

Mechanical and thermal properties of rigid PVC and graphene nanocomposites obtained by melt-mixing

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DOI: <https://doi.org/10.14314/polimery.2024.2.2>

Abstract: The effect of graphene (0.01, 0.1, 0.5 and 1 wt%) on the mechanical properties and thermal stability of rigid PVC was investigated. The morphology and thermal properties were analyzed by scanning electron microscopy (SEM) and thermogravimetric thermal analysis (TGA). Additionally, tensile properties, impact strength and hardness were determined. It was found that the addition of graphene can increase the impact strength and hardness and extend the thermal stability time of PVC.

Keywords: PVC, graphene, nanocomposites, mechanical properties, thermal stability.

Właściwości mechaniczne i termiczne nanokompozytów twardego PVC z grafenem otrzymanych w procesie mieszania w stanie stopionym

Streszczenie: Zbadano wpływ grafenu (0,01; 0,1; 0,5 i 1% mas.) na właściwości mechaniczne i stabilność termiczną twardego PVC. Strukturę i właściwości termiczne analizowano za pomocą skaningowej mikroskopii elektronowej (SEM) i termogravimetrycznej analizy termicznej (TGA). Ponadto określono właściwości mechaniczne przy rozciąganiu, udarność i twardość. Stwierdzono, że dodatek grafenu może zwiększyć udarność i twardość oraz wydłużyć czas stabilności termicznej PVC.

Słowa kluczowe: PVC, grafen, nanokompozyty, stabilność termiczna, właściwości mechaniczne.

Poly(vinyl chloride) (PVC) is used in many fields such as construction, packaging, transport, and electrical industries due to its good chemical properties and fire resistance. However, for some applications, rigid PVC requires modification, to enhance its impact strength [1, 2 it was focused on developing mechanically stronger and thermally more stable polyvinyl chloride (PVC)]. In this regard, improvement in the mechanical properties of rigid PVC attracts much attention from industry and science to develop high-performance PVC-based construction materials [1–4].

Graphene (GN) as a single layer of graphite, has been isolated by A. Geim and K. Novoselov in 2004. Their discovery, honored with the 2010 Nobel Prize in Physics, started a revolution in research on obtaining, modifying and using new two-dimensional carbon structures [5–7]. Due to its favorable mechanical, electrical and chemical properties, graphene has tremendous application poten-

tial in many areas, including developing multifunctional polymer composites with high mechanical properties [6, 8, 9].

Despite many literature reports on polymer nanocomposites with graphene, those based on poly(vinyl chloride) (PVC) as a matrix are still relatively poorly understood. Like other polymer nanocomposites, they are obtained by three main methods, i.e. solvent casting, melt-mixing and *in situ* polymerization [10–14]. The most extensively described in the literature are materials obtained from PVC solutions. The tensile strength of such PVC/GN nanocomposites was improved relative to the matrix material at low filler contents. However, higher GN contents (2–5 wt% depending on the method of obtaining and the structure of graphene) caused deterioration of strength, despite a constant increase in elastic modulus [11, 15–17]. Typically, improvements in thermal stability, storage modulus and glass transition temperature, were also observed, and their maximum values were characteristic of PVC/GN materials with the highest graphene content [1, 15, 18–20]. Much less research has been devoted to nanocomposites obtained by direct mixing in the melt state. Above that, most of the available works deal with plasticized PVC matrix materials [21–24].

As a filler in the rigid poly(vinyl chloride)-matrix materials, the multilayer graphene (MLG) was most

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often used [2, 25]. It was stated that the presence of MLG resulted in a reduction in microhardness, and these materials also exhibited a significantly lower coefficient of friction than unfilled PVC [25]. The small amount of nanofiller (about 0.4 wt%) led to significant increase in elongation at break and simultaneous decrease of elastic modulus and the impact strength whereas does not affect the tensile strength [2, 25]. Thermomechanical studies of these materials did not show a significant increase in storage modulus, and the glass transition temperature enhanced slightly in materials containing 2 wt% nanofiller compared to PVC.

Therefore, the article presents the influence of three-layer graphene (according to the manufacturer's data) on the mechanical, thermal, and morphological properties of rigid PVC. So far, no studies have been published in the available literature on this type of materials produced by direct melt mixing.

EXPERIMENTAL PART

Materials

To obtain the PVC/GN nanocomposites, rigid dry blend of poly(vinyl chloride) composed of PVC S61 (Anwil SA, Wloclawek, Poland) (100 phr), thermal stabilizer Mark MOK 17M (Acros, Renningen, Germany) (4 phr), and wax Loxiol G22 (Henkel, Düsseldorf, Germany) (1 phr) was used as the matrix. Three-layer graphene in nanopowder form (Graphene Laboratories Inc., Ronkonkoma, USA) with a flake thickness of 1.6 nm (maximum of 3 atomic monolayers), a flake length of 10 μm , and a specific surface area of 400–800 m^2/g was introduced into the PVC matrix as the filler.

Processing of PVC/GN nanocomposites

PVC nanocomposites with graphene were processed by extrusion and compression molding. The first step consisted of obtaining a dry mixture of PVC with processing additives by mixing for 15 minutes in a mixer heated to 100°C. Dry PVC mixture was then mixed with the filler in a mechanical mixer Ika Eurostar 6000 (Ika Werke, Staufen im Beisgau, Germany) for 10 minutes. This allowed to obtain a mixture of powders containing 0.01, 0.1, 0.5 and 1 wt% graphene. Then the mixtures were extruded using the laboratory single-screw extruder (Brabender GmbH & Co. KG, Duisburg, Germany) (screw diameter = 15 mm, L/D = 13), through a cylindrical nozzle with a diameter of 2 mm and a length of 30 mm. Processing temperatures were as follows: hopper 20°C; 1st zone 140°C; 2nd zone 165°C; head 175°C operating at the screw speed of 40 rpm. The extrudates obtained were cooled and granulated. Subsequently, the granulates were pressed at the maximum pressure of 15 MPa at the temperature of 185°C into plates, which were used to cut samples for further

testing. Finally, composites containing 0.01, 0.1, 0.5, and 1 wt% graphene were obtained.

Characteristics of PVC/GN composites

SEM analysis

Structure of the nanocomposites was studied using scanning electron microscopy (SEM) on a Zeiss Crossbeam 350 microscope (Carl Zeiss Microscopy GmbH, Germany); cryogenic breakthroughs of nanocomposites, with a sputtered gold layer were observed.

Mechanical properties

Tensile properties were determined in accordance with EN ISO 527. The standardized test specimens (type 5A) were cut using a CNC milling machine from a plate with dimensions of 120×120×2 mm. The measurement was carried out with a Zwick/Roell Z010 testing machine (Ulm, Germany) at 23°C. The crosshead speed was 5 mm/min (for modulus 1 mm/min). The impact strength was evaluated by using the Charpy method in accordance with EN ISO 179–1. Rectangular specimens with a length of 80 mm and a cross-section dimension of about 10×4 mm was used. Samples without notches were evaluated. The tests featured the use of a pendulum with a nominal impact energy of 4 J. The measurement was taken for 6 samples. The hardness of PVC and nanocomposites with GN was measured using a Shore D instrument (Zwick Roell, Ulm, Germany) and in accordance with PN EN 868. The test samples were 4 mm thick. The device was calibrated after each measurement. The hardness of the materials was read after 15 s.

Thermal stability

Thermogravimetric analyses were carried out using a TG 209 F3 Netzsch Group (Germany) device in the temperature range of 30–900°C at a heating rate of 10°C/min in the nitrogen atmosphere. A sample (approx. 10 mg) was taken from pressed plates prepared for mechanical tests. Thermal stability time was determined using the Congo red method. The materials were placed in a glass tube with an internal diameter of 4.7 mm and a wall thickness of 0.65 mm. Congo test paper was inserted into the upper part of the test tube to a depth of 5 mm. The test tube was then placed in an oil bath heated to 200°C. The test result was the time (in minutes) at which the first visible color change (from red to blue) was observed on the test paper. The change indicates the decomposition of PVC and the evaporation of hydrogen chloride as a decomposition product.

Statistical analysis

Origin 8.6 Pro software with implemented statistical analysis modules was used to analyze the obtained

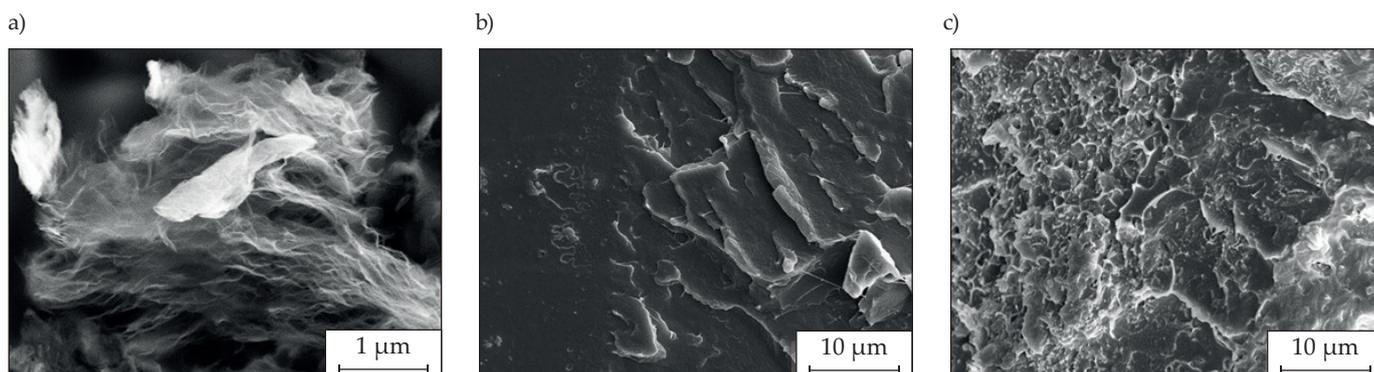


Fig. 1. SEM images: a) graphene, b) PVC, c) PVC/1%GN

results. To compare the significance of the difference for the mean values of the obtained results, ANOVA with Tukey's post-hoc test was used. The Shapiro–Wilk test confirmed normal distribution, and homogeneity of variances by Levene's test. All analyzes were performed assuming a significance level below 0.05.

RESULTS AND DISCUSSION

SEM analysis

Fig. 1 shows SEM images of graphene (GN), unmodified PVC and PVC containing 1 wt% GN. The graphene used was characterized by a flake structure typical for this material. The large lateral surface of the filler in relation to its thickness gives it a characteristic wrinkled morphology [2, 21]. The image of unmodified PVC was typical of thermoplastics brittle fracture. The nanocomposite fracture surface was more jagged than that of the unmodified polymer. Fig. 1c shows that the graphene flakes are completely covered with PVC. The filler was characterized by good dispersion in the PVC matrix, as evidenced by the lack of visible nanofiller agglomerates. This is confirmed by the correct selection of the two-stage preparation method and the parameters used. At the same time, the different nature of the crack indicates adequate adhesion at the graphene/PVC interface [2, 3, 22, 25, 26].

Mechanical properties

To determine the effect of GN on the mechanical properties of rigid PVC, the tensile modulus (E_t), tensile strength (σ_M), elongation at tensile strength (ε_M), elongation at break (ε_B), impact strength (a_{CN}) and hardness

(H) of the PVC/GN nanocomposites were examined. The results presented in Table 1 and Fig. 2 showed no statistically significant changes in E_t , σ_M , ε_M while a significant increase in elongation at break and impact strength were observed in materials with low graphene content, i.e., 0.01 and 0.1 wt%. In addition, a slight increase in hardness was observed in composites containing 0.1, 0.5, and 1 wt% graphene relative to matrix and PVC/0.01% GN nanocomposite.

The observed increase in impact strength and elongation at break of PVC/0.01% GN and PVC/0.1% GN samples differs from that typically observed for polymer-graphene nanocomposites, for which an increase in tensile modulus and tensile strength causes a decrease in elongation at break. The difference in the results obtained was due to the high flexibility of the nanofiller used, which was characterized by a crumpled structure resulting from a small number of layers and a large flake area. Moreover, graphene has high self-lubricating properties, which may also affect the mechanical properties of nanocomposites with their content [2, 25].

The observed increase in hardness (Table 1) of PVC/GN nanocomposites is typical for materials with graphene fillers. The uniform dispersion of the filler in the composite may hinder the movement of PVC macromolecules formed under the influence of external force (local plastic deformation), which contributes to an increase in hardness.

According to the literature, there is a relationship between the hardness and stiffness of composites, and their increase leads to an increase in the brittleness of nanocomposites compared to PVC [15]. In the case of the presented materials, no significant increase in E_t was observed, however, its values were higher compared to the PVC matrix in the case of materials characterized

Table 1. Mechanical properties

Sample	E_t MPa	σ_M MPa	ε_M %	ε_B %	a_{CN} kJ/m ²	H , °Sh
PVC	1522±104.3	60.1±0.4	5.5±0.2	13.3±5.1	3.0±1.2	72.0±3.9
PVC/0.01% GN	1486±108.7	60.1±0.9	5.4±0.4	61.5±26.0	8.6±2.1	72.5±3.3
PVC/0.1% GN	1578±85.8	60.5±0.9	5.5±0.3	146.9±28.5	6.2±1.3	76.6±0.7
PVC/0.5% GN	1612±39.6	60.1±0.7	5.2±0.1	18.6±13.1	4.0±1.9	77.0±0.6
PVC/1% GN	1568±108.1	59.4±1.2	5.1±0.4	5.5±0.6	2.5±0.8	77.5±0.8

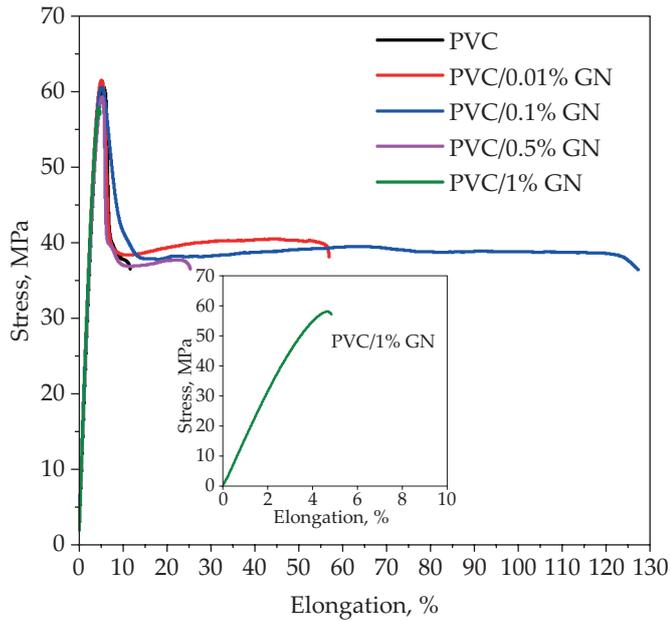


Fig. 2. Stress-strain curves of investigated samples

by higher hardness. In Fig. 2, it can be observed that the PVC/1% GN nanocomposite was characterized by typically brittle fracture, which further confirms the relationships discussed above.

Thermal properties

The rest of the work focused on characterizing the thermal properties of the obtained materials. For this purpose, thermogravimetric analysis and stability time measurement using the Congo Red method were performed. Based on the results presented in Fig. 3a) and 3b), it was found

that the decomposition of nanocomposites, similarly to PVC, takes place in two stages. The first stage of degradation (230–400°C) was associated with dehydrochlorination of the matrix material and the formation of conjugated polyene structures. The second stage occurring in the higher temperature range (400–600°C) corresponded to the thermal cracking of carbonaceous conjugated polyene sequences and the formation of residual chars [19, 27].

To compare the thermal stability of the materials, temperature corresponding to 1, 5, and 50% of their mass loss (T_1 , T_5 , T_{50}) and the maximum temperature of the first stage of decomposition were determined on the differential thermogravimetry curves (max. DTG I). The results of T_1 , T_5 and T_{50} analyzes presented in Table 2 did not show a statistically significant change in the thermal stability of the nanocomposites compared to PVC.

However, an increase in the maximum DTG I temperature was observed for the PVC/1% GN sample by approximately 6.4°C compared to PVC. The thermal stability time determined using the Congo red test was also longer in this case by about 1.5 minutes.

This improvement in PVC thermal stability associated with the use of graphene is not significant from the point of view of industrial processing, but nevertheless indicates that well-dispersed graphene nanoparticles in the PVC matrix can create a physical barrier to hydrogen chloride and thus delay the dehydrochlorination process of the polymer. GN is known for its barrier properties to gas molecules [28, 29]. Therefore, the likely mechanism is the creation of a more tortuous diffusion path for hydrogen chloride gas molecules. The consequence of this is the extension of its release time and the reduction of unfavorable catalytic effects [30]. The presented effects allow us to assume that improve the GN dispersion in the

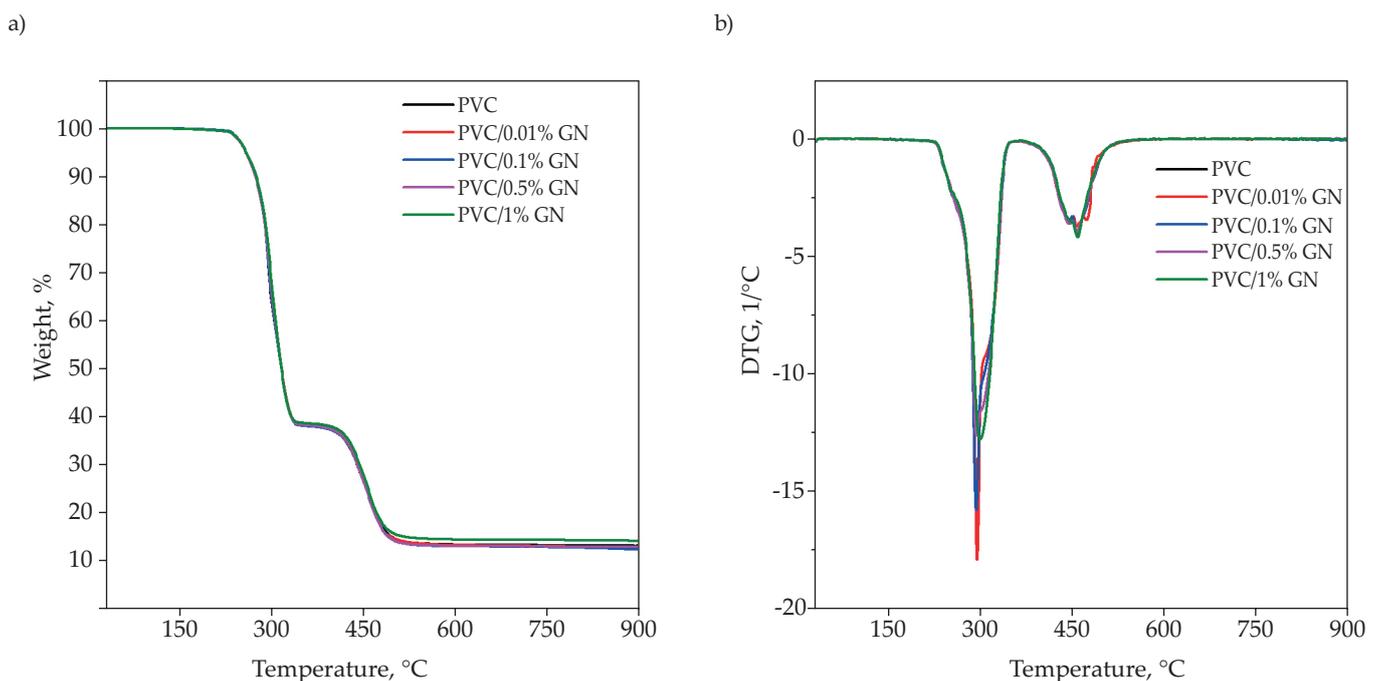


Fig. 3. Thermal properties: a) TGA curves, b) DTG thermograms

Table 2. Thermal properties

Material	$T_{1'}^{\circ}\text{C}$	$T_{5'}^{\circ}\text{C}$	$T_{50'}^{\circ}\text{C}$	Max. DTG I, $^{\circ}\text{C}$	Congo Red Test, min
PVC	235.3±1.2	258.7±0.4	316.3±0.3	293.2±0.8	16.7±0.1
PVC/0.01% GN	235.6±0.7	258.7±0.3	316.4±0.3	293.3±0.7	16.8±0.2
PVC/0.1% GN	235.6±0.8	258.8±0.3	316.4±0.4	293.4±0.9	17.4±0.3
PVC/0.5% GN	235.5±1.1	258.8±0.3	316.5±0.3	293.4±0.6	17.4±0.4
PVC/1% GN	235.6±0.5	258.8±0.4	316.4±0.3	299.6±0.5	18.1±0.2

PVC matrix or the use of single-layer graphene should positively increase the thermal stability of the polymer by creating an effective physical barrier hindering the permeability of volatile degradation products.

CONCLUSIONS

Homogeneous nanocomposites of rigid PVC with three-layer graphene were obtained using the melt mixing method. The use of graphene can significantly improve the impact strength of PVC at low filler content, i.e., 0.01 and 0.1 wt%. At the same time, the higher graphene content increased its hardness and brittleness. Graphene did not improve the thermal stability of PVC, but it did increase the thermal stability time measured by the Congo red test, especially for the PVC/1%GN sample. This was due to the formation of a physical spatial barrier of graphene in the PVC matrix, which delayed the autocatalytic dehydrochlorination reaction of the polymer. However, considering the low heat resistance of PVC, the improvement in thermal properties of nanocomposites with simultaneous enhancement of mechanical properties is beneficial having regard to the application of such materials. Although new materials with favorable properties were obtained, it is necessary to conduct further research focusing on improving the GN dispersion in the PVC matrix, which should result in a significant increase in the thermal stability of the nanocomposites.

Author contribution

S.W. – conceptualization, methodology, validation, investigation, writing-original draft, writing-review and editing, visualization; K.S. – methodology, investigation, writing-original draft; J.T. – conceptualization, writing-original draft, writing-review and editing, supervision; K.L. – methodology, investigation, writing-original draft; Ö.F.Ş. – methodology, validation, investigation.

Funding

The results presented in this paper were funded with grants for education allocated by the Ministry of Science and Higher Education in Poland.

Conflict of interest

The authors declare no conflict of interest.

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Received 28 XI 2023.
Accepted 11 XII 2023.

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