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Structure and thermal stability of phosphochlorinated polybutadiene/carbon black composite synthesized *via* oxidative chlorophosphorylation reaction

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Abstract: The aim of the presented work was to obtain a new type of homogeneous composite based on an industrial polymer (polybutadiene, PB) and a well-known inexpensive filler (carbon black P-234, CB). For this purpose, the reaction of oxidative chlorophosphorylation (OxCh) was used. This makes it possible to introduce CB into the cross-linked structure of the modified polymer and ensure optimal distribution of the filler in it. The structure and thermal stability of the composite synthesized by the OxCh reaction were studied. Analysis of the composite by Fourier-transform infrared spectroscopy indicates a uniform distribution of carbon black in the network structure of the matrix and the physical interaction of the phases of the composite. Ultraviolet-visible spectrum data confirmed the improvement in light absorption in a wide range of the electromagnetic spectrum and the decrease in the optical band gap energy of the phosphochlorinated PB (PhPB) matrix with the addition of CB (E_g of PhPB = 3.25 eV; E_g of PhPB/CB composite = 2.28 eV). The influence of CB on the thermal stability of the PhPB matrix was studied using thermogravimetric and differential thermogravimetric analysis. After thermal analysis, the char yield for PhPB was 41 wt. %, and for PhPB/CB composite was 35.2 wt. %. Compared to PhPB, the increase in char yield, the decrease in maximum thermal decomposition temperature, and the high-integrated thermal decomposition temperature for the PhPB/CB composite show the improvement in the thermal stability of PhPB due to CB.

Keywords: rubber; filler; spectroscopy; chemical modification; matrix; infrared spectroscopy.

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INTRODUCTION

Polymer/carbon black (CB) composites are unusual materials that find versatile applications in a variety of industrial, electronic, and biotechnological devices. For example, they are used as temperature sensors in many systems,[1,2] including sensors for volatile organic compounds with a wide range of applications such as toluene, acetone, cyclohexane and carbon tetrachloride.[3,4] The authors of the studies[5,6] discussed the improvement of wear resistance, erosion resistance of protective coatings, and electromagnetic shielding through the use of polymer/CB composites. Nakashima *et al.*[7] and Inan *et al.*[8] presented feasible membrane fuel cells operating over a wide range of temperatures and humidity levels in their studies. Nonwoven materials with modified CB nanoparticles in a Nylon-6 matrix polymer have been obtained and proposed as an adsorbent material (hemodialysis membrane).[9] A new structure of carbon nanofibers is discussed, which will be potentially useful for energy and water purification.[10] Harraz and colleagues[11] successfully created a new gold nanoparticle-decorated polypyrrole–CB/SnO_2 photocatalyst that was used to remove the insecticide imidacloprid and methylene blue under visible light illumination. A new scheme for harvesting solar energy was also demonstrated, based on the pyroelectric effect using absorbers from nanocomposite polymers of graphene and CB.[12]

Improving the performance of polymer/CB composites in all areas of application mainly depends on improving their mechanical, electrical and thermal properties, which are greatly influenced by CB.[13–15]

CB has the appropriate physical and chemical properties and is used in industry as a reinforcing rubber filler, UV stabilizer, sorbent and pigment.[16–18] CB is an amorphous particle with pores, it consists of more than 97 % carbon with a very low content of oxygen, hydrogen, sulfur, and organic compounds. CB has an interesting surface with various functional groups such as quinine, hydroxyl and carboxyl groups, which are necessary to create a cross-linked structure to improve the mechanical properties of polymers, especially rubbers. CB particles oriented in various morphologies by van der Waals forces exhibit structures with medium and high aggregates, as well as graphite-like structures.[19,20] Various CB structures are important for the thermal and electrical properties of polymer composites.[14,21,22]

Analysis of literature data shows that the properties of polymer composites using CB are determined not only by the nature of the polymer matrix, but also by the degree of uniform distribution of the filler in the matrix. In addition, structural studies of polymer/CB composites show that for designing such materials with the improved performance, it is necessary to achieve a higher degree of distribution of CB aggregates in the polymer. And the above mentioned, in turn, is established by the method of preparing composites.[22–25]

In this paper, we continue our previous studies of phosphochlorinated polybutadiene (PhPB) and its composites with various fillers, using the oxidative chlorophosphorylation reaction[26–28] as a tool. Using this reaction, we are for the first time conducting a study of the structure and thermal stability of the PhPB composite with the expedient commercially available CB P-234, with the assumption of further use. The results on the structure and thermal stability of the composite can be taken into account when using it as adsorbents.

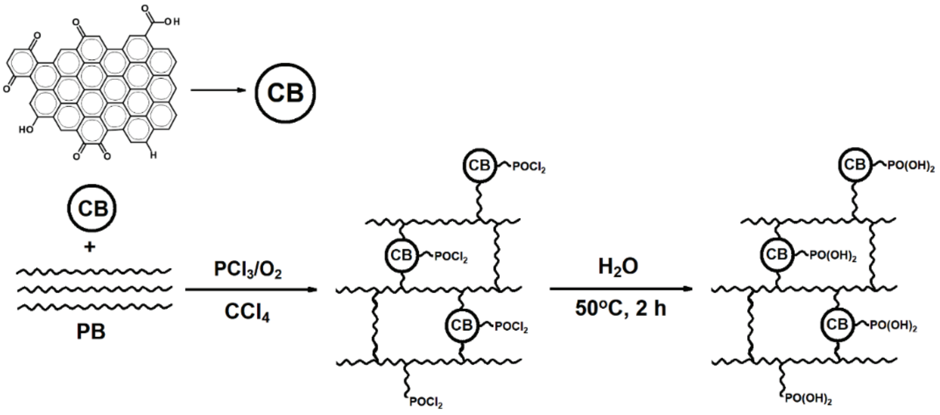
EXPERIMENTAL

Materials

PB was purchased from Voronezh Synthetic Rubber Plant (Russia). CB P-234 was purchased from ABA Providing (Russia). PCl_3 and CCl_4 were supplied by Gorex-Analyt GmbH and used without further purification. Oxygen was supplied to the reaction medium by purging through the concentrated H_2SO_4.

Preparation of PhPB/CB composite

The construction of the cross-linked structure of PB and the preparation of its composite with a CB filler was carried out by the OxCh reaction. Initially, a 6 % solution of PB in CCl_4 was prepared in a flat-bottomed three-necked flask. The flask was then equipped with a reflux condenser, a thermometer, and a bubbler to supply oxygen gas to the reaction medium. Then, CB was added to the PB in a ratio of 1:10 (PB to CB) and the mixing of the mixture was started. Oxygen was supplied to the reaction medium at a rate of 7 L h^{-1}. The reaction was started with the gradual dropwise addition of 10 ml of PCl_3. An increase in temperature to 56°C indicated the exothermic nature of the reaction. A black solid was formed in the reaction medium and the temperature dropped back to room temperature. After completion of the reaction, the liquid phase containing PCl_3, CCl_4, and intermediate product $POCl_3$ was separated from the solid by distillation using a water jet pump. The resulting product contains functional groups $–P(O)(Cl)_2$ and $–OP(O)(Cl)_2$ and was therefore subjected to hydrolysis at 50 °C for 2 h. Hydrolysis product, *i.e.*, the PhPB/CB composite was washed with deionized water until neutral pH and finally dried first in air and then in a vacuum drying oven. The synthesis mechanism of PhPB/CB composite is given in Scheme 1.



Scheme 1. Synthesis mechanism of PhPB/CB composite.

Preparation of PhPB

To compare the results obtained for the PhPB/CB composite, PhPB with a cross-linked structure was synthesized by the OxCh reaction of PB without CB filler.[29]

Characterization of CB, PhPB and PhPB/CB composite

The Fourier-transform infrared (FTIR) spectra of all samples were measured on a Perkin Elmer Spectrum 100 FTIR spectrophotometer in the range from 650 to 4000 cm^{-1}. UV–Vis spectroscopic studies of the samples were carried out on a Specord 210 Plus spectrophotometer (Analytik Jena, Germany) in the wavelength range from 200 to 700 nm. Absorption spectra obtained using UV–Vis spectroscopy were also used to estimate the optical band gap energies for the samples using Tauc's plot.[30] TG and DTG analysis of all samples was carried out on a Terra-ZA thermogravimetric analyzer in the temperature range from 26 to 750 °C (heating rate 10 °C min^{-1}) on a ceramic crucible in a nitrogen atmosphere. Approximately 4–4.5 mg of each sample was used.

RESULTS AND DISCUSSION

Characterization of CB, PhPB and CB/PhPB composite

A comparative analysis of the FTIR spectra of CB, PhPB, and the PhPB/CB composite was carried out firstly, to characterize the functional groups on the CB secondly, to study the modification of PB by the OxCh reaction and finally, to study the possibility of interaction between the CB filler and the modified PhPB.

The FTIR spectra of CB, PhPB and PhPB/CB composite are shown in Fig. 1. In the spectrum of CB the broad band at 3467 cm^{-1} (Fig. 1c) refers to the stretching of the –OH hydroxyl groups. The smaller absorption bands at 1239 and 1787 cm^{-1} are associated with the elongation of the carboxyl group C–O and C=O, respectively. The slightly intense band at 2328 cm^{-1} is usually associated with the C=O force, also the band at 980 cm^{-1}, indicates C=C–H bending vibrations. The bands at 2106 and 2660 cm^{-1} were attributed to the –CH$_2$ tension. These results of the analysis confirmed the presence of hydroxyl (–OH) and carboxyl (–COOH) groups on the CB surface. The presence of these functional groups plays a significant role in the interaction of CB with the modified PB during the construction of the composite structure.[31,32]

In the spectrum of PhPB obtained by the OxCh reaction (Fig. 1a), peaks were found at 3384, 2931, 2868, 2280 and 2099 cm^{-1}, corresponding to the –OH vibration of –P(O)(OH)$_2$ functional groups. The associated P=O stretching vibrations and P–OH stretching vibrations appear at 1174 and 739 cm^{-1}, respectively. An intense peak at 983 cm^{-1} corresponds to C–O–P, which indicates the addition of the –PO(OH)$_2$ group to the rubber matrix chain through oxygen. The adsorption peak at 1446 cm^{-1} is attributed to –CH$_2$ groups.[33]

After the interaction of the filler with the polymer matrix by the OxCh reaction, the FTIR spectrum of the obtained PhPB/CB composite (Fig. 1b) shows a slight increase in the C–O–R intensity (broad band at 982 cm^{-1}), which is associated with the physical interaction of the PhPB with CB functional groups. As a rule, the absence of a significant effect on the FTIR spectra of PhPB after the addition of CB indicates a uniform distribution of CB particles throughout the polymer matrix. A similar result was observed in the FTIR spectra of HDPE, PP, PET and nylon/carbon black composites.[1,34]

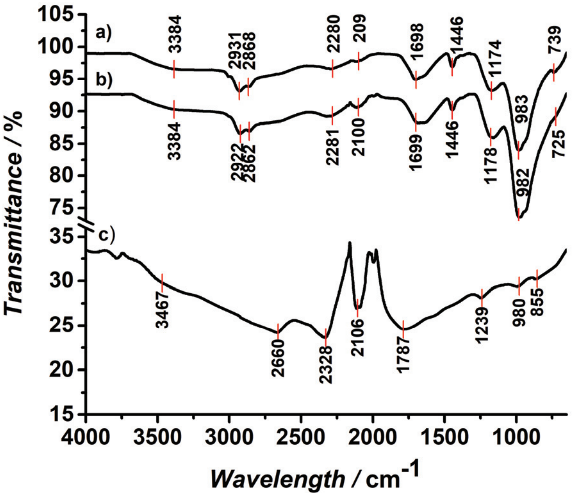


Fig. 1. FTIR spectra of PhPB (a), PhPB/CB composite (b) and CB (c).

UV–Vis analysis

UV–Vis measurements were carried out to study the effect of CB particles on the optical properties of the PhPB matrix. UV–Vis spectra of the PhPB matrix observe absorption at a wide range of 256 to 390 nm due to π–π* absorption of

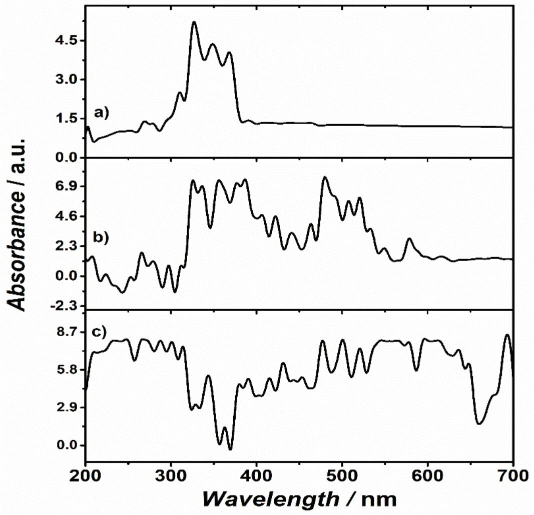


Fig 2. UV–Vis spectra of samples PhPB (a), PhPB/CB composite (b) and CB (c).

the conjugate system in the polybutadiene as shown in Fig. 2c.[35] This peak shifted to a wide range at the visible region in case of PhPB/CB composite as seen in Fig. 2b.

Direct allowed band gap of CB, PhPB and PhPB/CB composite was analyzed by Tauc's equation.[30] As can be seen in Fig. 3, the optical band gaps of PhPB (Fig. 3a) and PhPB/CB composite (Fig. 3c) are 3.25 and 2.28 eV, respectively. The smaller optical band gap of the PhPB/CB composite was attributed to disorder in the polymer matrix by the incorporation of CB particles, and thus the adsorption shift of the composite (Fig. 2b) into the visible region in the electromagnetic spectrum, due to the nature of the CB, that CB has black color and absorbs UV–Vis light as in Fig. 2a.[30] In addition, the decrease in the optical band gap of the polymer matrix is a good indicator of the increase in conductivity, which adapts the contribution of CB particles to the composite structure. Similar optical properties were observed in the polyethylene oxide/carbon black composite.[36]

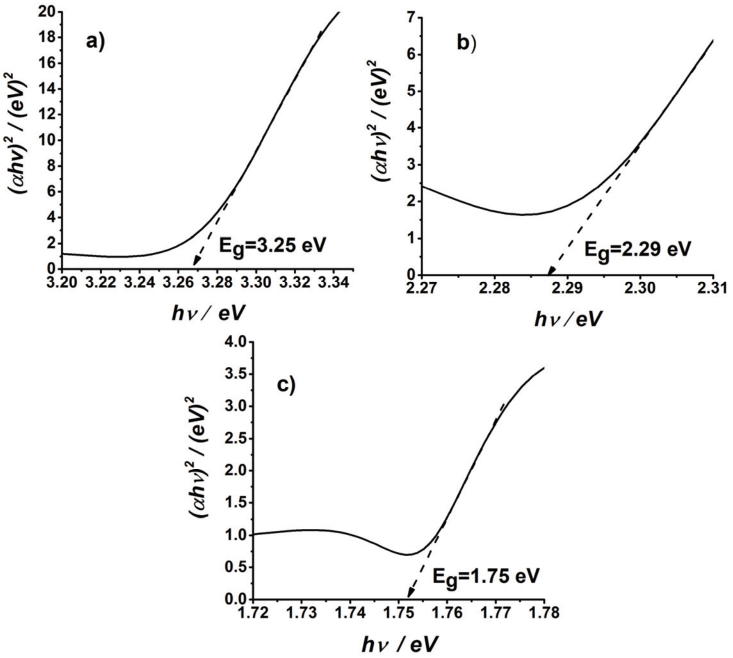


Fig. 3. The optical band gap energies of PhPB (a), PhPB/CB composite (b),and CB (c).

TG/DTG analysis

Based on the thermogravimetric analysis of CB (P-234), the TG curve in Fig. 4 shows two decomposition stages. The first stage below 120 °C is associated with the evaporation of adsorbed water from the sample. The second stage on the curve in the range of 120–750 °C is associated with the release of volatile oxygen-containing fragments of functional groups onto the surface of the CB.[32] The DTG curve clearly shows maxima (exo-peaks) characteristic of volatile fragments, which are associated with the release of CO_2 during the decomposition of carboxyl groups in the range of 120–470 °C, and a large amount of CO from all oxygen-containing functional groups, reaching a maximum at 700 °C.[37] A less intense peak in the region of lower temperatures may be associated with the release of residual water, which is physically associated with the CB.[36]

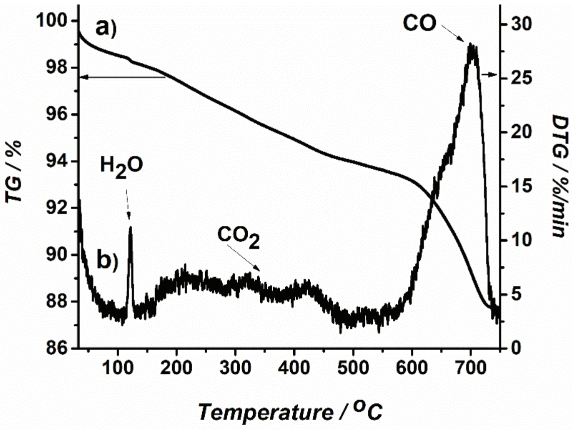


Fig. 4. TG (a) and DTG (b) thermogram CB (P-234).

To assess the effect of CB on the thermal stability of the polymer matrix, TG/DTG analyses of the PhPB matrix and the PhPB/CB composite were carried out. The results are presented in Fig. 5. The TG/DTG curves show three stages of thermal degradation for both PhPB and the PhPB/CB composite, indicating a similar degradation mechanism. A significant weight loss was observed in the range of 125–500 °C (second and third stages), weight loss below 125 °C (first stage) is due to the evaporation of physically bound water molecules, while the decomposition of functional groups and the polymer chain occurs in the second and third stages, respectively. The maximum decomposition temperatures and weight loss obtained for PhPB and the PhPB/CB composite are listed in Table I. The higher weight loss of PhPB compared to the PhPB/CB composite was observed in the second and third stages, and the apparent weight loss of the polymer matrix is due to the high amount of volatile components formed in the process of destruction. The composition exhibits greater thermal stability with less weight loss. This may be due to the presence of the CB filler, which has a shielding effect on the composite and slows down the thermal decomposition process. Accordingly, a comparison of the DTG curves of the polymer matrix and the composite showed a decrease in $t_{\max}$ in the second and third stages due to the addition of CB to the matrix, as indicated in Table I. This is due to the dispersion of the CB of the filler in the PhPB matrix, due to the effect on the matrix cross-link density, as well as by increase of t_{max} at the first stage due to a larger amount of evaporated water adsorbed on the CB filler. The split peak in the third stage of decomposition in the polymer matrix and composite results from parallel multiple decomposition reactions at higher decomposition temperatures. A large amount of residue is also obtained in composites with styrene-butadiene or natural rubber, including CB as a filler.[38,39]

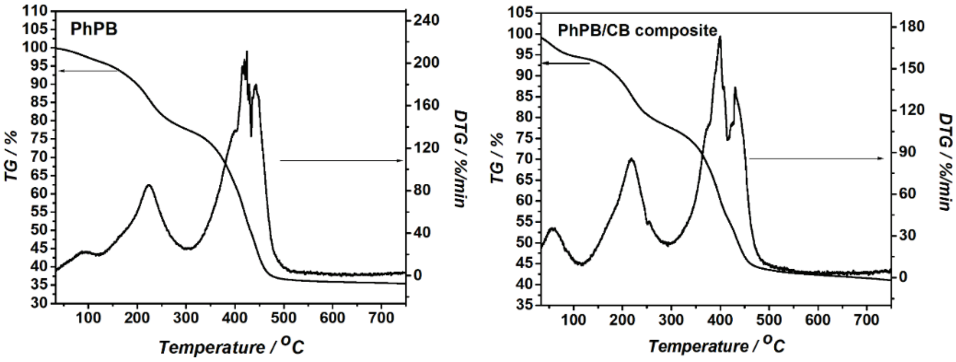


Fig. 5. TG/DTG Thermograms of PhBB and PhPB/CB composite.

TABLE I. Parameter obtained from TG and DTG thermograms

Sample	TG					DTG	
	Step	Temp. range °C	Mass loss wt. %	Yield at 750 °C wt. %	IPDT °C	T_{max} °C	DTG_{max} % min^{-1}
PhPB	1st	25–125	3.8	35.2	1064	98	0.31
	2nd	125–303	18.9			223.4	1.61
	3rd	303–750	42			424.3	4.16
PhPB/CB composite	1st	26–114	5.6	41	1316	55.7	0.84
	2nd	114–290	16.5			218.3	2.01
	3rd	290–750	36.9			400	4.06

Moreover, the PhPB/CB composite exhibits a higher resistance to thermal degradation according to integral decomposition temperature (IPDT) values calculated from the TG curve (Fig. 6) using the Doyle equation:[40]

$$IPDT = A^{*} K^{*} (T_{f} - T_{i}) + T_{i} \tag{1}$$

where A^* is $[(A_1+A_2)/(A_1+A_2+A_3)]$, K^* is a coefficient $[(A_1+A_2)/A_1]$, and T_i and T_f are initial temperatures and final temperature, respectively. A_1, A_2 and A_3 are area ratios in TG thermogram as shown in Fig. 4.

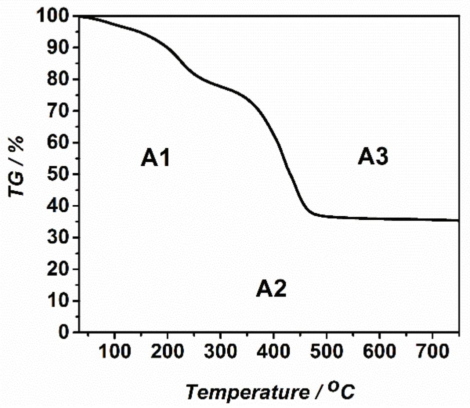


Fig. 6. Schematic representation of TGA area for calculation of IPDT values.

Probable structure of the produced polymer/CB composite

According to the results of analysis for the polymer/CB composite using IR, UV spectroscopy and TG/DTG, its structure has the following features:

– There is a chemical bond between the chains of macromolecules and CB in the composite;

– CB is evenly distributed in the polymer matrix.

The probable polymer/CB structure is shown in Fig. 7.

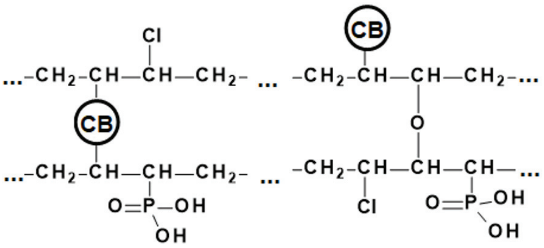


Fig. 7. Probable chemical structure of PhPB/CB composite.

CONCLUSION

PhPB/CB composite was synthesized by OxCh reaction. PhPB/CB composite and its constituent components, *i.e.*, CB and PhPB, were studied by FTIR, UV–Vis and TG/DTG analysis methods. According to the results of FTIR spectroscopy, we have found that the proposed OxCh reaction succeeded in modifying and constructing the cross-linked structure of PB obtaining well dispersed CB P-234 filler into a modified PB structure. The result of UV–Vis studies showed that due to the nature of the added CB, the PhPB/CB composite absorbs UV–Vis lights in a wider wavelength range than the PhPB matrix. The fact that the optical band gap width of the PhPB/CB composite is less than that of PhPB was attributed to the fact that CB imparts electrical conductivity to the polymer matrix.

According to the results obtained from the study of the thermal properties of the samples, PhPB/CB composite exhibits a higher resistance to thermal degradation.

Based on the overall results, it can be said that by using the OxCh reaction and CB as a filler, it is possible to improve the thermal, electrical, and optical properties of PB, as well as to synthesize a composite material with a cross-linked structure.

ИЗВОД

СТРУКТУРА И ТОПЛОТНА СТАБИЛНОСТ ФОСФОХЛОРИСАНОГ ПОЛИБУТАДИЕН-ЧАЂ КОМПОЗИТА СИНТЕТИСАНОГ ПУТЕМ ОКСИДАТИВНЕ ХЛОРОФОСФОРИЛАЦИЈЕ

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Циљ представљеног рада био је да се добије нови тип хомогеног композита заснованог на индустријском полимеру (полибутадиен, PB) и добро познатом јефтином пуниоцу (чађ P-234, CB). У ту сврху коришћена је реакција оксидативне хлорофосфорилације (OxCh). То омогућава увођење CB у умрежену структуру модификованог полимера и обезбеђивање оптималне расподеле пуниоца у њему. Проучавана је структура и топлотна стабилност композита синтетисаног OxCh реакцијом. Анализа композита FTIR методом указује на уједначену расподелу пуниоца у умреженој структури матрице и физичку интеракцију фаза композита. Подаци ултраљубичастог видљивог спектра потврдили су побољшање апсорпције светлости у широком спектру електромагнетног спектра и смањење оптичког енергетског јаза фосфохлорне PB (PhPB) матрице са додатком CB (E_g 3,25 eV; E_g PhPB/CB композита 2,28 eV). Утицај CB на топлотну стабилност PhPB матрице проучаван је коришћењем термогравиметијске и диференцијалне термогравиметријске анализе. Након термалне анализе, остатак за PHPB је био 41 мас. %, а за PhPB/CB композит 35,2 мас. %. У поређењу са PHPB, повећање остатка, смањење максималне температуре топлотног распадања и висока температура термалне декомпозиције за PhPB/CB композит показују побољшање топлотне стабилности PHPB због CB.

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