

Synthesis, Modification and Optical Characterization of Co-Cr Layered Double Hydroxide

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Abstract: Cobalt and chromium based layered double hydroxides (LDHs) have been successfully synthesized by the co-precipitation method at a constant pH of 10. The intercalation of stearic acid (C₁₈H₃₆O₂) into CoCr-LDH and preparation of their polymer nanocomposites using two different methods were studied in the paper. The obtained samples were characterized before and after modification by X-ray diffractometry (XRD) and Ultraviolet visible (UV-Vis) spectroscopy. It has been shown that different reaction temperature profoundly affects the band-gaps of inorganic and composite structures. Three optical band gap values (E_{g1}, E_{g2} and E_{g3}) for the samples obtained before and after modification. Two optical band gap values were estimated in polymer/LDH nanocomposites. The high-value band gaps for CoCr-LDH_(100°C)-NBR and CoCr-LDH_(100°C)-SA-NBR were determined to be 5.9 eV and 5.7 eV, respectively. The low-value band gaps for CoCr-LDH_(100°C)-NBR and CoCr-LDH_(100°C)-SA-NBR were determined to be 4.1 eV and 3.25 eV, respectively.

Keywords: CoCr-LDHs; polymer nanocomposites; stearic acid; nitrile butadiene rubber (NBR); optical properties.

1. Introduction

NBR is a family of unsaturated copolymers used in the automotive, aeronautical, nuclear industry, to create moulded goods, shoes, sticking materials, sponges, polyfoams, and composite materials. NBR has good resistance to oils, aliphatic hydrocarbons, benzene, petrol, ordinary diluted acids and alkalines although has low resistance to ozone, ketones, esters and aldehydes.

Three main modified NBR like hydrogenated- [1], carboxylated- [2] and chlorophosphorylated- [3] NBR (HNBR and XNBR, FNBR respectively) are very useful for industrial application commonly used to manufacture O-rings for automotive air-conditioning systems, rubber products and sorbents. Although there is still a need a convenient, cost-effective and environmentally friendly preparation methods. Being unstable at a high temperature and flammability make polymers not ideal materials for most high-temperature applications. Layered materials, especially, layered double hydroxides (LDH), layered triple hydroxides (LTH) and ternary layered double hydroxides are very influential and potential nanofillers for polymers and elastomers. LDH are a class of ionic solids represented by the general formula: $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^+[(A^m)_{x/m} \cdot nH_2O]$, where M²⁺ and M³⁺ are metal cations, and Aⁿ⁻ is an interlayer exchangeable anion.

LDHs are promising materials for the application in various fields such as catalysts [4], catalyst precursors [5,6], anion exchangers [7,8], CO₂ absorbents [9], bioactive nanocomposites [10], catalytic active compounds in the oxidation reaction [11, 12], pseudocapacitors [13], biomaterials, electrical and mechanical materials, etc. [14].

Synthesizing of P/LDH nanocomposites (since nanopolymer has emerged) it is possible to detect some new quality of the polymer and affect its important properties. In general, LDHs act as not only essential and effective ionic crosslinking agent, but also they are environmentally friendly curing agent and fillers. There are different approaches applying some methods (in situ and external polymerization, melt mixing, solution blending, deposited onto the surface of the polymer latex particles etc.) to increase polymers mechanical and thermal properties, fire resistance and decrease fragility. De-Yi Wang et al. [15] have successfully prepared PP/CoAl-LDH nanocomposite based upon organomodified CoAl-LDH via one step synthesis, finding the fire retardancy have been improved significantly with the increasing the CoAl-LDH concentration. The results

obtained from Friedman and Flynn-Wall-Ozawa methods in authors study suggest that the activation energies of thermal degradation of PP/CoAl-LDH nanocomposite are higher than that of neat PP, which could be the internal reason for improvement of the flame retardancy. Normally, PP/CoAl-LDH nanocomposite with high LDH concentration has higher activation energy of thermal degradation, while this activation energy also was influenced by the modified surfactant in the LDH.

Nitrile-butadiene rubber (NBR) based layered double hydroxide (LDHs) composites have been prepared through melt-compounding method using sodium lignosulfonate modified LDH (SLS-LDH) as a filler obtained by in-situ synthesis method [16]. Differential scanning calorimetry analysis data indicates the enhancement of interactions between NBR chains and LDH particles in the presence of SLS. These results indicated that this SLS will be a promising dispersant for LDH/ rubber composites.

Varun Thakur et al. have investigated the effect of LDH particles on the formation of ionic clusters between XNBR and ZnO and observed the properties of the resulting composites [17]. The dispersion of the filler particles have also been studied with the aid of XRD and STEM studies, which indicated that the dispersion was far better in modified LDH compared to unmodified LDH, and the filler particles exhibit mixed intercalated-exfoliated morphology with some aggregation tendency.

In this paper, we will discuss about the synthesis of CoCr-LDH-NO₃ by co-precipitation method, their anion exchange modification to form CoCr-LDH-SA in the presence of stearic acid and fabrication of NBR/LDH nanocomposites by the melt mixing method. The mechanism of the modification process and the effect of LDH / Polymer ratio on synthesis of nanocomposites were investigated by the studying of optical and structural properties of the samples. The effects of technological parameters (concentration of reagents, reaction temperature, aging time and annealing temperature of obtained powder samples) on the properties of the samples were also analyzed in detail.

2. Experimental

2.1. Materials and instrumentation

The starting reagents of cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), chromium (III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O), caustic soda (NaOH) and urea (CO(NH₂)₂) were of analytical grade and used for the preparation of LDHs by the co-precipitation method. Distilled water and absolute alcohol (C₂H₅OH) were used for the experiments as solvents and sample washing solution. Analytical grade stearic acid (C₁₇H₃₅COOH) was used for the modification of LDH-NO₃ compounds. Nitrile butadiene rubber (NBR-26) was purchased from Voronezh Synthetic Rubber Manufactory (Russia) [18] used in this study for the preparation of nanocomposites.

The structural characterization of the samples was carried out by the Powder X-ray diffractometer using Bruker D2 Phaser in CuK α radiation ($\lambda = 0.1541$ nm) in the angular range $2\theta = 5-80^\circ$ and 5° min^{-1} of scan rate.

The optical measurements and band gap calculation were carried out on a (Specord 250) UV-vis spectrophotometer in the wavelength range 190–1100 nm.

2.2 Preparation of CoCr-LDH-NO₃ at different condition

40 ml 0.375M of (Co(NO₃)₂·6H₂O) and 40 ml 0.125M of (Cr(NO₃)₃·9H₂O) water solution were mixed and added into 500-ml chemistry beaker. 0.625 M of NaOH water solution was drop wise added to the beaker containing Co²⁺ and Cr³⁺ ions under vigorous stirring. The pH of the slurry was kept at 10. Thus, the sample was prepared in 3 parts by this method. One part of obtained slurry was boiled for 18 hours under reflux at 100°C and called as CoCr-LDH_(100°C), second part of slurry was aged into the thermostat at 90°C for 36 hours and called as CoCr-LDH_(90°C), third part of slurry solution was allowed to age under room temperature for 36 hours and called as CoCr-LDH_(25°C). All LDH slurries obtained at different temperature were washed with distilled water then with absolute alcohol, filtered, air-dried and ground into powder.

2.3 Modification of CoCr-LDH-NO₃ to CoCr-LDH-SA

The obtained CoCr-LDHs were used to prepare CoCr-LDH-SA using stearic acid by the anion exchange process. 0.1 g of stearic acid was solved in 30 mL of ethanol. Three part of 10 mL of stearic acid - ethanol solutions were separately added to 0.5 g of CoCr-LDH_(25°C), CoCr-LDH_(90°C) and CoCr-LDH_(100°C) powders, mixed and aged for 24 hours into the thermostat at 75°C. The final products were washed with ethanol to remove the residual surfactant, filtered, dried at room temperature and ground into powder. The samples obtained after the modification with stearic acid were called as: CoCr-LDH_(25°C)-SA, CoCr-LDH_(90°C)-SA and CoCr-LDH_(100°C)-SA powders.

2.4 Synthesis of LDH–SA–NBR nanocomposites by two different methods.

LDH–SA–NBR nanocomposites were prepared by two different methods: solution blending and melt mixing.

Synthesis of nanocomposites by melt mixing method was carried out by adding 0.02 g of CoCr-LDH_(100°C)-SA to 0.2 g of NBR-26 and mixed at 80°C for 3 hours. The obtained nanocomposite was called CoCr-LDH_(100°C)-SA-NBR.

Synthesis of nanocomposites by solution blending method was carried by adding 0.01 g of CoCr LDH_(100°C) (or CoCr LDH_(90°C) and CoCr LDH_(25°C)) to 10 mL 1% solution of NBR-Chloroform (CHCl₃) which was prepared as before, mixed at room temperature for 24 hours and air dried. The obtained nanocomposite was called CoCr-LDH_(25°C)-SA-NBR, CoCr-LDH_(90°C)-SA-NBR and CoCr-LDH_(100°C)-SA-NBR.

3. Results and discussion

3.1 X-ray diffraction (XRD) study

The XRD patterns of CoCr-LDH_(25°C), CoCr-LDH_(90°C) and CoCr-LDH_(100°C) have shown in **Fig.1**. Five characteristic reflections at (003), (006), (009), (012) and (110) planes observed at the diffraction angles of $2\theta = 11.86^\circ, 23.1^\circ, 34.13^\circ, 38.76^\circ$ and 60.34° , corresponding to LDH materials (JCPDS file 38–0487) [8]. The first reflection (003) was used to calculate “c” lattice parameter and the fifth reflection (110) was used to calculate “a” lattice parameter and the basal spacing (d) of the layers equals to $c/3$. [19]. The basal spacing parameter of the layers (d) was calculated from the equation known as Bragg's Law (1):

$$d_{hkl} = n\lambda / 2\sin\theta \quad (1)$$

Where, n is an integer; λ is wavelength of the incident light; d_{hkl} is lattice spacing; θ is angle of incidence.

The basal spacings of CoCr-LDH_(25°C), CoCr-LDH_(90°C), CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were calculated from the (003) reflection which observed at the diffraction angles of $2\theta = 11.8^\circ, 11.85^\circ, 12^\circ$ and 11.9° equal $7.490\text{\AA}, 7.459\text{\AA}, 7.366\text{\AA}$ and 7.428\AA , respectively. $d_{(006)}$ values of CoCr-LDH_(25°C), CoCr-LDH_(90°C), CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were calculated from the (006) reflection which observed at the diffraction angles of $2\theta = 23.45, 23.25, 23.416$ and 23.3 equal $3.789\text{\AA}, 3.821\text{\AA}, 3.794\text{\AA}$ and 3.813\AA , respectively. $d_{(110)}$ values of CoCr-LDH_(25°C), CoCr-LDH_(90°C), CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were calculated from the (110) reflection which observed at the diffraction angles of $2\theta = 59.5^\circ, 60.32^\circ, 59.82^\circ$ and 60.34° equal $1.551\text{\AA}, 1.532\text{\AA}, 1.544\text{\AA}$ and 1.532\AA , respectively.

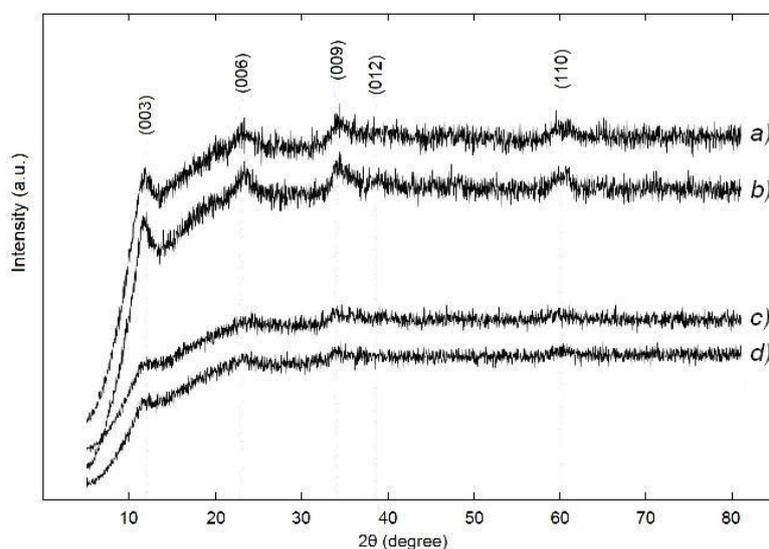


Fig.1. XRD patterns of a) CoCr-LDH_(25°C), b) CoCr-LDH_(90°C) c) CoCr-LDH_(100°C) and d) CoCr-LDH_(100°C)-SA compounds.

The average crystallite sizes of crystals were calculated from the average values of (003) and (006) diffraction peaks using the Scherrer equation (2) [20]:

$$D = \alpha\lambda / \beta\cos\theta \quad (2)$$

where, D – is the diameter of particles, α - is constant (0.9), λ -is the X-ray wavelength equals to 1.5418\AA , and β -is the half-width of diffraction peaks. The average crystallite sizes of CoCr-LDH_(25°C), CoCr-LDH_(90°C),

CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were estimated as 3.79nm, 4.17nm, 2.93nm and 3.34nm, respectively.

3.2 Optical properties by UV-vis and FTIR spectroscopy

Optical properties of CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds have studied at room temperature (25°C). The UV-vis absorbance and transmission spectra for unmodified nanoparticles (CoCr-LDH_(100°C)) and modified nanocomposites (CoCr-LDH_(100°C)-SA) are shown in **Fig.2**. The band gap values of the modified and unmodified samples were estimated by the extrapolation to the “x” axis of the absorbance spectra and also calculated the mathematical treatment of the data obtained from the optical absorbance versus wavelength data with the following relationship for near-edge absorption: [21].

$$A=[k(h\nu-E_g)]^{n/2} / h\nu \quad (3)$$

Where, ν is the frequency, h is the Planck's constant; k equals a constant while ν carries the value of either 1 or 4. The band gap, E_g , could be obtained from a straight line plot of $(\alpha h\nu)^{2/n}$ as a function of $h\nu$ [22]. There are three optical band gap values (E_{g1} , E_{g2} and E_{g3}) for the samples obtained before and after modification (**Fig.3**). The band gap observed at high energy level (E_{g1}), attributed to the presence of NO_3^- groups in the LDH interlayer galleries [20][23-25]. The optical band gap E_{g1} for CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were determined 3.96eV and 3.78eV from absorbance spectra which extrapolated to 315nm and 330nm, respectively (**Fig. 2A**). The optical band gap E_{g1} for CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were also determined 4.1eV and 3.79eV from the extrapolation of the straight lines section of $(\alpha h\nu)^2$ vs. $h\nu$ curve (**Fig. 3**).

Two optical band gap values were estimated in polymer/LDH nanocomposites. The high-value band gaps for CoCr-LDH_(100°C)-NBR and CoCr-LDH_(100°C)-SA-NBR were determined to be 5.9 eV and 5.7 eV, respectively. The low-value band gaps for CoCr-LDH_(100°C)-NBR and CoCr-LDH_(100°C)-SA-NBR were determined to be 4.1 eV and 3.25 eV, respectively.

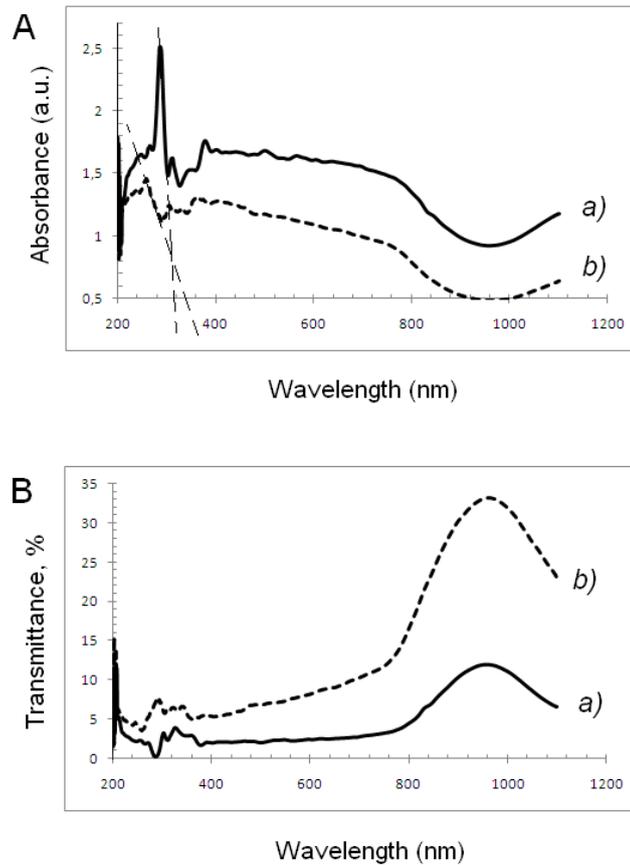


Fig.2. Optical absorbance (A) and transmittance (B) of CoCr-LDH_(100°C) (a) and CoCr-LDH_(100°C)-SA (b)

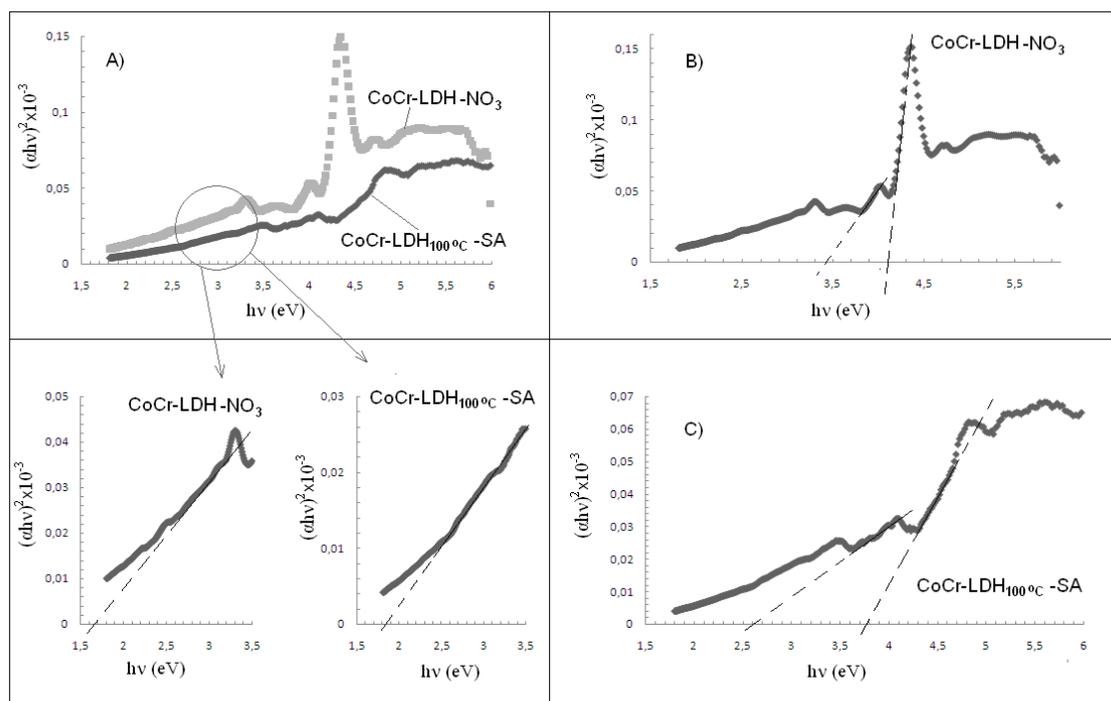


Fig.3. Optical band gap for CoCr-LDH_(100°C) (a) and CoCr-LDH_(100°C)-SA (b) compounds determined from the extrapolation of the straight lines section of $(\alpha hv)^2$ vs. $h\nu$ curve.

4. Conclusions

In this paper, we discussed about the synthesis of CoCr-LDH-NO₃ by co-precipitation method, their anion exchange modification to form CoCr-LDH-SA in the presence of stearic acid and fabrication of NBR/LDH nanocomposites by the melt mixing method. The structural and cell parameters of the compounds obtained at different temperature and modified by stearic acid were analyzed in detail. The basal spacings of CoCr-LDH_(25°C), CoCr-LDH_(90°C), CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were calculated from the (003) reflection which observed at the diffraction angles of $2\theta=11.8, 11.85, 12$ and 11.9 , respectively. The average crystallite sizes of CoCr-LDH_(25°C), CoCr-LDH_(90°C), CoCr-LDH_(100°C) and CoCr-LDH_(100°C)-SA compounds were estimated as $3.79\text{nm}, 4.17\text{nm}, 2.93\text{nm}$ and 3.34nm , respectively.

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