$  increase from  $\sim 10^2$  to  $\sim 10^5$  at filler contents from 5 to 6 wt%. However, in the case of SAN/CNT samples the same permittivity  $\epsilon'$  increase from  $\sim 10^2$  to  $\sim 10^5$  was observed already at the CNT content of 1 and 2 wt%.

Besides permittivity (Fig. 6) also conductivity measured in AC mode showed a percolation threshold in the CNT range from 0.5 to 1 wt% (Fig. 7), thus testifying on the development of an effective CNT conductive network in the polymer matrix at such small concentrations and an effect on nanocomposite electrical properties.

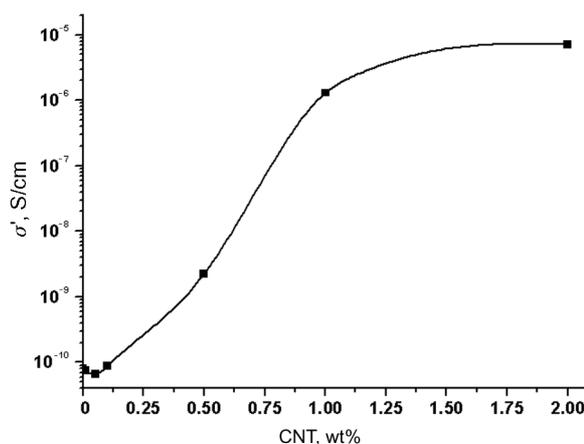


Fig. 7. AC conductivity  $\sigma'$  as a function of CNT wt% at 1 kHz frequency.

## CONCLUSIONS

A simple solution casting method was applied to prepare SAN/CNT nanocomposites with enhanced mechanical and electrical properties. Mechanical tests showed that, compared with pure SAN, the tensile modulus of the composite was improved by a factor of 1.3 at a significantly small CNT loading amount of 0.5 wt%. TGA measurements showed  $T_g$  increase from  $\sim 15^\circ\text{C}$  to  $\sim 19^\circ\text{C}$  by adding CNTs from 0.01 to 2 wt%. Measurements of thermal properties testified on a noticeable increase in the thermal conductivity (34% increase at 0.5 wt% CNT). This increase in the thermal properties leads to a higher thermal decomposition point.

Similarly to the improvement of the mechanical properties of the nanocomposite, a significant improvement was observed in their electrical properties at CNT concentration of 0.5 wt%. This indicates that a good CNT dispersion was achieved by using a common CNT dispersion technique.

The results on SAN/CNT nanocomposites presented in this paper may lead to some practical applications, for example in the manufacture of antistatic adhesives and coatings.

## ACKNOWLEDGEMENTS

The research was carried out within the framework of the COST Action FA0904 “Eco-sustainable Food Packaging based on Polymer Nanomaterials”. The authors are grateful to the Thermophysical Properties Section of the NETZSCH Applications Laboratory for support with thermophysical properties measurements.

## REFERENCES

1. Maciej, O. Carbon nanotube composites – mechanical, electrical, and optical properties. Dissertation zur Erlangung des Doktorgrades (Dr. rer. nat.). Bonn, 2006.
2. Chen, W., Tao, X., Xue, P., and Cheng, X. Enhanced mechanical properties and morphological characterizations of poly(vinyl alcohol)–carbon nanotube composite films. *Appl. Surf. Sci.*, 2005, **252**, 1404–1409.
3. Tang, C., Zhou, T., Yang, J., Zhang, Q., Chen, F., Fu, Q., and Yang, L. Wet-grinding assisted ultrasonic dispersion of pristine multi-walled carbon nanotubes (MWCNTs) in chitosan solution. *Colloids Surf. B*, 2011, **86**, 189–197.
4. Maa, P. C., Siddiqui, N. A., Marom, G., and Kim, J. K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. *Composites: Part A*, 2010, **41**, 1345–1367.
5. Bauhofer, W. and Kovacs, J. Z. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Compos. Sci. Technol.*, 2009, **69**, 1486–1498.
6. Morcom, M., Atkinson, K., and Simon, G. P. The effect of carbon nanotube properties on the degree of dispersion and reinforcement of high density polyethylene. *Polymer*, 2010, **51**, 3540–3550.
7. Wang, M., Pramoda, K. P., and Goh, S. H. Enhancement of the mechanical properties of poly(styrene-co-acrylonitrile) with poly(methyl methacrylate)-grafted multiwalled carbon nanotubes. *Polymer*, 2005, **46**, 11510–11516.
8. Zhao, C., Hu, G., Justice, R., Schaefer, D. W., Zhang, S., Yang, M., and Han, C. C. Synthesis and characterization of multi-walled carbon nanotubes reinforced polyamide 6 via in situ polymerization. *Polymer*, 2005, **46**, 5125–5132.
9. Coleman, J. N., Khan, U., Blau, W. J., and Gun'ko, Y. K. Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites. *Carbon*, 2006, **44**, 1624–1652.
10. Regev, O., El Kati, P. N. B., Loos, J., and Koning, C. E. Preparation of conductive nanotube–polymer composites using latex technology. *Adv. Mater.*, 2004, **16**, 248.
11. Wu, T. M. and Chen, E. C. Preparation and characterization of conductive carbon nanotube–polystyrene nanocomposites using latex technology. *Compos. Sci. Technol.*, 2008, **68**, 2254–2259.
12. Zhaoxia, J., Pramoda, K. P., Guoqin, X., and Suat, H. G. Dynamic mechanical behavior of melt-processed multi-walled carbon nanotube/poly(methyl methacrylate) composites. *Chem. Phys. Lett.*, 2001, **337**, 43–47.
13. Shi, J. H., Yang, B. X., and Goh, S. H. Covalent functionalization of multiwalled carbon nanotubes with poly(styrene-co-acrylonitrile) by reactive melt blending. *Eur. Polym. J.*, 2009, **45**, 1002–1008.
14. Spitalskya, Z., Tasisb, D., Papagelisb, K., and Galiotis, C. Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties. *Progr. Polym. Sci.*, 2010, **35**, 357–401.
15. Bartholome, C., Miaudet, P., Derré, A., Maugey, M., Roubeau, O., Zakri, C., and Poulin, P. Influence of surface functionalization on the thermal and electrical properties of nanotube–PVA composites. *Compos. Sci. Technol.*, 2008, **68**, 2568–2573.
16. Machado, M. A. L., Valentini, L., Biagiotti, J., and Kenny, J. M. Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing. *Carbon*, 2005, **43**, 1499–1505.
17. Chen, L., Pang, X. J., and Yu, Z. L. Study on polycarbonate/multi-walled carbon nanotubes composite produced by melt processing. *Mat. Sci. Eng., A*, 2007, **457**, 287–291.
18. Bin, Y., Mine, M., Koganemaru, A., Jiang, X., and Matsuo, M. Morphology and mechanical and electrical properties of oriented PVA–VGCF and PVA–MWNT composites. *Polymer*, 2006, **47**, 1308–1317.
19. Fritzsche, J., Lorenz, H., and Klüppel, M. CNT based elastomer-hybrid-nanocomposites with promising mechanical and electrical properties. *Macromol. Mater. Eng.*, 2009, **294**, 551–560.
20. Tapas, K., Saswata, B., Partha, K., Nam, H. K., Kyong, Y. R., and Joong, H. L. Characterization and

- properties of in situ emulsion polymerized poly(methyl methacrylate)/graphene nanocomposites. *Composites: Part A*, 2011, **42**, 1856–1861.
21. Rajendra, A. K. and Jyoti, P. J. Copolyester nanocomposites based on carbon nanotubes: reinforcement effect of carbon nanotubes on viscoelastic and dielectric properties of nanocomposites. *Polym. Int.*, 2008, **57**, 114–123.
22. Panwar, V. and Mehra, R. M. Study of electrical and dielectric properties of styrene-acrylonitrile/graphite sheets composites. *Eur. Polym. J.*, 2008, **44**, 2367–2375.

### **Stüreen-akrülaat-/süsiniknanotorudega nanokomposiidid: mehaanilised, termilised ja elektrilised omadused**

Juris Bitenieks, Remo Merijs Meri, Janis Zicans, Roberts Maksimovs, Cornelia Vasile  
ja Valentina Elena Musteata

Süsiniknanotorudest (CNT) armatuuri ja polümeerse maatriksiga nanokomposiididel on erilisi omadusi, mis muudavad need mitmete eriotstarbeliste materjalisüsteemide jaoks ideaalseks valikuks. Süsiniknanotorude lisamisega komposiididele on nende mehaanilised, elektrilised ja termilised omadused paranenud. On teada, et süsiniknanotorudel on väga kõrge Youngi moodul – kuni 1 TPa – ja tõmbetugevus ulatub 10–200 GPa. Need omadused võimaldaksid kergeid, suure elastsusega ja väga tugevaid süsiniknanotorusid laialdaselt komposiidides armatuurina kasutada.

CNT-/polümeernanokomposiidide arengut takistavaks asjaoluks on CNT piisava dispersiooni puudumine polümeeri maatriksis. On teada, et mehaaniliste omaduste parandamine on piiratud polümeeri maatriksi ja CNT faasi halva segunemise tõttu. CNT hajutatuse parandamiseks on erinevaid viise: *in situ* polümerisatsioon, ultraheli ja lahustiga valamine, lateksi kontsept jne.

Nende tehnoloogiate abil on CNT-sid kasutatud termoplastsete ja reaktoplastsete polümeeride maatriksis. Palju vähem on kasutatud sellistes polümeerides, nagu polüvinüülakrülaat (PVAc), stüreen-akrülonitril-kopolümeer (SAN) ja polüvinüülalkohol (PVA). On teada elektriliste ja mehaaniliste omaduste paranemisest CNT-ga nanokomposiidides.

Artikli autorite läbi viidud uuringus on tutvustatud lihtsat meetodit SAN-i/CNT komposiidkilede ettevalmistuseks. Segu valmistati lihtsal lahustimeetodil, kasutades vesilahust. Hea CNT dispersiooni saamiseks kasutati intensiivset ultraheliga segamist. Komposiidist katsekehad valmistati erineva CNT kontsentratsiooniga.

Leiti, et “puhta” SAN-i materjaliga võrreldes paranesid oluliselt materjali mehaanilised, elektrilised ja termofüüsikalised omadused. Tõmbemooduli paranemise tegur oli 1,3 (lisades vaid 0,5 massiprotsenti CNT-d). TGA mõõtmised näitasid, et lisades CNT-d 0,01 kuni 2 massiprotsenti, tõusis  $T_g \sim 15^\circ\text{C}$ -lt  $\sim 19^\circ\text{C}$ -ni. Termiliste omaduste mõõtmised näitavad märgatavat soojusjuhtivuse tõusu (34% tõus 0,5 massiprotsendi CNT lisamisel). Termiliste omaduste paranemine viib kõrgema termilise lagunemise temperatuurini.

SAN-i/CNT elektriliste omaduste märgatav tõus 0,5 massiprotsenti CNT kontsentratsiooni juures on sarnane mehaaniliste omaduste paranemisele, mis näitab, et tavapärasest dispersioonitehnoloogiast kasutades saavutati suurepärane CNT hajuti.

Selles uuringus saadud tulemused võivad olla aluseks praktilistele kasutusvõimalustele näiteks antistaatilistes liimides ja pinnakattematerjalides.