

EFFECT OF EPOXY MATRIX VISCOSITY ON THE DISPERSION OF GPL GRAPHENE LAYER SEPARATION FOR COATING APPLICATIONS

Dimithar Dimitrov, Anna Staneva

University of Chemical Technology and Metallurgy,
8 Kliment Ohridski Blvd. Sofia 1797, Bulgaria, dimithar@uctm.edu (D.D.);
ani_sta@uctm.edu (A.S.)

Received 26 June 2025

Accepted 15 July 2025

DOI: 10.59957/jctm.v60.i6.2025.12

ABSTRACT

Coatings application is among the most accessible methods of surface modification. Many materials exhibit the desired bulk properties (e.g. mechanical strength), but their surface needs to be protected from the environment to have an additionally functionalized surface - heat and electrically conducting or isolating, optical or aesthetic considerations.

When adding nanosized materials to a matrix the main concern is the retention of separation of nanoparticles and the prevention of aggregation. In the following study, dispersion of Graphene nanoplatelets (GPL) in bisphenol-a based epoxy is investigated. GPL is initially sonicated in methanol and introduced into a series of liquid epoxies with varying dry weight concentration and thus, varying viscosity. The working hypothesis that increased viscosity aids to stabilize the suspension and delamination of graphene layers, has been confirmed. The samples have been characterized by Transmission Electron Microscopy (TEM) and Raman spectroscopy. TEM confirms that the best delamination is retained in the most concentrated matrix. Increased Raman signal intensity testifies to the increase of stabile suspended fraction of GPL before coating, which leads to a higher concentration of active additives in the coatings. Furthermore, adhesion and delamination testing by the crosshatch method confirms that adding GPL does not negatively affect the mechanical properties of the coatings, as compared to coatings without the addition of GPL.

Keywords: coatings, graphene layers, epoxy matrix, bisphenol-a, delamination.

INTRODUCTION

Antimicrobial resistance is a current challenge which is reaching worrying dimensions [1]. The growing number of microorganisms which are resistant to traditional antimicrobials and antiseptics imposes urgent reconsideration of current protocols for treatment and disinfection. A potential solution to reduce microorganism load would be the application of coatings which slow down and/or kill microorganisms on contact. Such coatings can find applications in healthcare [2], food and beverage industry [3, 4], and domestically.

Graphene, graphene oxide, and reduced graphene oxide have shown promising results in antimicrobial activity studies [5]. Graphene is a two-dimensional carbon nanostructure consisting of a single layer of

carbon atoms. Its chemical preparation consists of the oxidation of graphite powder to graphene oxide, and subsequent chemical reduction to obtain reduced graphene oxide. These materials are well studied due to their more accessible synthesis compared to single-layer graphene (which is prepared by vacuum methods) [6, 7]. The antimicrobial activity of nanosized metal particles is also the subject of much research. Some popular choices are silver nanoparticles [8], zinc oxide [9], zinc titanate [10], among others.

The materials proposed as additives in the current study (graphene structures and nanosized particles) show promising results for antimicrobial activity in. Due to the poorly studied solubility and dispersibility features of graphene materials, it is difficult to predict the most suitable matrices in which they can be dispersed. In

addition to not being dispersible, graphene material can also change the polymerization conditions [11, 12]. Graphene oxide has been successfully added to epoxy coatings in previous studies [14 - 16].

In addition to their biological activity, antimicrobial coatings can also contribute in cases where they have anti-adhesive and/or hydrophobic properties. In all cases, the coating must also meet mechanical requirements - a coefficient of thermal expansion like that of the substrate, low risk of flaking, resistance to aging under the influence of UV rays. There are standardized tests for the qualification of coatings according to these indicators.

The dispersion and delamination of GPL layers remains a key challenge in obtaining isotropic properties of the coatings. Using a higher or lower concentration of the precursor epoxide, the viscosity of the suspension can be influenced. With its increase, more limited sedimentation and a higher concentration of GPL particles in the suspension are expected.

EXPERIMENTAL

For the purposes of the study, suspensions of GPL in methanol were prepared by sonication. The obtained suspensions were added to BADGE precursor with different amounts of solvent and applied as coatings by dip coating. Due to the volatility of the solvents, the amount of dry mass after polymerization of the epoxy was calculated using Eq. (1):

$$M\% = \frac{M_c}{M_m} \cdot 100 \quad (1)$$

where: M% - calculated dry weight, M_c - weight of sample after polymerization, M_m - weight before drying and polymerization

The control sample (K) contains the factory-prepared precursor and does not undergo further modification and additives. In sample T0 the polymer matrix is unmodified, but the GPL suspension is added. T1 and T2 are subjected to stirring with heating to 40°C for 8 and 16 h respectively, to remove part of the volatile fraction, thus increasing the viscosity and dry concentration. A working suspension of 0.128 g GPL in 50ml methanol was prepared in a beaker. The suspension was sonicated for 15 min at an amplitude of 30 %, maximum permissible probe temperature 70°C. 3 mL of the working suspension was added to samples T0., T1.,

Table 1. Mass percentage by weight after polymerization.

Sample	Mass, %
Control (K)	31.6
T0	32.3
T1	34.5
T2	36.7

T2. under constant stirring with a magnetic stirrer. The coatings were applied by dip coating on glass substrates, which were subjected to polymerization at 100°C for 1 h. The synthesis steps are shown in Fig. 1.

RESULTS AND DISCUSSION

To characterize the morphology and dispersion of GPL in the polymer composites, samples T0, T1 and T2 were examined by TEM. Selected area electron diffraction (SAED) was also performed to characterize the crystallographic structural data.

Fig. 2. shows partial retention of graphene layers in the GPL structure in sample T0. Aggregation of the layers within microstructures can be observed, while the nanosheets remain whole. SAED shows weak reflexes in addition to amorphous halo, which points towards incomplete delamination. Additional research is needed for further characterization.

Sample T1 shows folded sheets with initiated fragmentation and a high degree of association between nanoparticles with some degree of stabilization at a certain distance. SAED shows weak reflections pointing to a hexagonal structure, but the signal is too weak (Fig. 3).

Fig. 4. shows that the lamination of the graphene layers is superior in the composition of the polymer with the highest concentration of precursors T2. Clearly delaminated single layers are observed, at the expense of the integrity of the sheets. The amorphous halo in SAED does not show any reflexes, which is in accordance with the expectations in the presence of well-delaminated graphene layers.

The results confirm the working hypothesis that the higher viscosity of the polymer matrix helps to stabilize the graphene layers and prevents their aggregation.

Raman spectroscopy results

The analysis was performed with a RENISHAW inVia Raman spectrometer with microscopy capabilities,

model: inVia Qontor Microscope with Leica objectives, and a CCD detector at a working room temperature of 21°C. The apparatus was calibrated with a silica standard, and a peak was obtained at 521 cm^{-1} . Each sample was placed on a glass substrate (2 mm), scanned for 30 sec, with 5 scans, using Wire 5.6 software. A laser with a wavelength of 532 nm and an output power of 50 mW was used for excitation. The nominal power used in the analysis was 5 mW in accordance with the concentration in the studied sample. In order to

focus the laser beam and collect the scattered light in a backscattering configuration, an X50 objective was used. The diameter of the illuminated spot on the surface of the sample was about 1 μm . The studied spectral range was 10.00 cm^{-1} - 3500.00 cm^{-1} .

The obtained data were processed with Origin 2024. Fig. 5 shows the original data plotted. Even at first glance, the shape of the curves shows that no shifts are observed, but there are differences in the intensities and the ratio between the intensities of the obtained peaks.

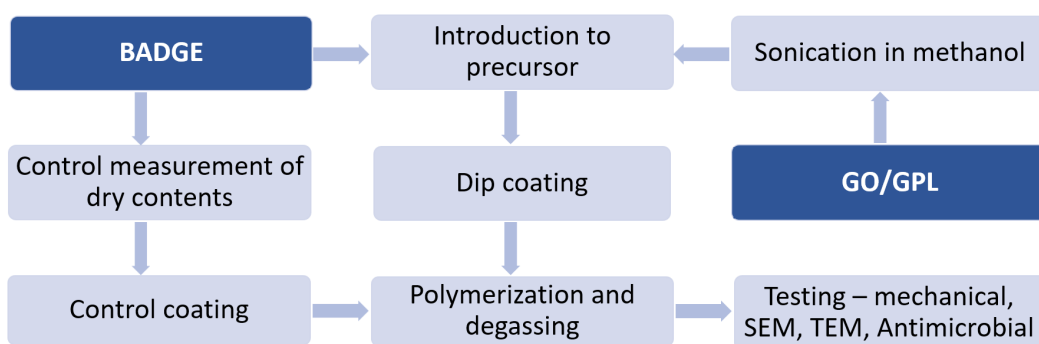


Fig. 1. Method of synthesis.

BPA + G_T0

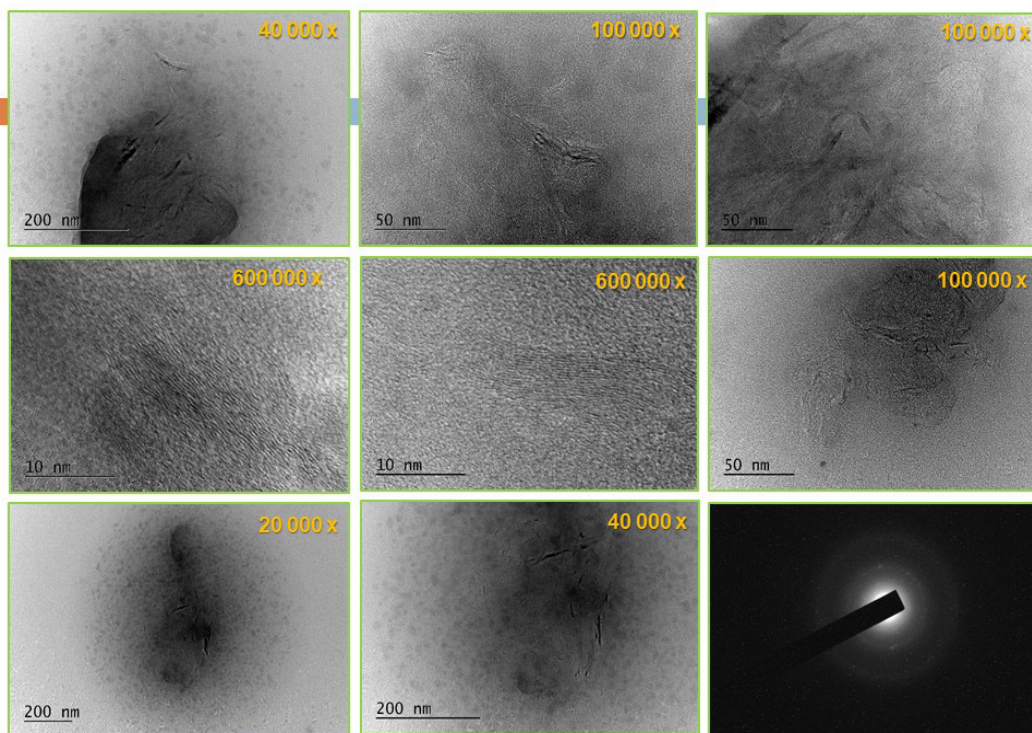


Fig. 2. TEM of sample T0 - GPL dispersed in epoxy with no additional evaporation.

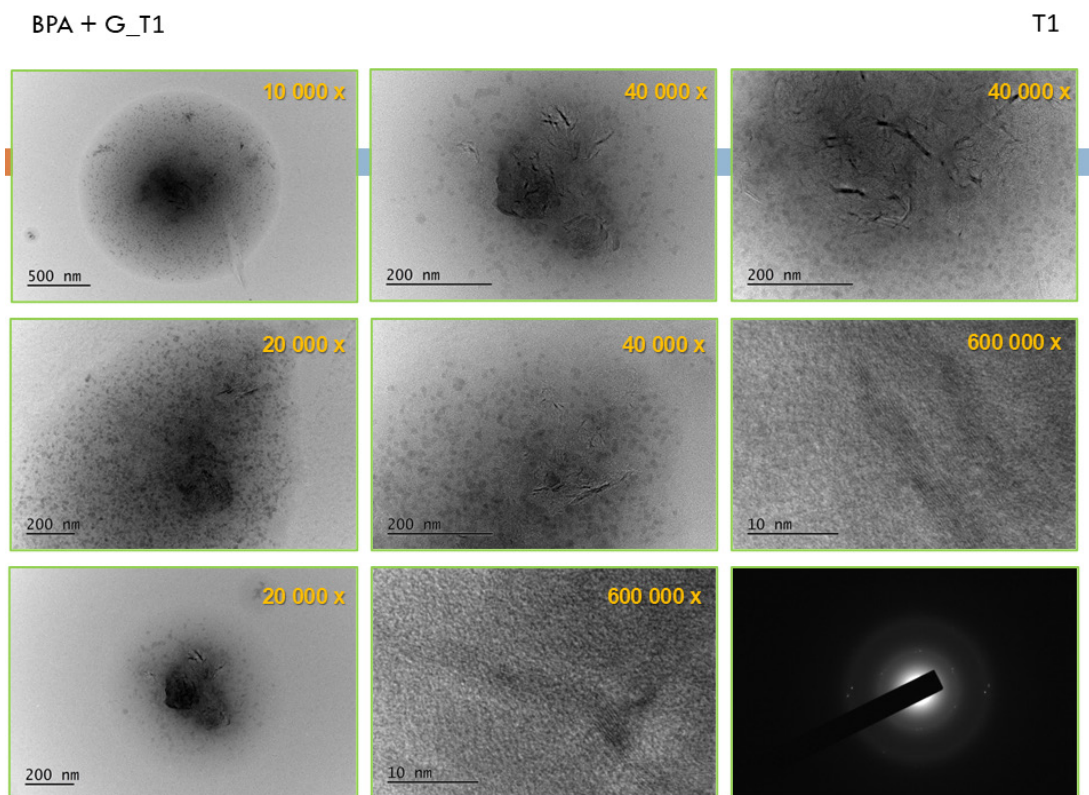


Fig. 3. TEM of sample T1 - GPL dispersed in epoxy with 8h of evaporation.

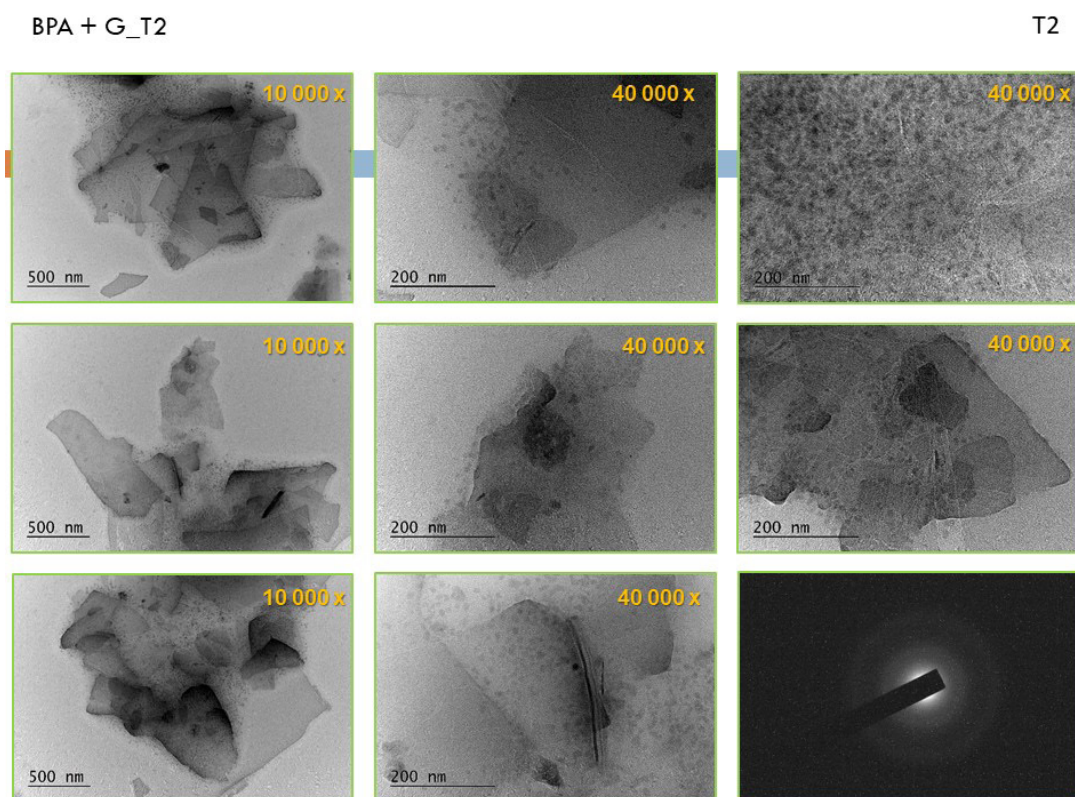


Fig. 4. TEM of sample T2 - GPL dispersed in epoxy with 16 h of evaporation.

The control sample as well as the other samples show a peak at 1100 cm^{-1} , which we attribute to the polymer matrix. In the samples with GPL additives, peaks appear at around 1300 , 1456 , 1600 and 2900 cm^{-1} , which are of interest for the measurement.

At the next stage of the analysis, the least squares method was applied to remove background noise. The processed data are positive, so the asymmetry factor was

set to 0. The obtained function was subtracted from the experimental data, and a smoother curve was obtained - the minima are assigned to the same value. Since the intensity is in relative units, its absolute value does not give an analytical information - the graphs were factured to a common zero Fig. 6.

In this form, the data shows a regular increase in the intensity of both the 2D and G bands with each

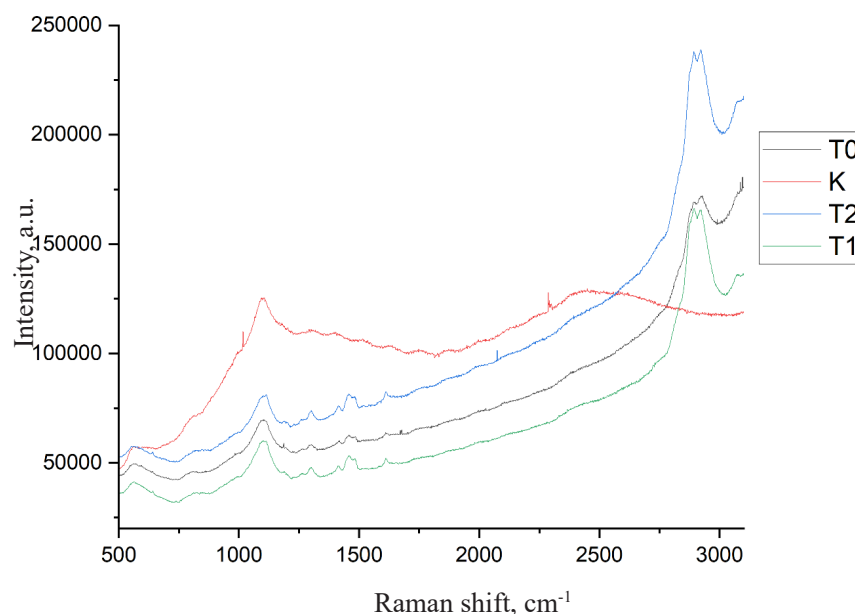


Fig. 5. Raman spectra of samples K, T0, T1, and T2 before signal processing.

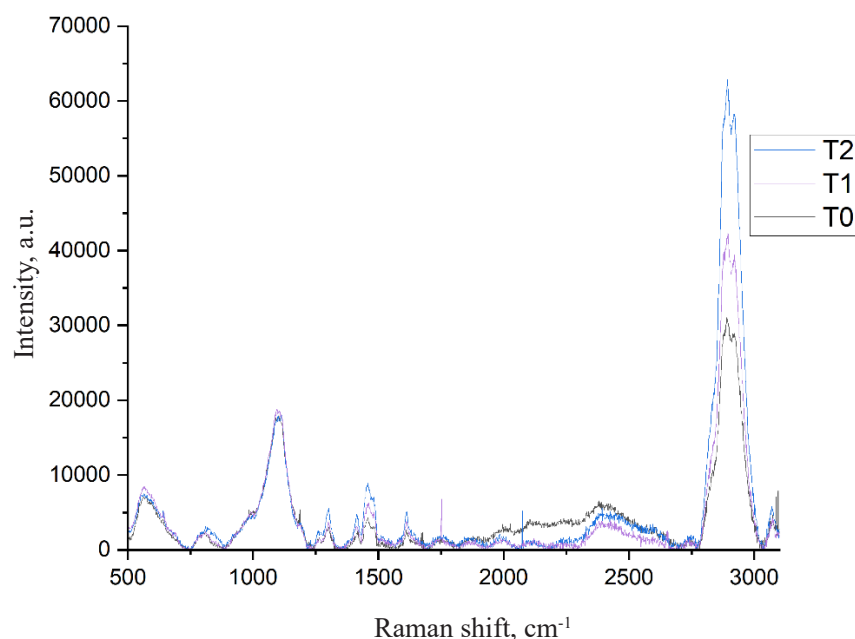


Fig. 6. Raman shift of samples K, T0, T1, and T2 after background noise removal.

successive sample. Although the ratio between the 2D/G band also increases, it would be premature to draw a conclusion about a change in the number of layers in the sample. The proposed hypothesis is about an increase in the concentration of the non-precipitated GPL in the suspension, which remains bound in the coating.

For greater clarity, the data are compared together in Fig. 7.

No shifting is observed between the samples. The shape of the peaks in also identical, which eliminates the need for deconvolution and additional mathematical analysis.

Main conclusions from the Raman spectroscopy study:

- The obtained signal corresponds in shape to expectations based on the literature review.
- The lack of shifts between the samples indicates a minor influence of the structure and number of GPL layers.
- The change in intensities is most likely due to a higher concentration of the stable fraction in the suspension, which has significant implications for further studies.
- It is important to note that the liquid samples did not give a good enough signal for processing.

- Although GPL concentrations comparable in scale to those other studies were used, it would be beneficial to increase them to make the signal more distinct.

Crosshatch delamination test results

The addition of additives to the coating carries the risk of hindering polymerization and adhesion to the substrate. Furthermore, one of the objectives of the study is to utilize a polymer that has been discarded from production and to prevent its scrapping by finding alternative applications. For this purpose, it is necessary to study the mechanical properties of the coating, and in particular - adhesion strength and delamination resistance.

One of the main concerns with the chosen method (as stated in ASTM standard) is the operator approach. The study in this case was conducted by the author after many years of experience in applying the method in industrial conditions. It is important to note that the coating is usually applied to polymer products, while the present study is on glass substrates. Thus, of greatest importance in such a case will be the comparison between the control sample K, which represents the coating on a glass substrate without GPL additives on the one hand, and the sample T0, which represents the coating with added GPL. Samples T0, T1 and T2 should

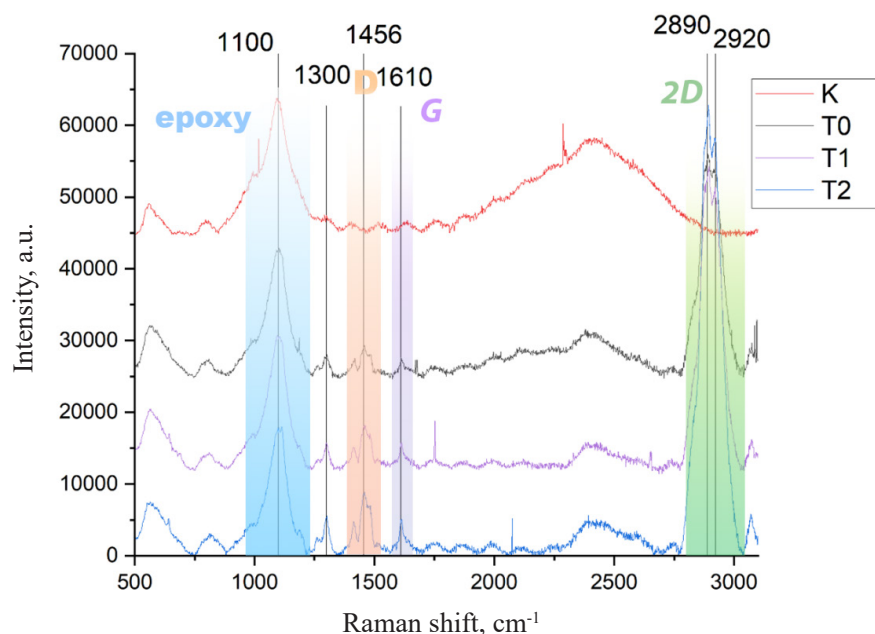


Fig. 7. Raman spectra of K, T0, T1, and T2.

be compared separately with one another, as they show a change in the concentration of dry polymer in the coating.

The following conclusions can be drawn from the crosshatch test:

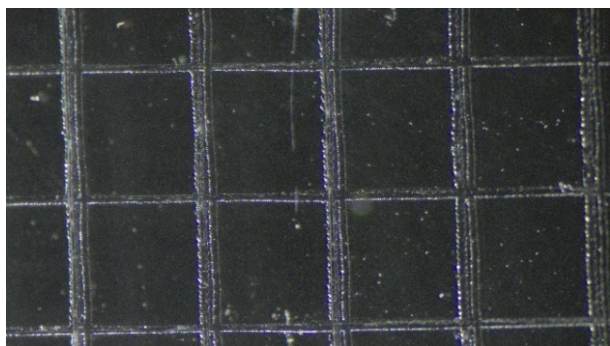
1. All coatings except sample T0 can be categorized as level 5 or 4.
2. Coating T0 shows delamination parallel to the grooves with a length of more than 1.6mm, therefore it falls into level 2.
3. The results do not show correlative behaviour with respect to the varied factors:
 - a. Comparing the control sample K with samples T0, T1 and T2, it cannot be stated that the addition of GPL improves or worsens the mechanical resistance of the coating.
 - b. Comparing the samples T0, T1 and T3 with the participation of GPL among themselves, it cannot be stated with confidence whether the variation of the dry matter concentration leads to a deterioration in the mechanical resistance of the coating.

Antimicrobial activity test using the agar diffusion method.

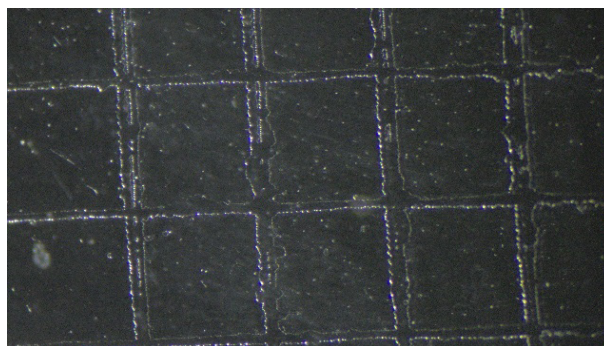
The studies were conducted at the Department of Biotechnology at the UCTM. No classical zones of inhibition were observed. The results suggest that the GPL sheets are firmly cross-linked in the polymer matrix and immobilized, therefore they do not diffuse into the agar. On the one hand, this extinguishes the antimicrobial properties, but on the other hand, it has the advantage that the active additives in the coating will not leech into the environment. In view of these results, two potential approaches are outlined:

1. Conducting studies on antibiofouling resistance by another method - for example, by immersion in an aqueous medium to study the resistance to fouling by unicellular and multicellular algae, cyanobacteria and other biofilm-forming organisms. Such coatings may find applications in shipping.
2. Studying the stabilizing role of GPL in epoxy coatings to prevent leaching of active components into the environment.

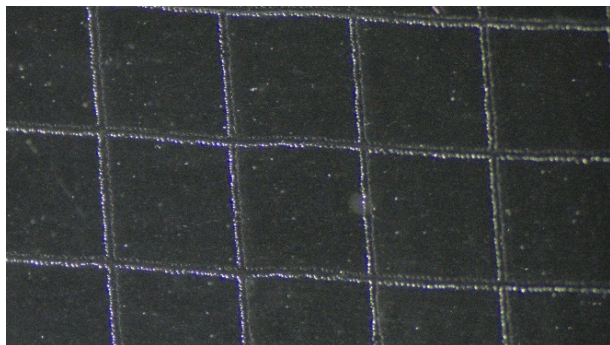
1. K



2. T0



3. T1



4. T2

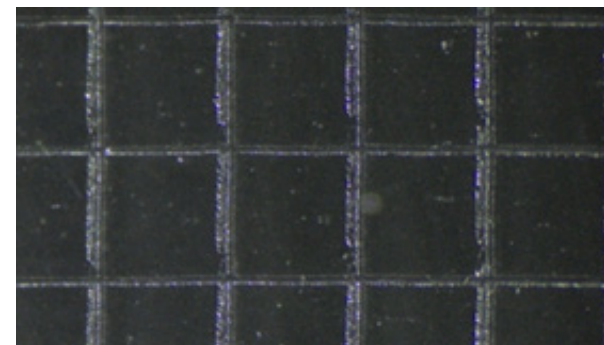


Fig. 8. Results of ASTM-standard crosshatch adhesion test: 1. Control, 2. T0, 3. T1, 4. T2.



Fig. 9. *S. aureus* NBIMCC 3703 white strain, samples K, T0, T1, T2.

Fig. 9 shows the results of the antimicrobial study. We note the absence of zones of inhibition and partial fouling of samples K and T1.

CONCLUSIONS

A suitable method for obtaining epoxy polymer coatings with the participation of GPL has been developed. When varying the concentration of the epoxy resin, the viscosity changes, which affects the dispersed graphene materials. Better preservation of the delaminated layers is obtained at a higher concentration of the resin, and TEM shows stabilized separated single graphene layers. Raman spectroscopy confirms the graphene layers are undisturbed by the polymer matrix, and that the higher dry weight concentration contributes to the obtaining of more stable suspensions, thus leading to a higher concentration of the active additives to the coating.

Acknowledgments

This work is developed as a part of Contract №: BG-RRP-2.004-0002-C01, „BiOrgaMCT“ (Bioactive organic and inorganic materials and clean technologies) By procedure: BG-RRP-2.004, Creation of a network of research universities in Bulgaria under the National Recovery and Resilience Plan and Project No. 23-ДC-37/15.12.2023 on the topic: “Low-adhesive, antibacterial coatings with the participation of graphene structures, peptides, metal and oxide nanoparticles”.

Authors' contributions: D.D.: Conceptualization, Experimental work, Writing - review & Editing,

Formal analysis, Design of the research; A.S.: Conceptualization, Methodology, Validation, Formal analysis, Writing - review & Editing, Design of the research, Project management and funding acquisition.

REFERENCES

1. J. Hou, X. Long, X. Wang, L. Li, D. Mao, Y. Luo, R. Hongqiang, Global trend of antimicrobial resistance in common bacterial pathogens in response to antibiotic consumption, *J. Hazard. Mater.*, 442, 130042, 2022.
2. S. Pandit, K. Gaska, R. Kádár, I. Mijakovic, Graphene-Based Antimicrobial Biomedical Surfaces, *Chem. Phys. Chem.*, 22, 3, 2021, 250-263.
3. V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, S. Seal, Graphene based materials: Past, present and future, *Progress in Materials Science*, 56, 1, 2011, 1178-1271.
4. B. Garg, T. Bisht, Y.C. Ling, Graphene-based nanomaterials as heterogeneous acid catalysts: A comprehensive perspective, *Molecules*, 19, 9, 2014, 14582-14614.
5. S. Liu, T.H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R. Jiang, J. Kong, Y. Chen, Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: Membrane and oxidative stress, *ACS Nano*, 5, 9, 2021.
6. W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *J. Am. Chem. Soc.*, 80, 6, 1958, 1339
7. S. Park, R.S. Ruoff, Chemical methods for the production of graphenes, *Nature Nanotechnology*, 4, 2009, 217-224.
8. G. Magdy, E. Aboelkassim, S.M. Abd Elhaleem.

- A comprehensive review on silver nanoparticles: Synthesis approaches, characterization techniques, and recent pharmaceutical, environmental, and antimicrobial applications, *Microchemical Journal*, 196, 2024, 109615.
9. V.P. Klienchen de Maria, F.F. Guedes de Paiva, J.R. Tamashiro, L.H.P. Silva, G. da Silva Pinho, F. Rubio-Marcos, A. Kinoshita, Advances in ZnO nanoparticles in building material: Antimicrobial and photocatalytic applications - Systematic literature review. *Constr. Build. Mater.*, 417, 2024, 135337.
 10. R. Abirami, C.R. Kalaiselvi, L. Kungumadevi, T.S. Senthil, M. Kang, Synthesis and characterization of ZnTiO_3 and Ag doped ZnTiO_3 perovskite nanoparticles and their enhanced photocatalytic and antibacterial activity, *J. Solid State Chem.*, 281, 2020, 121019.
 11. J.M. Parente, R. Simões, P. N. B. Reis, Effect of graphene nanoparticles on suspension viscosity and mechanical properties of epoxy-based nanocomposites, *Procedia Structural Integrity*, 37, 2022, 820-825.
 12. P. M. Biranje, A.W. Patwardhan, J.B. Joshi, K. Dasgupta, Exfoliated graphene and its derivatives from liquid phase and their role in performance enhancement of epoxy matrix composite. *Composites Part A: Appl. Sci. Manuf.*, 156, 2022, 106886.
 13. K. Verma, S.H. Siddiki, C.K. Maity, R.K. Mishra, M. Moniruzzaman, Development of reduced graphene oxide (rGO) reinforced poly(lactic) acid/cellulose nanocrystal composite through melt mixing: Effect of nanofiller on thermal, structural, biodegradation and antibacterial properties. *Industrial Crops and Prod.*, 204, B, 2023, 117307.
 14. M.H. Wang, Q. Li, X. Li, Y. Liu, L.Z. Fan, Effect of oxygen-containing functional groups in epoxy/reduced graphene oxide composite coatings on corrosion protection and antimicrobial properties. *Applied Surf. Sci.*, 448, 2018, 351-361.
 15. J.S. George, P.P. Vijayan, J.K. Paduvilan, N. Salim, J. Sunarso, N. Kalarikkal, N. Hameed, S. Thomas, Advances and future outlook in epoxy/graphene composites for anticorrosive applications, *Progress in Organic Coatings*, 162, 2022, 106571.
 16. A.A. Bahraq, M.A. Al-Osta, I.B. Obot, O.S. Baghabra Al-Amoudi, T.A. Saleh, M. Maslehuddin, Improving the adhesion properties of cement/epoxy interface using graphene-based nanomaterials: Insights from molecular dynamics simulation, *Cement and Concrete Composites*, 134, 2022, 104801.

