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Investigation of the thermal, mechanical and biological properties of PVC/ABS blends loaded with cobalt chloride for biomedical and electronics applications

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Abstract: New PVC/ABS and $CoCl_2$ composites with various concentrations of cobalt chloride (≤10 wt. %) were synthesized by solution casting techniques and investigated by spectro-chemical, morphological and thermal mode of characterization. The FT-IR, XRD and SEM analyses proved the smooth distribution and uniformity of the constituents of the composite materials. Thermal behavior showed that the addition of $CoCl_2$ to the PVC/ABS blends enhanced the thermal stability and improved mechanical properties of composites due to crosslinking between PVC/ABS blend and $CoCl_2$. Thus based on their remarkable morphology, thermomechanical stability and promising bioactivities, the synthesized composites could be applied for high performance polymeric materials in the field of biomedics and electronics.

Key words: poly(vinyl chloride); acrylonitrile; composites; metal salt.

INTRODUCTION

A composite substance comprises two phases named as matrix and reinforcing phases, which are continuous and discontinuous, respectively. Both these phases collectively work together and enhance different properties of the resulting material. During the manufacturi of composite materials two or more different substances having different properties, including morphology and macroscopic composition, are mixed together.[1] Composite materials exhibit better properties than those of the constituents from which they are synthesized. Due to their extraordinary properties, including corrosion resistance, high tensile strength, light weight, high loadbearing capacity, and better surface finishing and

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higher fatigue strength, composite materials are superior to the pristine components in various fields.[2] During the past few decades, composite material have attracted intense attraction as compared to neat and pure organic materials because of their great and novel properties, including mechanical, thermal stability, flame retardancy, recyclability, aging resistance, dimension stability, *etc.*[3–9] Polymeric composite substances containing either a bio or synthetic polymer matrix and reinforcing natural fibers, having excellent biocompatibility, are especially employed in different biomedical fields, mainly dental, regenerative medicine, tissue engineering, and for the manufacture of artificial body parts.[10] Poly(vinyl chloride) is a globally used thermoplastic material, over about 23 million ton per year in various fields.[11] Poly(vinyl chloride) (PVC) polymer (40 % of dedicated polymeric materials) is suitably employed in the fields of biomedicine and food. Medical and food grade poly(vinyl chloride) are considered as the major polymer for the matrix of antimicrobial composite materials. In spite of being an outstanding building material, PVC has some disadvantages especially concerning human health and environmental hazards. Acrylonitrile–butadiene styrene (ABS) has very interesting features in the polymeric class of compounds with respect to its structures, composition and manufacturing quality. ABS has been applied in a variety of fields because of phase system, mechanical properties, recyclability and cost effective.[12] Acrylonitrile–butadiene styrene comprises two composite systems one of which is the polybutadiene rubber phase and the second is the styrene–acrylonitrile copolymer rigid phase. Polybutadiene–styrene is dispersed and imprinted in the styrene–acrylonitrile co-polymer rigid phase that behaves as a matrix.[13] Inorganic additives, such as CNTs,[14–18] graphene,[19] carbon black,[20] clay,[21] MMTs,[22] Cal. carbonate,[23] Al_2O_3[24] and SiO_2,[25] were selected to dope into different polymer matrices for the manufacture of novel composites. The hydrophilic nature of the inorganic additives and their weak interaction with the organic matrix result in inhomogeneous dispersions. To minimize such difficulties a series of research projects consisting of chemical modification and physical coating were performed.[12]

Keeping in mind previous results, the present research work was based on the synthesis of ternary composites of PVC/ABS and $CoCl_2$, which was used as a filler attached onto the polymeric chains and disperses through the disordered regions (amorphous regions) forming aggregates between the polymeric chains. Different concentration of $CoCl_2$ ($\leq$10 weight) were used to enhance the thermo mechanical properties of the composite materials. Structural and morphological studies were performed using FT-IR, SEM and XRD. Thermogravimetric analysis (TGA) was used to investigate the thermal stability and degradation behavior of the ternary composites. Furthermore, such composite materials were subjected to antibacterial and antioxidant investigations.

MATERIALS AND METHOD

Materials

Poly(vinyl chloride) (PVC, M_w 48000 D), acrylonitrile–butadiene styrene (ABS) and cobalt chloride of analytical grade were purchased from Sigma Aldrich and employed as such without further purification. Tetrahydrofuran (THF) as the solvent was purchased from Sigma Aldrich and dried before use.

Instrumental techniques

Various techniques were used to confirm the formation of composite material. An FT-IR spectrophotometer (Bruker) was used for the confirmation of functional groups in the composites. The IR spectra were recorded at room temperature in the range 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1}. For the thermogravimetric analyses, a DSC 404C Netzsch and a Perkin Elmer TGA-7 under nitrogen atmosphere were used. Crystallites of the composites were examined by single-crystal XRD from wide-angle (WA) diffractograms obtained using a 3040/60 X'Pert PRO diffractometer. The thermal stabilities, investigated by heating the composites at a rate of 10 °C min^{-1}, were characterized by the initial decomposition temperature (T_0), temperature for 50 % gravimetric loss (T_{50}), maximum degradation temperature (T_{max}) and residual weight at 800 °C.

Preparation of PVC/ABS/$CoCl_2$ composite

The films of PVC/ABS/$CoCl_2$ composite were prepared by the solution casting technique.[26] Typically, different weight ratios of PVC/ABS (80:20), were homogenized in dried THF by constant stirring for about 8 h. At 40 °C, a solution of $CoCl_2$ was dropped into the resulting viscous solution at different weight percents (2.5, 5.0, 7.5 and 1 0 %) and then the resulting mixtures were stirred overnight at ambient temperature. The films of PVC/ ABS/ /$CoCl_2$ were casted onto glass Petri dishes and air dried.

RESULTS AND DISCUSSION

Structural elucidation by FT-IR analysis

The FT-IR absorption spectra of PVC/ABS blends loaded with various concentrations of $CoCl_2$ are shown in Fig. 1. The characteristic absorption band at 2919 cm^{-1} (–CH), 2915 and 2820 cm^{-1} $(–CH_2)_{asym}$ and 1423, 1329, 1256, 968, 615 cm^{-1} were attributed to (–CH) bending of pure PVC.[24] The absorption band at 698 cm^{-1} was attributed the $–CH_2$ rocking vibration and the band at 2235 cm^{-1} was attributed with the CN^- functional group, characteristic of acrylonitrile in ABS and absent in this region for PVC. Mixing of constituents (PVC/ABS) of polymer showed characteristic absorption bands, the small band at 1465 cm^{-1} vanished and sharp bands at 1680, 1140 and 759 cm^{-1} become smaller, while the sharp band at 610 cm^{-1} increased in intensity, which may be due to interaction among the functionality of the polymers back bone with the cation of the inorganic additive cobalt.[27]

X-Ray diffraction analysis

The degree of crystallinity of synthesized ternary composite of PVC/ABS blended with different contents of cobalt chloride (2.5, 5, 7.5 and 10 %) was studied by wide angle X-ray diffraction analysis. The X-ray spectra depicted a semi-crystallinity pattern and indicated two halos functional are present at 2θ 18° and 26° under the two peaks having broad areas while ABS have a shoulder at 13° and broad peak at 23.9° because of the amorphous structure of the copolymer, as shown in Fig. 2. The X-ray spectra showed the merging of ABS shoulder and the broad peak of ABS in two halo peaks of PVC, which indicated the uniform dispersion of ABS in PVC. Furthermore, as the content of $CoCl_2$ increased, intensity of the two halos decreased without any change in the halo position. Such results indicate that different weight ratios of $CoCl_2$ resulted in changes in the polymeric matrices.[28] However, a significant difference between blend doped with $CoCl_2$ and PVC/ABS blend was observed, which may be due to the good dispersion of $CoCl_2$ in the polymeric matrices, except the decrease in area under the peaks. It is clear that there are decreases in the area under the two peaks as the contents of $CoCl_2$ increased (Fig. 2d, e and f) that indicated that $CoCl_2$ may affect the degree of crystallinity and increased the amorphous regions.[29]

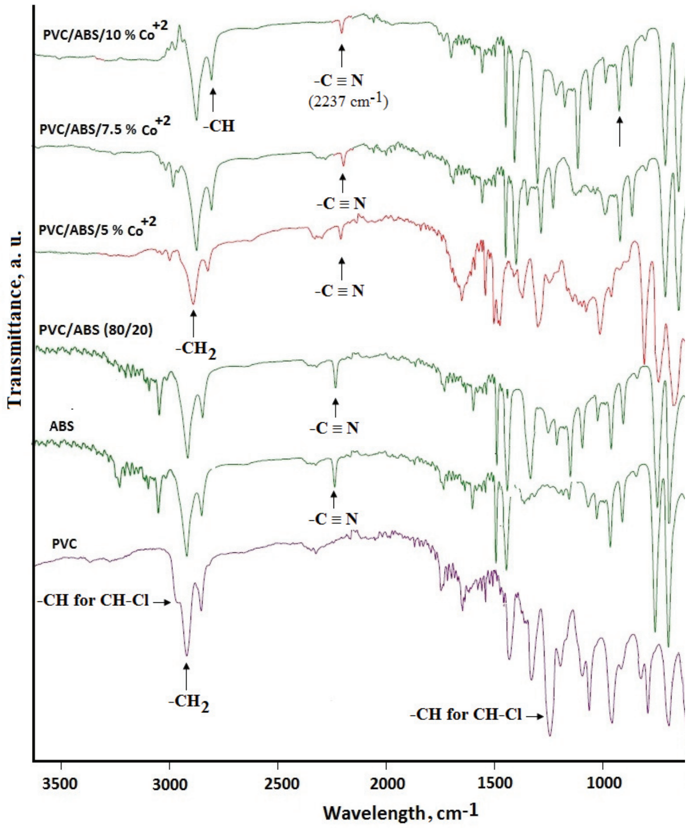

Fig. 1. The FT-IR spectra of PVC/ABS/ Co^{2+} ternary composites.

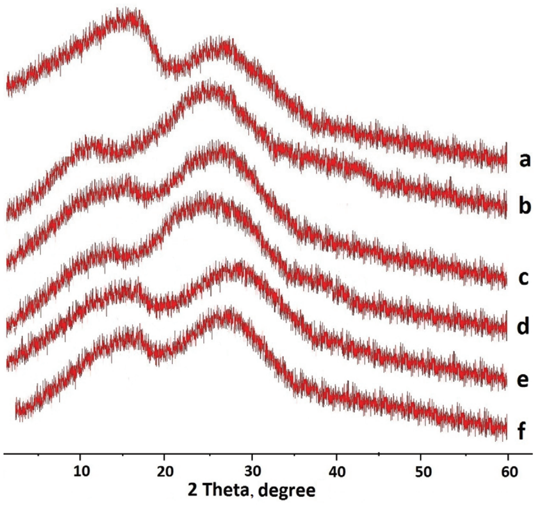

Fig. 2. XRD pattern of PVC/ABS/Co^{2+} composite a: PVC, b: ABS, c: PVC/ABS, d–f: ternary composite with 5, 7.5 and 10 % of Co^{2+}.

Thermogravimetric analysis (TGA)

The thermal stabilities of the PVC/ABS blend as well as the blends with various contents of cobalt chloride were evaluated up to 800 °C at a heating rate of 10 °C min^{-1} in terms of initial decomposition temperature (T_0), the temperature for 50 % mass loss (T_{50}), maximum degradation temperature (T_{max}) and residual weight at 800 °C, as calculated from the respective degradation curves (Fig. 3) and the results are presented in Table I. The thermogram curves showed that ABS decomposed in a single stage that was initiated at about 250 °C with sharp weight loss which was complete at 400 °C; almost 100 % decomposition occurred within an interval of 56 °C. The degradation process of PVC was a two-step process in agreement with literature.[30] The first step of the decomposition occurred between about 260–400 °C due dehydrochlorination resulting in the production of unsaturated HCs corresponding to 63 % of weight loss. Then, a stable temperature zone of around 60 °C was found. The next second stage of degradation was initiated at about 470–540 °C. During second stage of decomposition there was 28 % weight loss resulting in breakage of backbone of the polymer. While for the PVC/ABS blend and the blends doped with different contents of $CoCl_2$, three regions of weight loss were visible. Initially, a total of 8 % of water molecules physically bound with composite. Secondly, a substantial weight loss of about 7–93 %, attributed the main degradation of blend, occurred within the temperature range from 280 up to 485 °C. After 510 °C, a sharp weight loss of the blend occurred due to the breakage of the skeleton of organic matrix by the introduction of $CoCl_2$ to the cross-linked polymers. The data showed that thermal stability of PVC/ABS blend increased as the concentration of $CoCl_2$ increased.[31] Furthermore, the activation energy was calculated using the Coats and Redfern Equation.[32] The values of activation energy decreased on increasing cobalt chloride used as filler in the PVC/ABS blend.

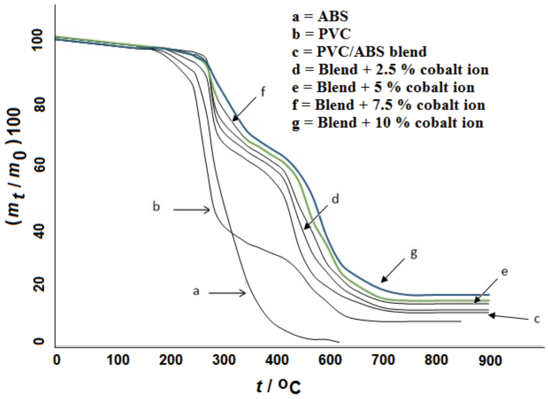

Fig. 3. TGA curves of the prepared ternary (PVC/ABS/$CoCl_2$) composites.

TABLE I. Results of TGA of PVC/ABS (80:20 weight ratio) with different contents of $CoCl_2$

$CoCl_2$ content, wt. %	T_0 / °C	T_{50} / °C	T_{max}./ °C	E_a / J mol^{-1}
0	250	425	610	128.75
1.0	255	432	625	105.31
2.5	260	445	640	95.74
5.0	268	450	652	84.63
7.5	272	460	663	76.25
10.0	280	475	680	65.46

Hygroscopic analysis

The moisture absorption capability of composite materials depends on their chemical structure. The water absorption abilities of PVC/ABS blend as well as salt containing composites was determined by weighing the changes of the dried composites before and after immersion in ionized water for 24 h at 25 °C. The water uptake was determined by applying Eq. (1):

$$W_A = 100(W–W_0/W) \quad (1)$$

where W_0 and W are the weights of dried specimens just after removal from oven and tissue-dried samples after immersion in water, respectively, and found in the range 0.35–0.66 %. Water absorption is due to presence of Co^{2+}. Composites having a lower water uptake value have great importance in the microelectronic industry.[33]

Mechanical properties

The effect of the different contents of cobalt chloride on mechanical properties, such tensile strength, elongation at break and Young's modulus, was investigated and the results are presented in Table II. For all types of the studied synthesized materials, the typical behavior of hard and brittle material was observed. The result showed that the mechanical properties of PVC/ABS/$CoCl_2$ composites increased many folds as compared to the pure PVC/ABS blend.[33]

TABLE II. Mechanical properties of the PVC/ABS (80:20 weight ratio) blend with different contents of $CoCl_2$

$CoCl_2$ content wt.%	Impact strength ±*SD*, J mol^{-1}	Tensile strength ±*SD*, MPa	Young's modulus ±*SD*, GPa	Elongation at break ±*SD*, %
0	25±0.15	43± 0.15	0.95	15±0.25
1.0	28±1.34	41±0.15	0.84±0.06	18±0.13
2.5	30±2.41	38±0.15	0.81±0.02	20±0.24
5.0	35±1.05	35±0.15	0.77±0.04	22±0.43
7.5	39±1.16	31±0.15	0.70±0.07	26±0.38
10.0	44±1.42	30±0.15	0.69±0.03	31±0.22

Scanning electron microscopy

Scanning electron microscopy is an outstanding tool to estimate the smooth distribution and uniformity of the constituents of composite materials. The micrographs of composite investigated under different magnification are shown in Fig. 4. In the absence of fillers, cracks were observed but the application fillers resulted in good distribution and homogeneity. As the contents of cobalt chloride increases, no agglomeration was indicated, which means maximum compatibility of the inorganic fillers with the organic matrix. When the contents of the components of the organic matrix (PVC/ABS) were up to 80:20 weight ratio, the maximum dispersion of phases was observed.[34] As the concentration of cobalt chloride was increased, a large number of large particles appeared equally distributed on the fractured surface.

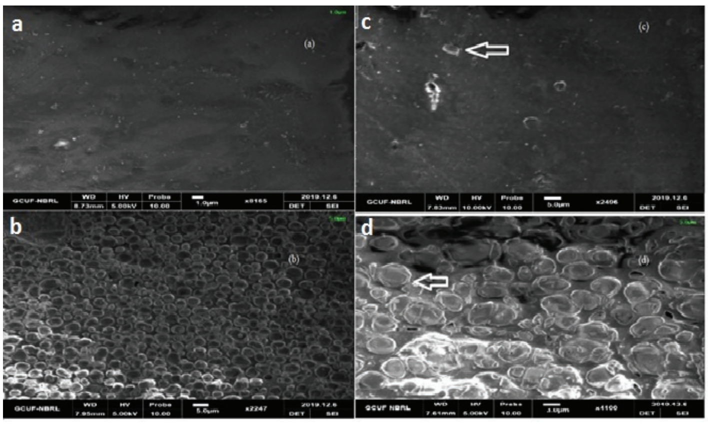

Fig. 4. SEM images of: a) pure PVC; b) PVC/ABS; c) 10 % $CoCl_2$; d) 5 % $CoCl_2$ at low and high magnification of 300 and 2000×.

BIOLOGICAL INVESTIGATIONS

Antibacterial activity

In order to check the structural–activity relationship, synthesized ternary composites (PVC/ABS/$CoCl_2$) were screened against six bacterial strains (three Gram-positive strains, *Staphylococcus aureus*, *Bacillus subtilis* and *Streptococcus pyogenes*, and three Gram-negative strains, *Pseudomonas aeruginosa*, *Escherichia coli* and *Salmonella typhi*) by the disc-diffusion method.[35–37] The strains were cultured at 37 °C in agar–agar nutrient broth for 24 h. The broth culture of the test organisms of approximately 10^4–10^6 colony forming units (CFU mL^{-1}) were added to agar medium into sterile Petri dishes at 45 °C and left to solidify. Five μL solution of PVC/ABS/$CoCl_2$ in DMSO was poured onto sterile paper disks and placed on the nutrient agar plates. Triplicate plates of each organism were prepared and incubated at 37 °C for 24 h and then the zone of inhibition (mm) was measured and compared with standard antibiotic drug (cefixime). In each plate cefixime (1 mg mL^{-1}) served as the reference antibacterial drug. The results are presented in Table III. The PVC/ABS blend and PVC/ABS/$CoCl_2$ composites showed varying degrees of antibacterial activity with a zone of inhibition. The antibacterial activity of $CoCl_2$-doped PVC/ABS blends were compared with the standard drug cefixime and it was found that increased contents of $CoCl_2$ showed remarkable effect from moderate to strong against different bacterial strains. This may be due to the chloro group present in the PVC polymers, which is itself bactericidal.

TABLE III. Antibacterial activity of the PVC/ABS blend with different contents of $CoCl_2$; 5–10 mm zone of inhibition = activity present, 11–25 mm zone of inhibition = moderate activity, 26–40 mm zone of inhibition = strong activity

Test compounds	Zone of inhibition ± *SD*, mm					
	S. aureus	*S. pyogenes*	*B. subtilis*	*E. Coli*	*S. Typhi*	*P. aeruginosa*
PVC/ABS blend	30±1	22±1	28±1	21±1	28±1	24±1
Blend + 2.5 % $CoCl_2$	17±1	15±1	16±1	10±1	14±1	16±1
Blend + 5.0 % $CoCl_2$	21±1	19±1	19±1	15±1	19±1	17±1
Blend + 7.5 % $CoCl_2$	24±1	23±1	22±1	19±1	21±1	18±1
Blend + 10.0 % $CoCl_2$	26±1	25±1	24±1	20±1	24±1	21±1
Cefixime (stand. drug)	33±1.5	31±1	35±1	29±0.5	36±1	31±2

Total antioxidant activity

The free radical scavenging activities of the synthesized composites (PVC/ABS/$CoCl_2$) were evaluated by the standard DPPH (1,1-diphenyl-2-picrylhydrazyl) method.[38] 1,1-Diphenyl-2-picrylhydrazyl (DPPH) is a relatively stable azo radical used to investigate the antioxidant properties of compounds by measurement of the molar absorbivity of DPPH at 517 nm after reaction with a test compound. Stock solutions of the composites (5 mg mL^{-1}) were prepared in DMSO and different concentrations (5, 10, 20, 40, 100, 200 μg mL^{-1}) were obtained by serial dilutions. Each concentration of the composites was mixed with freshly prepared DPPH solution in methanol in glass vials. The vials were sealed and incubated at 37 °C in the dark for 30 min. The deep-violet color of DPPH changed to light-yellow and the absorbance at 517 nm on spectrophotometer (Agilent 8453) was noted. The scavenging activity was calculated.

The antioxidant activity was measured as ascorbic acid equivalent which served as a reference (positive control). The determined results for the antioxidant activity of the PVC/ABS blend and PVC/ABS/$CoCl_2$ composites are presented in Table IV. The results showed that scavenging activity increased as the concentration of the synthesized composites increased. Comparing the IC_{50} values of the blends and their composites doped with $CoCl_2$, it was found that such ternary composites are more active in the DPPH activity test than their parent PVC/ABS blends.

TABLE IV. Antioxidant activity of the PVC/ABS blend with different contents of $CoCl_2$ expressed as the content of DPPH free radical scavenging (±*SD*, %)

Compounds	*c* / μg mL^{-1}						IC_{50} / μg mL^{-1}
	200	100	50	30	15	5	
PVC/ABS blend	69±1	42±1	34±1	20±2	10±1	–	>100
Blend + 2.5 % $CoCl_2$	41±1	33±1	26±1	21±1	15 ±1	10±1	>250
Blend + 5.0 % $CoCl_2$	53±1	44±2	32±2	29±2	18±1	13±1	>150
Blend + 7.5 % $CoCl_2$	57±1	41±2	29±1	22±1	19±1	15±1	>150
Blend + 10.0 % $CoCl_2$	61±2	46±1	39±1	31±1	28±2	15±1	>150
Ascorbic acid	87±1	84±1	80±1	70±1	56±1	35±1	8.75±1

CONCLUSIONS

PVC/ABS blend and ternary composites decorated with various concentration of $CoCl_2$ were synthesized and characterized by means of FT-IR, XRD, TGA, mechanical and SEM techniques. The FT-IR analysis showed that the blending of PVC and ABS revealed some characteristic absorption bands for both PVC and ABS due to interaction between them. Shifting of absorption spectra show the interaction between the constituents of polymer and inorganic additives ($CoCl_2$). The crystalline nature of the synthesized composite was observed by XRD and the area under the peaks was measured. It may be inferred from the result that as the concentration of $CoCl_2$ increases, the crystallinity is affected due to more defects in the polymer matrices, which reduces the area under the peaks. The thermograms of all the composites (PVC/ABS/$CoCl_2$) show a similar mode of three step degradation. It could be concluded that enhancing the doping concentration of $CoCl_2$ in the blend (PVC/ABS) results in higher order, reduced thermal motion and enhancement of the thermal stability due to the predomination of random scission initiated degradation of the macromolecule chains in the polymeric matrices and decreased activation energy of the process. The mechanical properties of PVC/ABS/$CoCl_2$ composites are greatly influenced by the composition. The incorporation of cobalt chloride in PVC/ABS enhances the thermal stability of the composite due to interfacial interaction and coordination between cobalt ions (Co^{2+}) and nitrile groups (−CN) of ABS in solid state, which result in enhancement in mechanical properties. SEM analysis proved the smooth distribution and uniformity of the constituents of composite materials. Concerning bioactivity, the PVC/ABS blend as well as blends with different concentrations of $CoCl_2$ showed activity against bacterial strains and free radical scavenging activity. Thus, based on their remarkable morphology, thermomechanical stability and promising bioactivity, the synthesized composites could be applied for high performance polymeric materials in the fields of biomedics and electronics.

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И З В О Д

ИСПИТИВАЊЕ ТЕРМИЧКИХ, МЕХАНИЧКИХ И БИОЛОШКИХ СВОЈСТАВА МЕШАВИНЕ PVC/ABS СА ДОДАТКОМ КОБАЛТ-ХЛОРИДА ЗА ПРИМЕНУ У БИОМЕДИЦИНИ И ЕЛЕКТРОНИЦИ

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Нови PVC/ABS и $CoCl_2$ композит са различитим концентрацијама кобалт-хлорида (≤10 мас. %) синтетисани су техникама изливања из раствора и истражени су спектрохемијском, морфолошком и термичком карактеризацијом. FT-IR, XRD и SEM анализа доказале су глатку расподелу и уједначеност састојака композитних материјала. Термичко понашање показало је да додавање $CoCl_2$ мешавини PVC/ABS побољшава термичку стабилност и побољшава механичка својства композита услед умрежавања мешавине PVC/ABS и $CoCl_2$. Тако се на основу изузетне морфологије, термомеханичке стабилности и обећавајуће биоактивности, синтетизовани композити могу применити за полимерне материјале високих перформанси у области биомедицине и електронике.

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