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THERMOMECHANICAL AND ELECTROCHEMICAL PROPERTIES OF GRAPHENE/PVB FUNCTIONAL COATING

TERMOMEHANIČKA I ELEKTROHEMIJSKA SVOJSTVA FUNKCIONALNIH PREVLAKA GRAFEN/PVB

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Keywords
- poly(vinyl butyral) (PVB)
- epoxy resin
- graphene nano-platelets
- graphene in supercapacitor applications
- supercapacitive properties

Abstract

This study investigates the thermomechanical resistance and electrochemical behaviour of a composite coating, based on a thermoplastic polymer, poly(vinyl butyral) (PVB), known for its great adhesion to various surfaces, with incorporated single-layer graphene nanoplatelets. Composite coating samples are produced by solvent-casting technology, in form of thin films in teflon moulds for the mechanical and thermal analyses, and on a thin carbon mat as a coated carrier for experimental electrode specimens. By employing Fourier-transform infrared spectroscopy the interaction of the incorporated graphene nanoplatelets with the polymer matrix is examined. Differential scanning calorimetry is applied to examine the thermal resistance of the hybrid material. For the obtained polymer/graphene films, mechanical properties are determined: indentation hardness and tensile strength. Electrochemical properties of the samples are investigated by cyclic voltammetry. Results obtained for samples with graphene nanoplatelets are compared to neat polymer and neat carbon mat and indicate that the inclusion of graphene significantly improves the materials' thermomechanical resistance and their potential for use as an electrode material in electrochemical energy storage devices. These findings suggest that PBV/graphene composites and coatings are promising materials for advanced electrochemical applications.

Ključne reči
- poli(vinil butiral) (PVB)
- epoksidna smola
- grafenske nano-pločice
- grafen u superkondenzatorima
- superkapacitivna svojstva

Izvod

U ovom istraživanju ispitani su termomehanička otpornost i elektrohemijsko ponašanje kompozitnog premaza, na bazi termoplastičnog polimera, poli(vinil butirala) (PVB), poznatog po odličnoj adheziji na različite površine, sa ugrađenim jednoslojnim grafenskim nano-pločicama. Uzorci kompozitnih premaza izrađeni su tehnologijom livenja iz rastvora, u obliku tankih filmova u teflonskim kalupima za mehaničke i termijske analize i na tankom ugljeničnom matu kao nosač premaza za eksperimentalne uzorke elektroda. Interakcija inkorporiranih grafenskih nano-pločica sa polimernom matricom ispitivana je pomoću infracrvene spektroskopije sa Furijeovom transformacijom. Diferencijalna skenirajuća kalorimetrija primenjena je za ispitivanje termičke otpornosti hibridnog materijala. Za dobijene polimer/grafen filmove određena su mehanička svojstva: tvrdoća utiskivanjem i zatezna čvrstoća. Elektrohemijska svojstva uzoraka ispitana su cikličnom voltametrijom. Rezultati dobijeni za uzorke sa grafenskim nano-pločicama, u poređenju sa čistim polimerom i čistim ugljeničnim matom ukazuju da grafen značajno poboljšava termomehaničku otpornost materijala i povećava njihov potencijal za primenu u elektrodama i u uređajima za skladištenje elektrohemijske energije. Ova saznanja sugerišu da su PVB/grafenski kompoziti i premazi obećavajući materijali za napredne elektrohemijske primene.

INTRODUCTION

Rapid advancements in modern electronics have led to an increasing demand for highly efficient energy storage systems /1-3/. Among them, supercapacitors have attracted significant attention due to their high power density, rapid charge/discharge rates, and exceptional cycling stability /4-6/. Notably, flexible and lightweight supercapacitors have emerged as ideal power sources for wearable and portable electronic devices /7, 8/. As an essential element of flexible electrodes, the flexible current collector is critical to the performance of supercapacitors. It must combine high conductivity to reduce internal resistance with lightweight and bendable properties to ensure mechanical integrity and enhance mass-specific capacitance /10/. Non-woven fabric (NWF) is a promising candidate for flexible current collectors due to its flexibility, mechanical stability, along with benefits such as lightweight, ease of fabrication, and low cost /9, 10/. Carbon-based materials are widely used as electrode materials in supercapacitors for their high specific surface area and abundance /10-12/. Among these, graphene and graphene-based materials have emerged as particularly promising /13-15/. Integration of graphene into polymer matrices has been widely studied, due to its overall remarkable mechanical, electrical, and thermal properties /16, 17/. Due to its planar shape, flexibility, lightweight and strength, it can be incorporated in various composites or applied onto various surfaces in order to form flexible electronics, wearable and compliant electronics, portable energy harvesting devices, and even artificial electronic skin /13, 18-22/. Aside its good thermomechanical and electrical properties, graphene is proven to be biocompatible, so it was studied in various biocomposites and bioelectronic devices /23, 24/. Fabricating electrodes from carbon-based powders requires blending the carbon particles with polymer binders to ensure mechanical integrity by holding active materials together and maintaining strong adhesion to the current collector /25/. While binder materials are less critical than active materials in determining the capacitance of supercapacitors, they play a vital role in providing mechanical support and electrode stability. Among various polymeric materials, poly(vinyl butyral) (PVB) stands out due to its unique combination of flexibility, transparency, and adhesion properties. PVB is a thermoplastic polymer, compatible with various surfaces/substrates. It has a good resistance to water, good compatibility with numerous compounds, and that is why it is widely used in preparation of composites and coatings /26-28/. When combined with conductive materials like graphene, the resulting composite retains these attributes while achieving enhanced electrical conductivity and energy density /10, 29/. Furthermore, graphene and graphene oxide can improve the limitations of polymer based composites due to high electrical conductivity, superior strength, and excellent thermal conductivity /30-32/.

The aim of this study is to evaluate the thermomechanical resistance and electrochemical behaviour of a composite coating made of PVB and graphene nanoplatelets (GNPs). The starting assumption of this study is that incorporation of graphene into PVB would not only enhance the mechanical integrity but would also bring up specific electrochemical properties which are essential for applications in energy storage devices. Hopefully, this may lead to a development of new functional coatings based on the two selected components, towards a reliable structural and mechanical durability and electrochemical performance stability.

Based on the previously stated properties of selected constituents, proposed graphene/PVB composites, as functional coatings, should have the following properties:

- increased tensile strength: the addition of graphene to PVB should improve its tensile strength, making the composite more resistant to deformation under stress;
- improved hardness and toughness: graphene reinforcement should enhance the hardness of the composite, making it more resistant to mechanical wear;
- better thermal resistance: excellent thermal conductivity of graphene might be transferred to the graphene/PVB composite. It could enhance its ability to withstand higher temperatures prior to phase transition, which allows them to perform well under a wider range of temperatures;
- improved heat dissipation: the composite material's ability to conduct heat more efficiently makes it suitable for applications in electronics and other heat-sensitive environments. Graphene/PVB composites might exhibit good charge transfer properties, characteristic for energy storage devices like supercapacitors and electrodes.

The next step in this study is the application of this composite coating onto a carbon fibre mat, as a simple model of a supercapacitor material characterised by great flexibility: PVB is flexible, and the inclusion of graphene can preserve these properties while enhancing other characteristics of the material, such as mechanical and thermal performance.

MATERIALS AND METHODS

Preparation of composite coatings

For the preparation of composite coatings in this study, the following materials are used:

- PVB powder, fine grade, Mowital B60H (Kuraray);
- graphene single-layer nanoplatelets (US Research Nanomaterials, SEM image given in Fig. 1, and main properties given in Table 1);
- ethanol, 96 % (Reachem);
- carbon mat non-woven, 20 g/m^2 (Faserverbundwerkstoffe, Composite Technology).

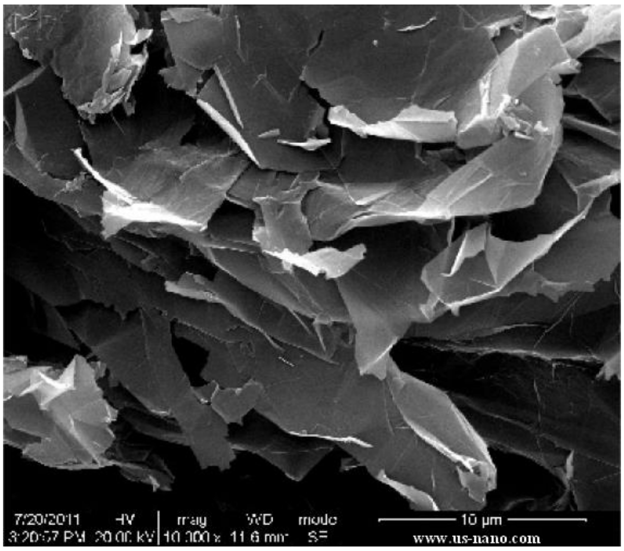


Figure 1. SEM image of single-layer graphene nanoplatelets (provided by the supplier).

Table 1. Main characteristics of graphene nanoplatelets.

Research grade single layer graphene	
graphene purity	> 99.3 wt.%
thickness	0.55-1.2 nm
platelets diameter	1-12 μm
specific surface area	500-1200 m^2/g
conductivity	1000-1500 S/m
COA	C = 99.6 %, O < 0.4 %

Graphene/PVB composite films are prepared using the solvent-casting method which involves ultrasonic deagglomeration and dispersion of graphene into an appropriate solvent (ethanol) using an ultrasonic processor, Bandelin Sonopuls HD 4100 (40 W, 20 kHz, 5 min), followed by dissolving the polymer in a dispersion, on magnetic stirrer, and then casting the resulting solution onto a flat surface to evaporate the solvent. This technique is advantageous for producing uniform thin films suitable for further analysis. Thin films are cast in polytetrafluoroethylene (PTFE) moulds, ensuring smooth and even film thicknesses which are important for the precision required in mechanical analyses.

The next step is the preparation of PVB/GNP coated carbon mat. Non-woven carbon fibre mat is used as the electrode carrier for electrochemical testing. Carbon mat is selected as a robust substrate that supports the thin film during electrochemical measurements, due to its good conductivity, chemical stability, and the ease with which it can be coated. In this study, the graphene/PVB solution is applied onto the carbon mat and left to dry, in the following three immersion methods:

- carbon mat in a glass beaker with PVB solution (as a reference sample without GNPs);
- carbon mat in a glass beaker containing GNPs dispersed in PVB solution;
- carbon mat in a glass beaker containing GNPs in PVB under ultrasonic probe during 1 min;
- PVB/coated carbon mat in a glass beaker containing GNPs dispersed in ethanol under ultrasound, 1 min.

Experimental steps in preparing composite coatings, as well as the appearance of specimens cut from the mechanical tests, are given in Fig. 2.

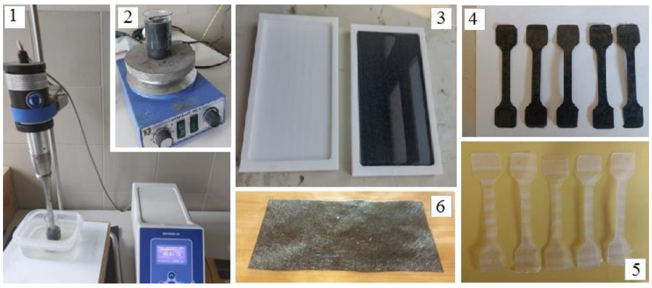


Figure 2. Preparation of the composite material: 1-ultrasonic deagglomeration and dispersion of GNPs in ethanol; 2-dissolving of PVB in the ethanol dispersion of GNPs; 3-solvent-casting of PVB and PVB/GNPs composite films; 4-specimens for tensile test cut out from PVB/GNPs; 5-specimens for tensile test cut out from PVB film; 6-carbon mat coated with PVB/GNPs.

Characterisation techniques

Several characterisation techniques are utilised to assess the properties of graphene/PVB composite films, independent and on a carbon mat, including their thermal, mechanical, and electrochemical behaviour.

Fourier Transform Infrared Spectroscopy (FTIR) is employed to investigate interactions between the PVB polymer matrix and graphene within the composite material. FTIR is a powerful technique that provides valuable information about the chemical bonds and molecular structure of a material. By analysing the absorption spectra, it is possible to detect shifts or changes in the functional groups of the polymer and graphene, which can reveal insights into the degree of interaction between the two components. FTIR device Nicolete i10 is used, with ATR sampling technique.

Differential Scanning Calorimetry (DSC) is used for the thermal analysis of graphene/PVB composites in order to provide information about the thermal transitions of the material, such as glass transition temperature (T_g) for the polymer matrix with or without GNPs. This analysis is carried out using DSC Q20 device (TA Instruments), with data acquisition programme Universal V4.7A, in a three-step process: heating from 20 to 160 °C, with heating speed 5 °C/min, then controlled cooling down back to 20 °C, and finally heating again to 160 °C at the same speed. The glass transition temperatures are considered relevant when taken from the second cycle of heating /33, 34/.

Mechanical testing included measurement of indentation hardness and tensile strength tests. The indenter is a square pyramid with an angle between opposite sides of 136° /35/. The hardness number (HV) is defined by the applied load F (kg) and by the length of the diagonal indentation D (mm), according to the following equation:

$$\mathrm{HV}=\frac{F}{0.5D^2}\sin\frac{136^\circ}{2}=2\sin 68^\circ\left(\frac{F}{D^2}\right)=1.8544\left(\frac{F}{D^2}\right).$$

Indentation hardness testing is performed to obtain insights into the material's resistance to surface localised deformation. To determine the microhardness of composite films/coatings, the Vickers method is applied using the device Micro Vickers TH710 Beijing Time Vision AI Instrument Ltd. (Marseille, France) /35/. This device combines optic, mechanical and electronic techniques for testing microhardness. All testing data such as indentation length, hardness value, the dwell time of the test force and the number of measurements, are all shown on the LCD screen. Testing specifications in this experiment are: 1) test force: 0.245 N (25 gf); 2) optical system ×400 (measurement); 3) dwell time of the test force is 15 s. The measurement was performed on both sides of the film, since the upper surface was glossy and smoother than the bottom. The reason for this is a moderate sedimentation of graphene in the PVB solution after the solvent-casting in the mould, during solvent evaporation, as well as the remaining roughness of the mould surface as a consequence of the production of the mould (machining of the flat PTFE piece). Five punctures are made in the middle and at each end of the specimen, and the diagonals are recorded on tester, directly. These measurements are repeated in the same way for all specimens.

Tensile strength testing is performed on a universal testing machine Instron 1122, which has a maximal load capacity of up to 5 kN. The appearance of specimens is given in Fig. 2. They are cut from composite films using a standardised stencil, according to ASTM D882 standard /36/. Speed of the clamps was 5 mm/min, and specimen length between clamps was 33 mm. The test was performed at room temperature, -20 °C. Load, displacement and time are registered during the experiment via TRC Pro acquisition system connected to the tensile machine. Finally, maximum tensile strength and elongation at break are calculated from the recorded data.

The combination of these two tests offers a comprehensive understanding of the structural and mechanical resistance of graphene/PVB composites, which is important for their potential applications in electrochemical devices.

Electrochemical testing

Supercapacitive properties of PVB/graphene samples are investigated using cyclic voltammetry (CV). Experiments are conducted in a standard three-electrode configuration, with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The CV measurements are carried out in N_2-saturated 0.5 M H_2SO_4 electrolyte at a sweep rate of 50 $mV \cdot s^{-1}$, using a potentiostat/galvanostat (model SP-200, Bio-Logic SAS, France).

RESULTS AND DISCUSSION

The FTIR spectra of neat PVB and PVB/graphene composite are given in Fig. 3. From them we may observe the presence of the key absorption bands that indicate polymer-graphene interactions: C-C bonds, and PVB carbonyl stretch. In both spectra, the characteristic peaks of PVB are present, but the broad peak at 3451 cm^{-1} observed in Fig. 4a, corresponds to the -OH groups, is slightly shift to 3443 cm^{-1} as seen in Fig. 4b. This indicates that the curing reaction is completed which enhances the mobility of molecular chains and facilitates interactions of functional groups at the interphase zone on the surface of the particles. Other peaks reading at: 2956 and 2870 cm^{-1} (symmetric and asymmetric vibrations of aliphatic groups (-CH_3, -CH_2, -CH)); 1737 cm^{-1}, 1240 cm^{-1}, and 1138 cm^{-1} (vibrational stretching and valence vibrations of the ester group (C=O)), and additionally, the peak attributed to C–OH vibrational stretching in 999 cm^{-1}, are identical as peaks detected for neat PVB /34/. According to this, it can be observed that present of all examined peaks the FTIR spectra for both samples are highly similar. This similarity suggests that incorporated nanostructures are chemically inert, with their reinforcing effect arising primarily from physical interactions with the matrix and resulting from their mechanical resistance.

Figure 4 shows representative DSC curves obtained for neat PVB and the PVB/GNP composite. As expected, the PVB/GNP composite exhibits higher thermal stability. The glass transition temperature (T_g) of nanocomposite PVB/GNP is slightly higher than that of neat PVB, as shown in Table 2. The 3.45 °C increase in T_g suggests that GNPs reduce the mobility of polymer chains. This reduction in chain mobility explains the observed changes in mechanical properties of PVB. Generally, the mechanical properties of thermoplastics with incorporated GNPs are influenced by the change in their T_g /37/.

Table 2. Glass transition temperatures read from DSC.

Sample	T_g, 1st cycle (°C)	T_g, 2nd cycle (°C)
PVB	67.05	67.66
PVB/graphene	68.08	71.11

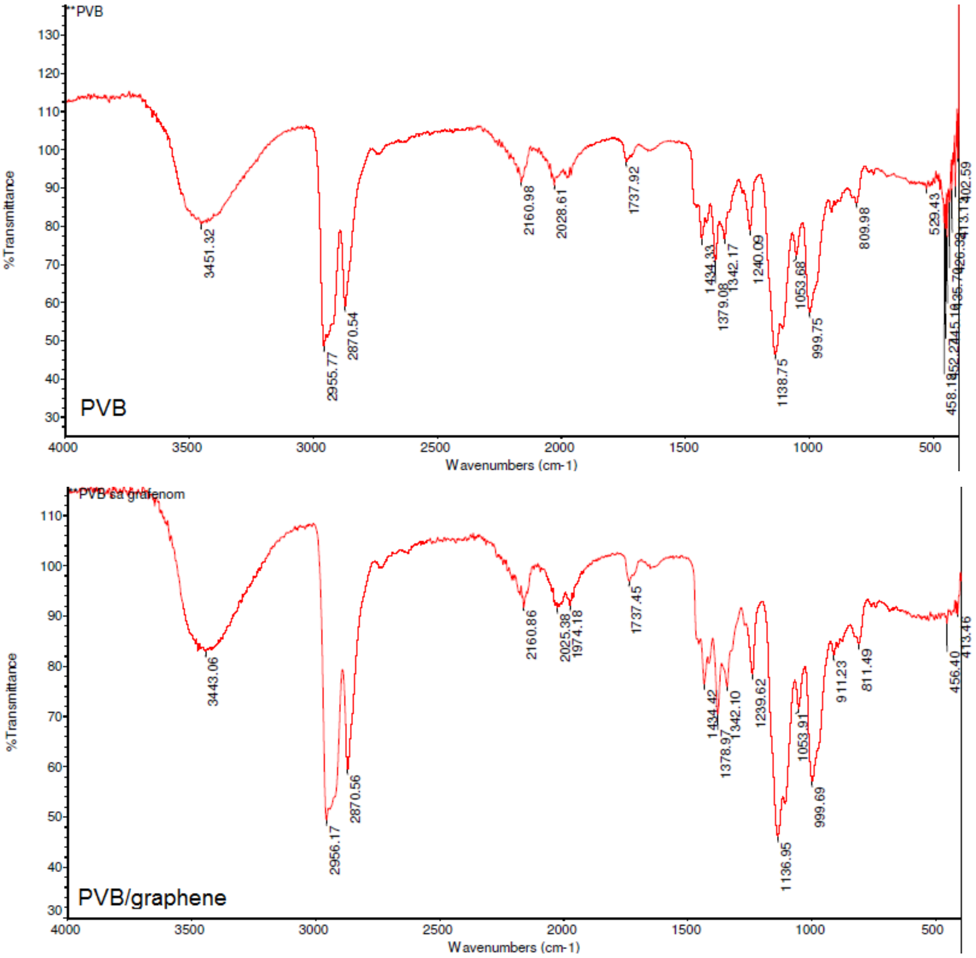


Figure 3. FTIR spectra of neat PVB and PVB/GNP composite.

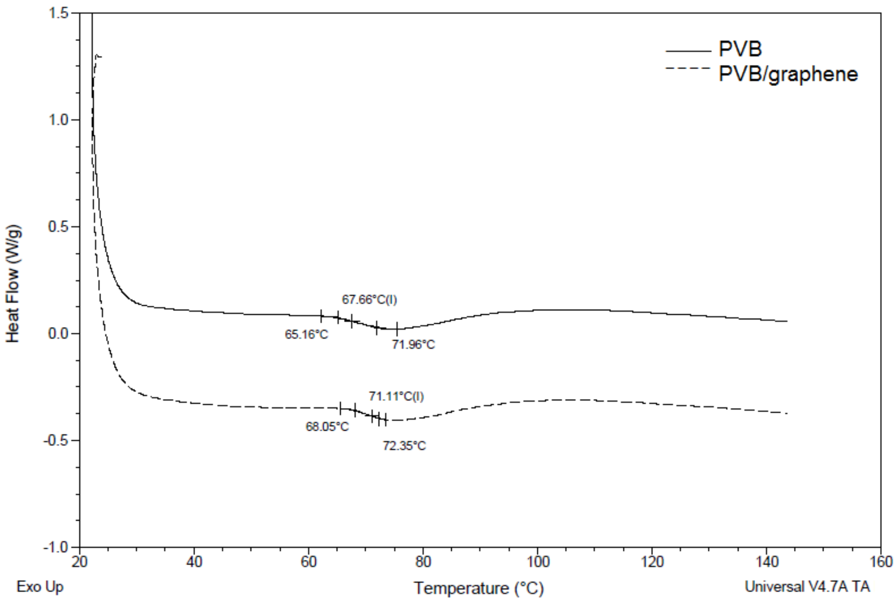


Figure 4. DSC thermographs for neat PVB and PVB/graphene composite.

Tensile test results are given in Table 3, showing the values and standard deviations (SD) of maximum force (F_{max}), stress (σ_{max}), maximum strain (ε_{max}), strain at break (ε_p), and modulus of elasticity (E).

The composite with incorporated GNPs has a slightly decreased tensile strength which is a common behaviour for polymers with particulate fillers, as each particle/each graphene platelet represents a discontinuity in the polymer matrix. Young`s modulus has slightly increased with the addition of graphene nanoplatelets.

Table 3. Tensile test results.

	PVB		PVB/graphene	
	Mean	St.dev.	Mean	St.dev.
F_{max} (N)	111.38	6.16	113.13	13.86
σ_{max} (MPa)	35.71	3.51	34.11	4.4
ε_{max} (%)	6.44	0.83	5.01	0.26
ε_p (%)	7.77	0.89	5.32	0.23
E (MPa)	548.03	56.27	565.1	51.13

Measured microhardness values of coatings are given in Table 4, for the top and bottom side of PVB/GNPs films. The polymer film thickness ranged from 0.30 to 0.36 mm. The mean value of the Vickers microhardness number (HV) with standard deviation errors are given, in accordance with standard ASTM E384, /36/.

Table 4. Microhardness of the coatings composite films.

Sample	Mean	st. dev.	st. dev. (%)
PVB top side	10.126	0.124	1.23
PVB bottom	10.702	0.177	1.66
PVB/graphene top side	12.844	0.138	1.08
PVB/graphene bottom side	13.652	0.125	0.91

There is evident increase in the overall hardness of the polymer with the incorporation of GNPs, as expected. However, there might be observed some differences between the microhardness of the two sides of the same samples. This difference is moderate in case of neat PVB, as a consequence of the manufacturing technology of the analysed samples, but in the case of the composite PVB/GNPs, this difference is more pronounced as a consequence of the GNPs tendency to agglomerate, and their mild sedimentation.

Cyclic voltammetry results

The characteristic cyclic voltammograms (CVs) of the neat carbon mat, carbon mat/graphene, and PVB/graphene composite coatings, are shown in Figs. 5 and 6.

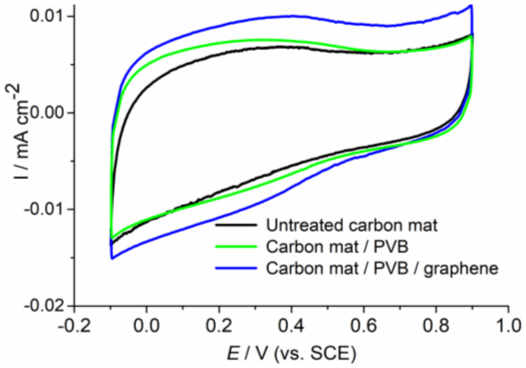


Figure 5. Cyclic voltammograms of carbon mat, and the carbon mat with PVB, and PVB/graphene composite coating.

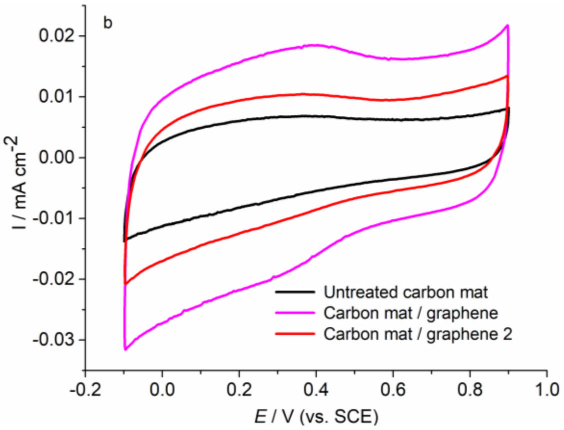


Figure 6. Cyclic voltammograms of carbon mat and carbon mat/ graphene, immersed and dried once and twice - graphene 2.

All recorded CV curves exhibit a quasi-rectangular shape, characteristic of capacitive materials where charge storage occurs through electric double-layer capacitance mechanism. Weak anodic peak around 0.4 V is observed in CV curves of composites with graphene, indicating a redox process, as corresponding cathodic peaks occur during discharge. These peaks are probably due to proton-coupled electron transfer reactions from residual oxygen-containing functional groups on graphene, such as quinone-like moieties, /38/.

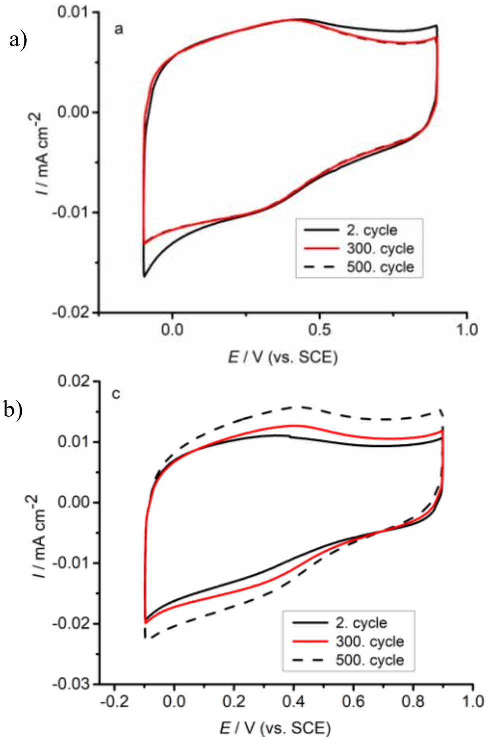
Values of specific capacitances of the prepared samples are calculated from CV curves according to the equation:

$$C_s = \frac{Q}{\Delta E \cdot A},$$

where: Q is the charge consumed in the potential range ΔE; and A is the geometric area of the electrode, /39/.

Incorporation of graphene into the carbon mat significantly increases the specific capacitance of resulting composites compared to the neat carbon mat or the carbon mat/PVB composite. This improvement can be attributed to the high conductivity and large surface area of graphene which enables efficient charge storage and electron transfer, /13/. Although PVB is electrochemically inert, its presence in the composites does not hinder their conductivity (Fig. 5a). The synergistic effect between graphene and the carbon mat improves the overall capacitive behaviour of the electrode. In comparison, the neat carbon mat and the carbon mat/PVB lacks the additional conductive properties and surface area provided by graphene, resulting in lower specific capacitances. These results highlight the critical role of graphene in improving the performance of carbon-based materials for supercapacitor applications.

The stability of the CV responses and corresponding capacitances as a function of cycle number of carbon mat/PVB and carbon mat/PVB/graphene composites to over 500 cycles are shown in Fig. 7.



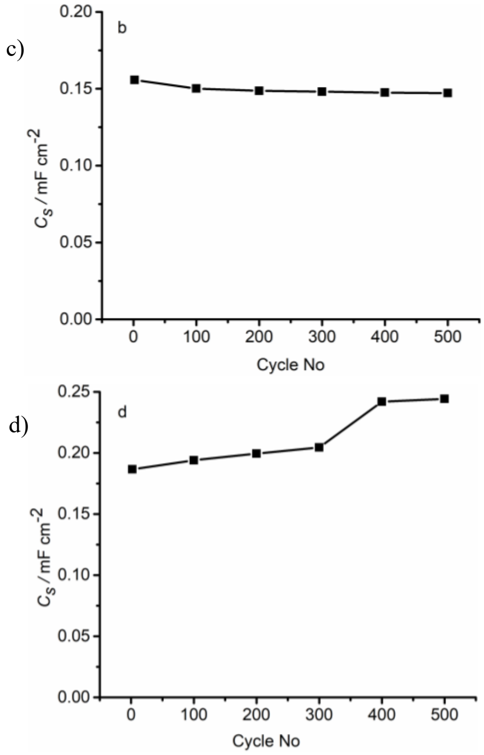


Figure 7. Cyclic voltammograms recorded over 500 cycles for: a) carbon mat/PVB; and b) carbon mat/PVB/graphene, along with the corresponding specific capacitances as a function of cycle number for: c) carbon mat/PVB; and d) carbon mat/PVB/graphene.

The carbon mat/PVB composite shows excellent stability, retaining 99.4 % of its initial capacitance after 500 cycles (Fig. 7b). On the other hand, the carbon mat/PVB/graphene composite shows an increase in CV currents over 500 cycles (Fig. 7c) which consequently leads to an increase in capacitance during cycling (Fig. 7d). With extended cycling, the electrolyte has more time to penetrate the graphene layers, allowing better access to the inner electrochemically active surface area. In addition, the PVB binder helps to maintain the structural integrity of the composite which contributes to stable and improved capacitive behaviour over longer cycles. The excellent stability of both composites can be attributed to the strong interaction between the PVB and the carbon mat which improves the overall mechanical strength and electrochemical performance of the electrodes.

CONCLUSIONS

New composite coating based on PVB and graphene nanoplatelets is developed and tested in the form of thin polymer films and as a coating applied on a carbon mat as a carrier material. FTIR spectra of neat PVB, graphene nanoplatelets, and PVB/graphene composite indicate polymer-graphene interactions (OH group, C–C bonds, PVB carbonyl stretch). Presence of the incorporated graphene nanoplatelets contribute to a higher hardness of the new composite coating, as well as altered mechanical behaviour, due to the inherent properties of graphene nanoplatelets (somewhat higher modulus of elasticity and smaller maximal tensile elongation and elongation at break). Also, improved thermal stability is observed with graphene inclusion, reflected in increased glass transition temperature.

The carbon mat/PVB/graphene and carbon mat/graphene composite showed promising properties for use in electrochemical energy storage devices such as supercapacitors. Further work might include optimisation of the composite structural design for specific electrochemical applications, as well as investigation of long-term stability and cycling performance.

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