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On the positron annihilation spectroscopy and tensile behavior of COOH-MWCNT/epoxy nanocomposites

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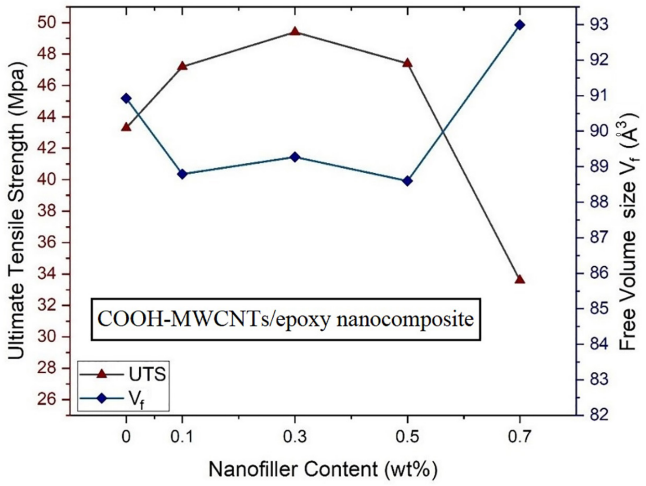
HIGHLIGHTS

- COOH - MWCNTs / epoxy nanocomposites with various filler loadings were fabricated.
- The positron annihilation spectroscopy and tensile behavior of the nanocomposites were investigated.
- Adding up to 0.5 wt% MWCNTs decreases the free volume size.
- The samples' tensile strength decreases as the free volume size increases.
- The maximum tensile strength was related to the sample containing 0.3 wt% MWCNTs.

GRAPHICAL ABSTRACT



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ABSTRACT

Positron Annihilation Lifetime Spectroscopy (PALS) is sensitive to the material voids/free volume on the atomic scale. For this reason, this method has been used as a unique technology to measure the free volume and structural defects in polymers in recent years. In the present study, epoxy-matrix nanocomposites with different carboxylic acid functionalized multiwalled carbon nanotubes (COOH-MWCNTs) loadings (0.1-0.7 wt% at a step of 0.2) were fabricated, and the influence of COOH-MWCNTs loading on the prepared nanocomposites' free volume properties and tensile behavior were explored. The measurement of positron annihilation lifetime was done using a conventional synchronization system based on a ^{22}Na radioactive source with 7 μCi activity. The detectors used in this work were fast plastic scintillators (type: NT-850) with ns time response. The results demonstrated that the tensile strength of the nanocomposites decreased with the increase in the lifetime of the ortho-positronium annihilation (increase in the radius and free volume) in the samples. The 0.3 wt% COOH-MWCNTs/epoxy nanocomposite showed the maximum tensile strength. Overall, the results of this work clearly revealed that there was a strong relationship between the tensile strength and free volume in the polymer nanocomposites.

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1. Introduction

Nanocomposites are a widely used class of materials that usually contain one or more components with dimensions less than 100 nm. In polymer-matrix nanocomposites, different types of nano-fillers, including carbon nanotubes (CNT) [1], graphene [2], nanoclay [3], nano-SiO_2 [4], nano-TiO_2 [5], nano-$CaCO_3$ [6], nano-ZrO_2 [7], etc. are used as reinforcement. Among these nano-fillers, CNTs have received much attention due to their unique properties, and several works have been done on various mechanical, physical, thermal, and electrical properties of CNTs-filled polymer composites [8-10].

CNTs are cylinders of carbon whose diameter is nanometers. These tubes have open or closed ends and are single- or multi-walled. Because of the strong bond between the carbon atoms in this structure, thermal conductivity and tensile strength are high. When nested by van der Waals forces, SWCNTs form multi-walled CNTs (MWCNTs). The diameter of MWCNTs is between 2 and 25 nm [11].

Positron annihilation lifetime spectroscopy (PALS) is sensitive to the size and density of the material volumetric free voids at the atomic scale. For this reason, as a unique non-destructive technology, it has been used to study the physical, mechanical, and structural properties of polymers in recent years [12,13]. In this method, positrons emitted from a radioactive isotope enter the sample, and in a few picoseconds, they lose a large part of their kinetic energy and become thermal. A thermal positron can be directly annihilated by an atomic electron. The result of annihilating a positron with an atomic electron is most likely the creation of two gamma rays [14]. The probability of creating more gamma rays is close to zero. In addition, there is the possibility of a thermal positron pairing with an atomic electron and forming an atom-like bound structure called positronium.

The probability of positronium formation strongly depends on the structure of the host environment. The formation of positronium is more likely in materials that have a relatively open structure. Positronium is formed in two ways. The singlet state with a total spin of 0 is called para-positronium, and the triplet state with a total spin of 1 is called ortho-positronium. In the absence of ortho-para transformations, 25% of positronium atoms are formed in the singlet state and 75% in the triplet state. The lifetime of para-positronium in its spontaneous state and becoming two photons is about 125 picoseconds, which is within the range of the lifetime of a free positron in dense material. Two-gamma decay is impossible for orthopositronium in a vacuum, so it decays to three-gamma with a lifetime of about 142 nanoseconds. The orthopositronium inside the material has a different fate, and with a high probability, it will explode into two gamma rays with a half-life of about a few nanoseconds in a process called desorption. In the annihilation process, the positronium atom positron is annihilated by an atomic electron with the opposite spin [15-17].

In the present work, the PALS method was employed to characterize the free volume size in the MWCNTs/epoxy nanocomposites. To do so, MWCNTs/epoxy samples having various MWCNTs loadings (0.1-0.7 wt% at a step of 0.2) were prepared, and the effect of MWCNTs addition on the free-volume voids and tensile behavior of samples were investigated.

2. Experimental

2.1. Materials

The present work employed EponTM epoxy resin 828, produced from bisphenol A and epichlorohydrin as the matrix phase. COOH-MWCNTs used as the reinforcing phase were supplied by US Research Nanomaterials, Inc. Table 1 gives the characteristics of the COOH-MWCNTs. The scanning electron microscopy (SEM) micrograph of the as-received COOH-MWCNTs is shown in Fig. 1.

2.2. Fabrication of the nanocomposites

The COOH-MWCNTs/epoxy nanocomposites were made in five steps as follows [4,6]:

1- 60 g of epoxy resin was poured into a plastic container. Then, according to the weight percentages of 0.1, 0.3, 0.5, and 0.7, the necessary amounts of COOH-MWCNTs as a reinforcing phase were added to the epoxy resin.

2- The resulting mixtures were stirred for 15 min using a high-speed mechanical stirrer.

3- The mixtures were placed in an ultrasonic homogenizer (150 W, TOPSONICS company, Iran) for 30 min to remove the existing MWCNT clusters, and to prevent temperature

Table 1. The characteristics of the COOH-MWCNTs.

Characteristic	Amount
Purity	> 95%
Outer diameter	50-80 nm
Inner diameter	5-15 nm
Length	10-20 μm
COOH wt%	0.49 %
Specific surface area	40 $m^2.g^{-1}$
Bulk density	0.18 $g.cm^{-3}$
True density	2.1 $g.cm^{-3}$

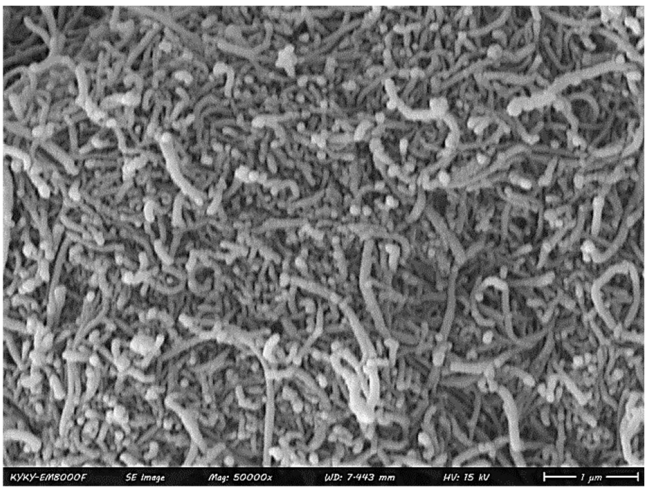

Fig. 1. SEM Micrograph of the as-received COOH-MWCNTs.

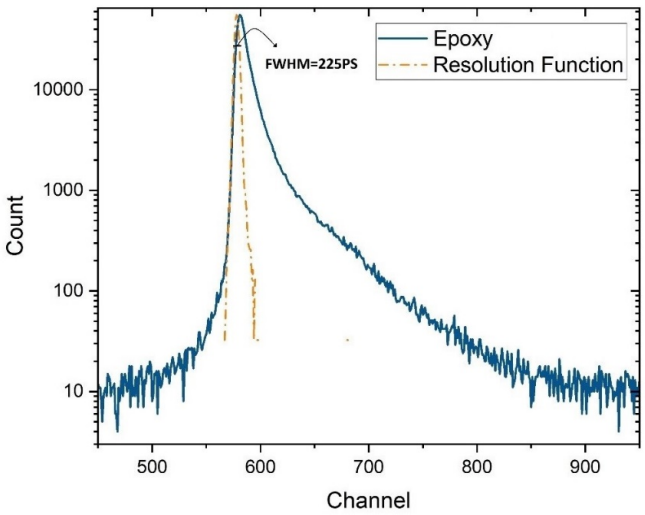

Fig. 2. Comparison of the positron annihilation lifetime spectrum of the epoxy resin and ^{60}Co source gamma-gamma synchronicity spectrum.

increase during this process, the mixture containers were placed in a water-ice bath.

4- Hardener was added to the suspensions as a curing agent (at a hardener/epoxy weight ratio of 1-10; 6 g), and the mixtures were slowly stirred for 3 min.

5- The resulting mixtures were slowly poured into pre-fabricated silicone molds well-greased with lubricant spray, and after 24 h, the samples were removed.

2.3. Measurement of positron annihilation lifetimes

In this work, a ^{22}NaCl positron emitter source with an activity of about 5 μCi consisting of thin Kapton layers was used. The lifetime of positron annihilation in the source was measured to be 376 ps. The time resolution of the positron annihilation lifetime spectroscopy system was obtained using a ^{60}Co gamma source equal to 225 ps. Fig. 2 compares the positron annihilation lifetime spectrum in the epoxy sample and the ^{60}Co radioactive isotope gamma synchronization spectrum as a measure of the time resolution function of the coincidence system. The fitting and analysis of the spectra obtained from the measurement of the positron annihilation lifetime were done using PAScual software. For each of the positron annihilation lifetime spectra, three lifetime components of τ_1 (related to the para-positronium annihilation), τ_2 (related to the positron annihilation in the source and also the sample free volume), and τ_3 (related to ortho-positronium annihilation), with intensities of I_1, I_2, and I_3, were resolved.

2.4. Tensile testing

Tensile tests were done on the various COOH-MWCNTs/epoxy nanocomposites according to the ASTM D 638 standard. Fig. 3 displays the samples prepared for the tension testing. All tensile tests were performed at room temperature with a universal testing machine (Hounsfield: H25K). The cross-head speed was 1 mm.min^{-1}. Three samples were tested for each composition, and the averaged values were reported. Finally, the fracture surfaces of the samples were evaluated using a KYKY-EM8000F field-emission SEM.

3. Results and discussion

The results of fitting the three components τ_1, τ_2, and τ_3 (with intensities I_1, I_2, and I_3, respectively) to the lifetime spectra of positron annihilation in MWCNTs/epoxy nanocomposites containing various MWCNT loadings are presented in Table 2. The τ_1 component with the intensity I_1 had the lowest value in these samples. This component could be related to para-positron annihilation in samples. The amount of this component in the epoxy sample is 114 ps, which decreases with the addition of MWCNTs up to 0.3

Fig. 3. The prepared samples for tension testing.

Table 2. Values of τ_1, τ_2, and τ_3 with corresponding intensities for MWCNTs/epoxy nanocomposites having various MWCNT loadings.

Sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)
Neat Epoxy	114 ± 7	23.2 ± 0.9	390 ± 4	59.8 ± 0.8	1930 ± 15	16.9 ± 0.2
0.1 wt% MWCNTs/Epoxy	99 ± 8	21.5 ± 0.7	383 ± 4	61.3 ± 0.6	1907 ± 14	17.2 ± 0.2
0.3 wt% MWCNTs/Epoxy	104 ± 11	18.5 ± 0.8	381 ± 4	64.1 ± 0.7	1912 ± 16	17.4 ± 0.2
0.5 wt% MWCNTs/Epoxy	114 ± 12	17.0 ± 1.1	381 ± 5	65.0 ± 1.0	1905 ± 16	18.0 ± 0.2
0.7 wt% MWCNTs/Epoxy	155 ± 13	22.1 ± 2.5	404 ± 8	60.9 ± 0.9	1952 ± 20	17.0 ± 0.3

wt% and then increases. The τ_2 component with the intensity I_2 represents the annihilation of the positrons with free electrons or positrons trapped in the boundary regions. The amount of this component initially decreases after adding 0.1 wt% MWCNTs, and remains unchanged at 0.3 and 0.5 wt%, but increases at 0.7 wt%. The third component τ_3 with the intensity I_3, the longest annihilation lifetime, represents the annihilation of ortho-positronium in the free holes formed in the disordered areas of the samples. This component shows the size of the free holes in the sample. The changes of the τ_3 indicate that the MWCNTs are dispersed in different forms in the free volume of the epoxy. This component's decrease is observed in the samples with 0.1, 0.3, and 0.5 wt% MWCNTs compared to the epoxy sample, and its value increased in the 0.7 wt% MWCNT-filled sample.

3.2. Catalyst performance

There are various models for the relationship between the ortho-positronium annihilation lifetime and the dimensions of the holes in the material. The Tao-Eldrup model is one of the most widely used models. This model was introduced by Tao and developed by Eldrup and is used for holes of less than 1 nm. This model ignores the annihilation rate in a vacuum and the possibility of ortho-positronium excited states. Ortho-positronium is considered a structureless quantum particle. In the Tao-Eldrup model, the annihilation rate of ortho-positronium (λ_{TE}) trapped in a spherical cavity with radius "R" is calculated by the Eq. (1) [18].

$$\lambda_{TE}(R) = \frac{1}{\tau_3} = \lambda_A[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin(\frac{2\pi R}{R+\Delta R})] \quad (1)$$

where, ΔR is the thickness of the electron layer in the cavity wall, which is usually considered equal to 0.166 nm. λ_A is the average annihilation rate of ortho-positronium in the material, which is assumed equal to $\lambda_A = 1/4\ \lambda_S + 3/4\ \lambda_T \approx 2$ ns.

Herein, using the τ_3 lifetime component, the radius of the holes (R) in the samples was calculated using the Tao-Eldrup model (Eq. (1)). Having the R values, the free volume size (V_f) was obtained via the Eq. (2).

$$V_f = \frac{4}{3}\pi R^3 \quad (2)$$

Table 3 gives the radius and free volume size of the MWCNTs/epoxy nanocomposites having various MWCNT loadings. According to the data in this table, adding up to 0.5 wt% MWCNTs decreased the free volume size while at 0.7 wt% MWCNTs increased the free volume again.

Uniaxial tensile testing was performed on the samples to find the relationship between the free volume size and tensile strength of the nanocomposites. Fig. 4 shows the relationship between the free volume size and the tensile strength in the MWCNTs/epoxy nanocomposites. As can be seen, the trend of tensile strength is opposite to the trend of free volume size. This means that the tensile strength of the samples decreases with the increase in the free volume size. The maximum tensile strength is related to the sample containing 0.3 wt% MWCNTs, which shows a 14% increase compared to the neat epoxy sample. This increase in strength is due to the very high specific surface area of MWCNTs, which increases the interaction between the matrix and the reinforcement [8]. In addition, the possible cause of the decrease in tensile strength and increase in free volume size in the 0.7 wt% MWCNTs/epoxy sample is due to the formation of agglomerates in higher MWCNT percentages, which act as stress concentration points in the matrix [19]. Fig. 5 demonstrates the fractured

Table 3. The radius and free volume size of the MWCNTs/epoxy nanocomposites having various MWCNT loadings.

Sample	R (nm)	ΔR	V_f (Å^3)
Neat Epoxy	0.2790	0.0014	90.9240
0.1 wt% MWCNTs/Epoxy	0.2768	0.0013	88.7905
0.3 wt% MWCNTs/Epoxy	0.2773	0.0015	89.2726
0.5 wt% MWCNTs/Epoxy	0.2766	0.0015	88.5982
0.7 wt% MWCNTs/Epoxy	0.2811	0.0019	92.9931

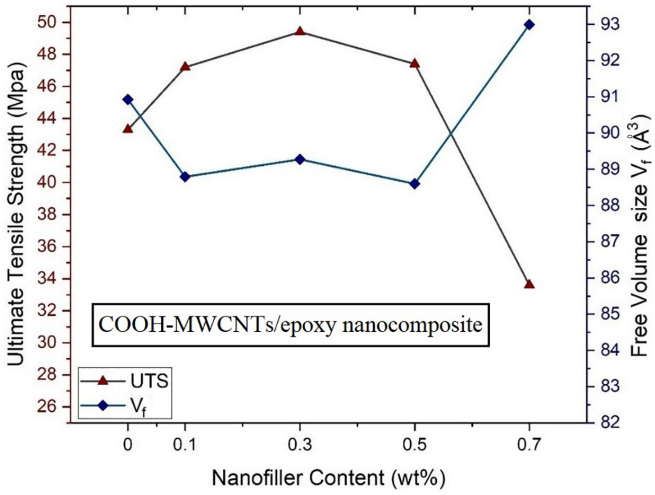

Fig. 4. Variation of the ultimate tensile strength (UTS) and free volume size versus MWCNT loadings.

samples after the tensile testing. As can be seen, all the samples are broken from the thin place.

Fig. 6 compares the fractured surface of the neat epoxy and 0.3 wt% MWCNTs/epoxy nanocomposite. As can be seen, the fracture surface of pure epoxy is smooth (Fig. 6(a)), which indicates a brittle fracture [20]. Shear stress easily transfers from one layer to another. However, the fracture surface of the nanocomposite sample (Fig. 6(b)) has a different appearance due to the presence of MWCNTs. For this sample, the growing crack interacts with the MWCNTs through the crack-bridging mechanism [21]. These results are in line with other research works.

4. Conclusion

The COOH-MWCNTs/epoxy nanocomposites were fabricated, and the effects of the COOH-MWCNT loading (0.1-0.7 wt% at a step of 0.2) on the free volume properties and tensile behavior of the prepared nanocomposites were explored. The obtained results are summarized as follows:

1) Adding up to 0.5 wt% MWCNTs decreased the free volume of voids and at 0.7 wt% MWCNTs, the free volume was increased again.

2) The samples' tensile strength decreases as the free volume size increases.

3) The maximum tensile strength was related to the sample containing 0.3 wt% MWCNTs, showing a 14% increase compared to the neat epoxy.

4) The fracture surface of the nanocomposite sample had a different appearance compared to the neat epoxy due to the presence of MWCNTs.

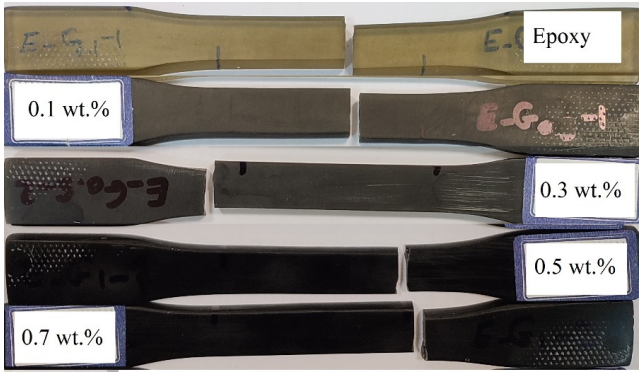

Fig. 5. Fractured samples after the tensile testing.

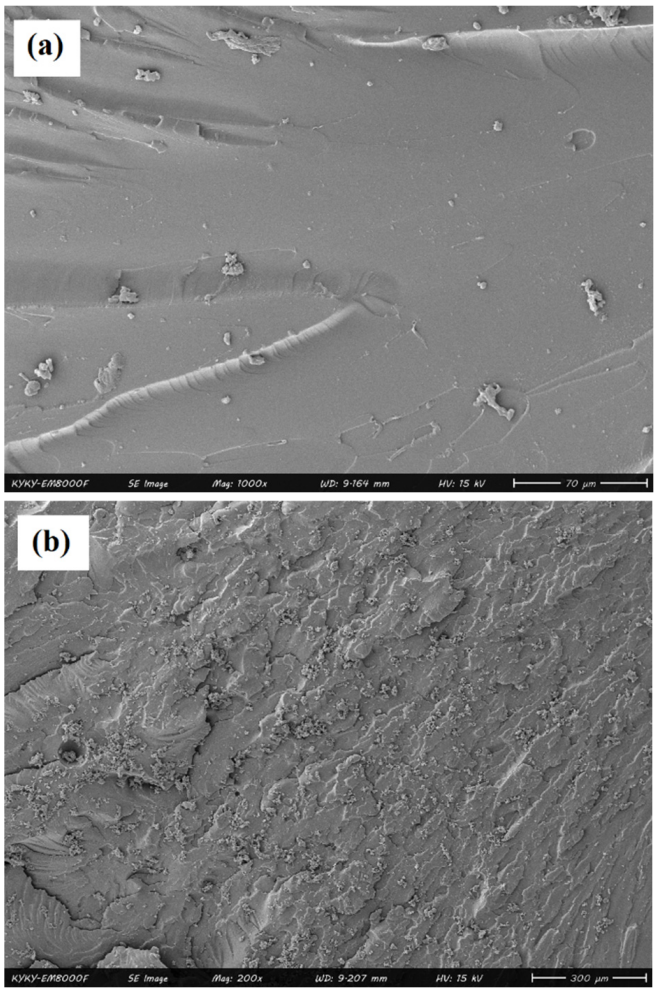

Fig. 6. Fracture surface of the (a) neat epoxy, and (b) 0.3 wt% MWCNTs/epoxy nanocomposite.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Bobbili, R., & Madhu, V. (2016). Sliding Wear Behavior of E-Glass-Epoxy/MWCNT Composites: An Experimental Assessment. *Engineering Science and Technology, an International Journal, 19*(1), 8-14. https://doi.org/10.1016/j.jestch.2015.07.008

[2] King, J. A., Klimek, D. R., Miskioglu, I. & Odegard, G. M. (2013). Mechanical Properties of Graphene Nanoplatelet/ Epoxy Composites. *Journal of Applied Polymer Science, 128*(6), 4217-4223. https://doi.org/10.1002/app.38645

[3] Karbhari, V. M., & Xian, G. (2022). Thermomechanical Characterization of Organo-Clay Epoxy Nanocomposites for Use in Civil Infrastructure. *Polymer Plastics Technology and Materials, 61*(2), 220-229. https://doi.org/10.1080/25740881.2021.1976205

[4] Hashemi, Z., & Khosravi, H. (2021). Effects of Functionalized Fumed-Silica on the Three-Point Bending and Sliding Wear Properties of Woven Basalt Fabric-Epoxy Composites. *Journal of Textile Institute, 112*(9), 1491-1499. https://doi.org/10.1080/00405000.2020.1827581

[5] Ponnuruthiyil Shaji, A., Shaik, M. A., & Golla, B. R. (2019). Mechanical, Wear, and Dielectric Behavior of TiO_2 Reinforced High-Density Polyethylene Composites. *Journal of Applied Polymer Science, 136*(23), 47610. https://doi.org/10.1002/app.47610

[6] Abdi, A., Eslami-Farsani, R., & Khosravi, H. (2018). Evaluating the Mechanical Behavior of Basalt Fibers/ Epoxy Composites Containing Surface-Modified $CaCO_3$ Nanoparticles. *Fibers and Polymers, 19*(3), 635-640. https://doi.org/10.1007/s12221-018-7755-x

[7] Rahmani, H., Eslami-Farsani, R., & Ebrahimnezhad-Khaljiri, H. (2020). High Velocity Impact Response of Aluminum - Carbon Fibers-Epoxy Laminated Composites Toughened by Nano Silica and Zirconia. *Fibers and Polymers, 21*(1), 170-178. https://doi.org/10.1007/s12221-020-9594-4

[8] Bigdilou, M., Eslami-Farsani, R., Ebrahimnezhad-Khaljiri, H. & Mohammadi, M. A. (2022). Experimental Assessment of Adding Carbon Nanotubes on the Impact Properties of Kevlar-Ultrahigh Molecular Weight Polyethylene Fibers Hybrid Composites. *Journal of Industrial Textiles, 51*, 3767S-3785S. https://doi.org/10.1177/1528083720921483

[9] Kim, M., Okoli, O. I., Jack, D., Park, Y. B., & Liang, Z. Y. (2011). Characterization and Modelling of CNT–Epoxy and CNT–Fibre–Epoxy Composites. *Plastics, Rubber and Composites, 40*(10), 481-490. https://doi.org/10.1179/1743289811Y.0000000003

[10] Chakraborty, A. K., Plyhm, T., Barbezat, M. Necola, A., & Terrasi, G. P. (2011). Carbon Nanotube (CNT)-Epoxy Nanocomposites: A Systematic Investigation of CNT Dispersion. *Journal of Nanoparticle Research, 13*, 6493-6506. https://doi.org/10.1007/s11051-011-0552-3

[11] Rathinavel, S., Priyadharshini, K., & Panda, D. (2021). A Review on Carbon Nanotube: An Overviewof Synthesis, Properties, Functionalization, Characterization, and the Application. *Materials Science and Engineering: B, 268*, 115095. https://doi.org/10.1016/j.mseb.2021.115095

[12] El-meniawi, M. A. H., Mahmoud, K. R., & Megahed, M. (2016). Positron Annihilation Spectroscopy and Mechanical Properties Studies for Epoxy Matrices Reinforced with Different Nanoparticles. *Journal of Polymer Research, 23*, 181. https://doi.org/10.1007/s10965-016-1074-6

[13] Patil, P. N., Sudarshan, K., Sharma, S. K., Maheshwari, P., Rath, S. K., Patri, M., & Pujari, P. K. (2012). Investigation of Nanoscopic Free Volume and Interfacial Interaction in an Epoxy Resin/Modified Clay Nanocomposite using Positron Annihilation Spectroscopy. *ChemPhysChem, 13*(17), 3916-3922. https://doi.org/10.1002/cphc.201200593

[14] Fang, M., Bartholomew, N., & Fulvio, A. D. (2019). Positron Annihilation Lifetime Spectroscopy Using Fast Scintillators and Digital Electronics. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 943*, 162507. https://doi.org/10.1016/j.nima.2019.162507

[15] Sharma, S. K., & Pujari, P. K. (2017). Role of Free Volume Characteristics of Polymer Matrix in Bulk Physical Properties of Polymer Nanocomposites: A Review of Positron Annihilation Lifetime Studies. *Progress in Polymer Science, 75*, 31-47. https://doi.org/10.1016/j.progpolymsci.2017.07.001

[16] Dehghani, E. S., Aghiano, S., Anwand, W., Consolati, G., Ferragut, R., & Panzarasa, G. (2018). Investigating the Structure of Crosslinked Polymer Brushes (Brush-Gels) by Means of Positron Annihilation Spectroscopy. *European Polymer, 99*, 415-421. https://doi.org/10.1016/j.eurpolymj.2017.12.042

[17] Biganeh, A., Kakuee, O., Rafi-Kheiri, H., Lamehi-Rachti, M., Sheikh, N., & Yahaghi, E. (2020). Positron Annihilation Lifetime and Doppler Broadening Spectroscopy of Polymers. *Radiation Physics and Chemistry, 166*, 108461. https://doi.org/10.1016/j.radphyschem.2019.108461

[18] Goworek, T. (2002). Comments on the Relation: Positronium Lifetime-Free Volume Size Parameters of the Tao-Eldrup Model. *Chemical Physics Letters, 366*(1-2), 184-187. https://doi.org/10.1016/S0009-2614(02)01569-5

[19] Ebrahimnezhad-Khaljiri, H., Eslami-Farsani, R., Khosravi, H., & Shahrabi-Farahani, A. (2020). Improving the Flexural Properties of E-Glass Fibers/ Epoxy Isogrid Stiffened Composites through Addition of 3-Glycidoxypropyltrimethoxysilane Functionalized Nanoclay. *Silicon, 12*, 2515-2523. https://doi.org/10.1007/s12633-019-00346-8

[20] Vakhshouri, M., & Khosravi, H. (2020). Synthesis of Nickel Nanoparticles on Graphene Oxide as a Promising Reinforcement for Epoxy Composites. *Polymer Composites, 41*(7), 2643-2651. https://doi.org/10.1002/pc.25563

[21] Khosravi, H., & Eslami-Farsani, R. (2018). Reinforcing Effect of Surface - Modified Multiwalled Carbon Nanotubes on Flexural Response of E-Glass/Epoxy Isogrid Stiffened Composite Panels. *Polymer Composites, 39*(52), E677-E686. https://doi.org/10.1002/pc.24118

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