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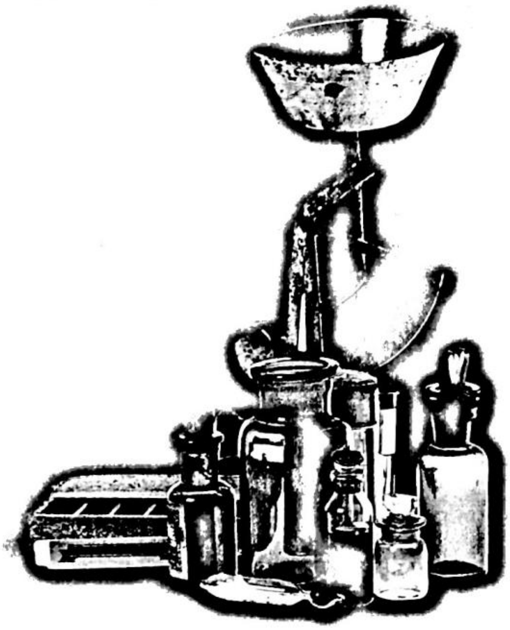

DEPARTMENT OF CHEMICAL ENGINEERING

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STRUCTURAL, MORPHOLOGICAL AND SWELLING PROPERTIES OF NOVEL POLY(NAAA-CO-HEA)/ MG-AL-CL LAYERED DOUBLE HYDROXIDE NANOCOMPOSITE HYDROGELS

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Abstract

the objective of this study is to investigate the effects of the Mg-Al-Cl layered double hydroxide (Mg–Al–Cl LDH) on the swelling, morphological and structural properties of the poly(sodium acrylate-co-2-hydroxyethyl acrylate) [poly(NaAA-co-HEA)] hydrogel. Acrylate monomer based novel nanocomposite hydrogels containing Mg–Al–Cl LDH [poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs] were synthesized by using the equal mole amounts of NaAA and HEA as monomers, potassium persulfate–bisulfite as initiator, N,N-methylenebisacrylamide (NMBA) as cross-linker and different amounts (1, 3, 5 % of total monomer weight) of Mg-Al-Cl LDH. The formation, morphological and structural properties of poly(NaAA-co-HEA)/Mg-Al-Cl LDHs were investigated by Fourier Transform Infrared (FTIR) Spectroscopy, X –ray Diffraction (XRD) Pattern and Scanning Electron Microscopy (SEM) analyses. Swelling behaviors of poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs were also examined in distilled water. The results show that poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs have been formed. As the content of Mg-Al-Cl LDHs increased, equilibrium swelling degree of the nanocomposite hydrogels in distilled water decreased due to the Mg-Al-Cl LDHs acting as crosslinking agent. It is then concluded that the poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs synthesized in this study may be used as an alternative water absorbent.

Keywords: Mg-Al-Cl Layered double hydroxides, nanocomposite hydrogels, 2-hydroxyethyl acrylate, sodium acrylate.

Introduction

The layered double hydroxides (LDHs), also called anionic clays, are composed of positively charged layers with interlayer exchangeable anions. LDHs have physical and chemical properties that are surprisingly similar to the properties of clay mineral. Its general composition can be represented as $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{x+} [A^{q-}_{x/q} .nH_2O]$, where M^{II} and M^{III} are divalent and trivalent cations, respectively, and A^{q-} is an exchangeable anion (Lee et al., 2005). The layer metal cations can be chosen among a wide selection, such as Mg^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, etc., as with the interlayer anion (Figure1), that can be inorganic or organic in nature (Ardanuy et al., 2010). In recent years, LDHs have been used as nanoparticles for preparing polymer-based nanocomposites. The use of LDHs as nanoparticles is advantageous due to their versatility in chemical composition and allow multiple interactions with the polymer (Özgümüş et al., 2013; Kovanda et al., 2010; Hoyo et al., 2007).

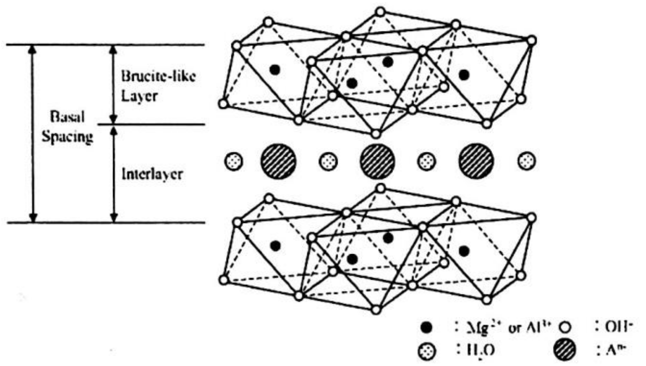

Figure 1. Schematic representation of Mg-Al LDH (Ardanuy et al., 2010).

In this study, the effects of the Mg-Al-Cl layered double hydroxide (Mg–Al–Cl LDH) on the swelling, morphological and structural properties of the poly(NaAA-co-HEA) hydrogel were investigated. In our previous study, Mg-Al-Cl LDH was prepared by the coprecipitation method and characterized using FTIR, XRD and SEM techniques (Özgümüş et al., 2013). Acrylate monomer based novel nanocomposite hydrogels containing Mg–Al–Cl LDH [poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs] were synthesized by using NaAA and HEA as monomers, potassium persulfate–bisulfite as initiator, NMBA as cross-linker and different amounts (1, 3, 5 % of total monomer weight) of Mg-Al-Cl LDH. The formation, morphological and structural properties of poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs were investigated by FTIR, XRD and SEM analyses. Swelling behaviors of poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs were also examined in distilled water.

Experimental

Preparation of Nanocomposite Hydrogels

Novel poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs (NH-LDHs) containing Mg–Al–Cl LDH, synthesized in our previous study (Özgümüş et al., 2013), were prepared by free radical chain polymerization of NaAA and HEA in Mg–Al–Cl LDH suspension. Firstly, Mg–Al–Cl LDH was suspended in water thoroughly under ultrasonic irradiation. NaAA and HEA monomers and NMBA (0.5% of total monomer moles) were dissolved in suspended Mg–Al–Cl LDH and taken in cylindrical glass tubes. After sealing the tubes with rubber caps, the solution was purged with nitrogen gas for 20 min eliminate dissolved oxygen in the system. The polymerization was performed at 80°C by introducing of initiator (1 X 10^{-4} mole) (1% of total monomer moles). After 3h reaction time at 80°C, the hydrogels were separated, cut into discs in 5-mm length and washed with water for 1 week. Then, nanocomposite hydrogels were dried under vacuum at 40°C. The hydrogel poly(NaAA-co-HEA) (H) was also prepared without using Mg-Al-Cl LDH to compare the results. Details about the conditions applied to synthesize the nanocomposite hydrogels are listed in Table 1.

Symbols of the hydrogels	Monomers NaAA/HEA (mole)	NMBA (mole %)	Mg–Al–Cl LDH (wt %)
H	0.005/0.005	$5x10^{-5}$	0
NH-1LDH	0.005/0.005	$5x10^{-5}$	1
NH-3LDH	0.005/0.005	$5x10^{-5}$	3
NH-5LDH	0.005/0.005	$5x10^{-5}$	5

Table1. The feed compositions of the nanocomposite hydrogels.

Swelling Studies of the Nanocomposite Hydrogels

The swelling characteristics of the nanocomposite hydrogels were measured in distilled water through, tea-bag method, gravimetric analysis (Dalaran et al., 2009). The amount of the water absorbed by the samples was given as the equilibrium swelling degree (Q_{eq}) and was calculated by eq. (1).

$$Q_e = (W_{wet} - W_{dry}) / W_{dry} \quad (1)$$

where W_{dry} is the weight of the dried sample and W_{wet} is the weight of the swollen sample.

Instruments

FTIR spectra of the samples were taken as KBr disks (sample/ KBr=1/250, w/w) using Digilab Excalibur-FTS 3000MX model FTIR Spectrophotometer operating in the range of 4000–650 cm^{-1}.

XRD patterns were obtained using a Rigaku D/Max-2200/PC X-Ray Powder Diffractometer (Japan) using Cu*Kα* radiation (λ=1.5406 nm) at 30 mA, 40 kV, a scanning speed of 1°/min from 2θ=5° to 2θ=30°.

The scanning electron microscopy (SEM) images of the samples were obtained using a Quanta FEG 450 Scanning Electron Microscopy (USA) scanning electron microscopy.

Results and Discussion

XRD Analysis

Figure 2 illustrates the typical diffraction peak from XRD powder patterns of Mg-Al-Cl LDH and the corresponding nanocomposite hydrogel incorporated with 3 wt. % Mg-Al-Cl LDH (NH-3LDH).

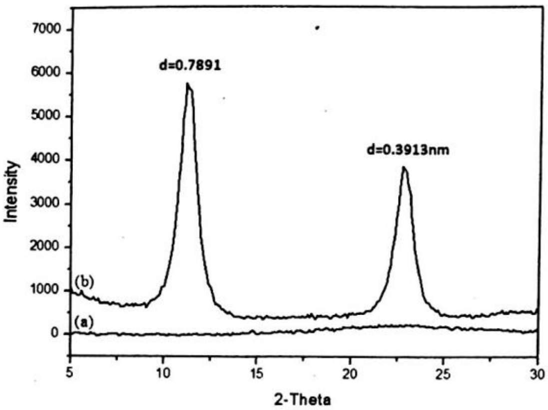

Figure 2. XRD patterns of (a) NH-3LDH (b) Mg-Al-Cl LDH.

There are two intense diffraction peaks for Mg-Al-Cl LDH, the main strong peak approximately at 2θ= 11.3° corresponding to d= 0.7891 nm and the other sharp peak approximately at 2θ= 22.9° corresponding to d= 0.3913 nm, while no diffraction peak appears for nanocomposite hydrogel sample NH-3LDH (3 wt% Mg-Al-Cl LDH), it was attributed that Mg-Al-Cl LDH sheets are exfoliated and uniformly dispersed in poly(NaAA-co-HEA) hydrogel network.

FT-IR Analysis

FTIR analysis reveals that the nature of change in hydrogel matrix and Mg-Al-Cl LDH during the formation of the nanocomposite. The FTIR spectra of Mg-Al-Cl LDH, H and NH-3LDH are shown in Figure 3a. FTIR spectrum of the Mg-Al-Cl LDH showed characteristic absorption bands; the intense and broad band at about 3200-3700 cm^{-1} region (max. at 3510 cm^{-1}) was related to the asymmetric and symmetric stretching mode of hydrogen-bonded OH groups in the hydroxyl layers; the small shoulder at approximately 3050 cm^{-1} was assigned to hydroxyl interactions with carbonate ions impurities in the interlayer, and has been attributed to the bridging mode H_2O-CO_3^{-2}. The weak absorption band corresponding to the H_2O deformation bending vibration was also seen at 1653 cm^{-1} as a function of the interlamellar anions such as CO_3^{-2}. The sharp absorption band at 1372 cm^{-1}, the small shoulder and weak band at 863 and 651 cm^{-1} attributed to unidentate carbonate symmetric stretching vibrations (O-C-O bond) for the LDH with CO_3^{-2} anions incorporated into the interlayer. An additional broad shoulder at 1500-1550 cm^{-1} regions attributed to the formation of bicarbonate ions due to the proton transfer from the hydroxide sheets to the carbonate ion. A series of bands in spectra which were recorded at 1000-400 cm^{-1} region are complicated due to the presence of lattice translational modes (Özgümüş et al., 2013).

In the spectra of the H Figure 3c the characteristic band at 3449 cm^{-1}, 2957 and 1579 cm^{-1} was attributed to the the asymmetric and symmetric stretching mode of OH groups in the HEA units on the copolymer structure, stretching vibration of CH_2 groups and C=O asymmetric stretching in the carboxylate anion,respectively. This was confirmed by another peak at 1405-1400 cm^{-1} region (max. 1415 cm^{-1}), which is related to the symmetric stretching mode of the carboxylate groups and OH groups of the HEA monomer units. The main contribution to the absorption band at 1732 cm^{-1} is from the C=O bonds stretching vibrations of the ester groups of HEA monomer units. Other bands at

1167, 1078 and 888 cm^{-1} corresponding to the C-O bonds vibrations of the monomers units, and OH groups vibrations of the monomer units were observed, respectively (Sadeghi et al., 2013).

The overall changes in the structure of Mg–Al–Cl LDH and H, depending on the formation of the NH-3LDH with exfoliated structure, were also investigated by FTIR analysis. A careful comparison of all the FTIR spectra indicates definite differences mainly in the absorption bands, appearing at approximately at 1750–1500 cm^{-1}, 1500–1300 $cm^{-1}$and 1000–600 cm^{-1}. As observed from the NH-3LDH spectra, the absorption bands observed at 3050, 1653, 1372 and 1000–600 cm^{-1} (max at 863, 750 and 651 cm^{-1}) in the FTIR spectra of the Mg–Al–Cl LDH disappeared. All these changes and the disappearances of the some bands are associated with the formation of the NH-3LDH with exfoliated structure. Namely, the monomers NaAA and HEA, the crosslinker NMBA and Mg–Al–Cl LDH physically or chemically interacted to form a network structure during the copolymerization reaction. Therefore, the layers of the Mg–Al–Cl LDH were exfoliated. These results are consistent with those of the powder XRD spectra for Mg–Al–Cl LDH, H and NH-3LDH.

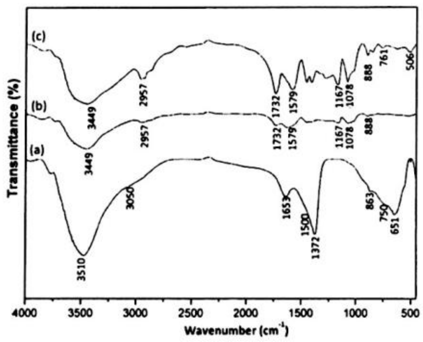

Figure 3. FTIR spectra of (a) Mg-Al-Cl LDH (b) NH-3LDH nanocomposite hydrogel and (c) H hydrogel.

SEM Analysis

In order to examine the surface morphology of the Mg-Al-Cl LDH, H and NH-3LDH, the SEM micrograph were taken at different magnification. Figure 4-6 represent the SEM micrographs for these products. Micrograph, is shown in Figure 4, revealed that Mg-Al-Cl LDH exhibits bead-like fine particle aggregates consisting of nanometer size (Özgümüş et al., 2013). The SEM images of H hydrogel (Figure

5) also demonstrate that H hydrogel has porous surface. NH-3LDH nanocomposite hydrogel showed some interesting morphological features when compared to H hydrogel (Figure 6). In addition, it can be seen from SEM images that the NH-3LDH nanocomposite hydrogel has a fiber-like structure, non-porous surface morphology and also exhibited large, open, channel-like structure, its shape is significantly different than that of the Mg–Al–Cl LDH and H. These results are also increasing evidence the occurrence of fully exfoliation between the Mg–Al–Cl LDH layers and H during the formation of the NH-3LDH nanocomposite hydrogel, as demonstrated our earlier study (Özgümüş et al., 2013).

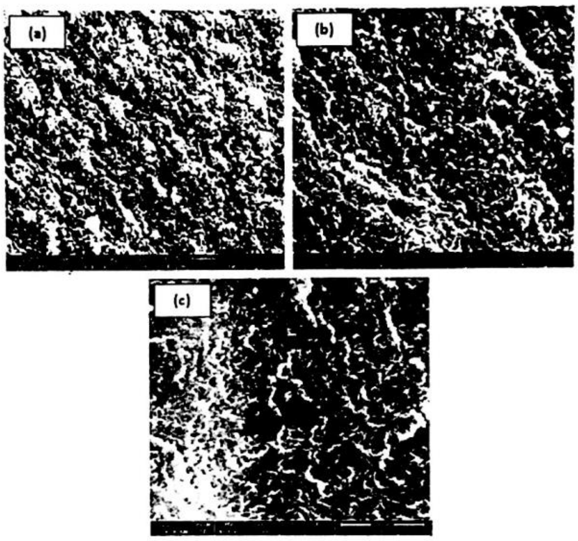

Figure 4. SEM images of Mg-Al-Cl LDH at different magnification: (a)40000x, (b) 80000× and (c) 150000x.

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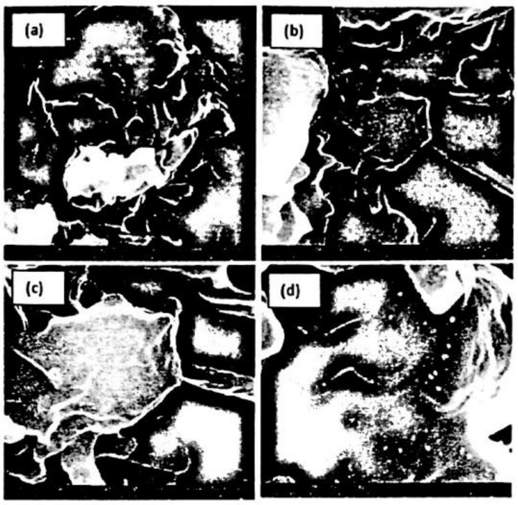

Figure 5. SEM images of H hydrogel at different magnification: (a)40000x, (b) 80000×, (c) 150000x and (d) 300000×.

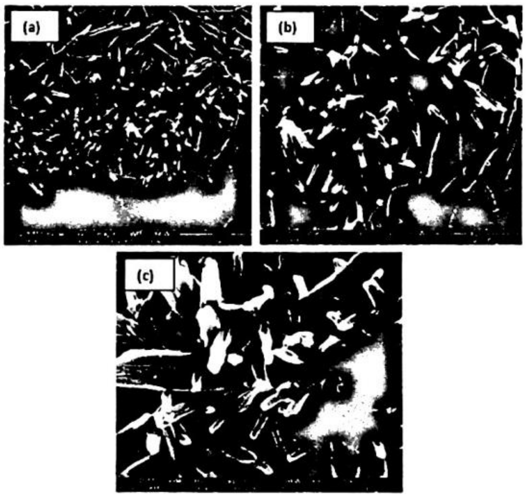

Figure 6. SEM images of NH-3LDH at different magnification: (a)40000x, (b) 80000× and (c) 150000x.

Effect of Mg–Al–Cl LDH Content on Swelling Capacity

The data in Figure 7 clearly showed also that, swelling capacity of the nanocomposite hydrogels decreased 30%, 48% and 82% with increasing amount of Mg–Al–Cl LDH from 1 to 5 wt%, respectively. Mg–Al–Cl LDH, which are called hydrotalcite-like compound, it is incorporated into the polymer matrix, may acts as additional co-crosslinking points similar to clay powder. The reason for the decrease in the Q_e value of the NH-LDHs is most likely due to the additional co-crosslinking points effect of the Mg–Al–Cl LDH (Özgümüş et al., 2013).

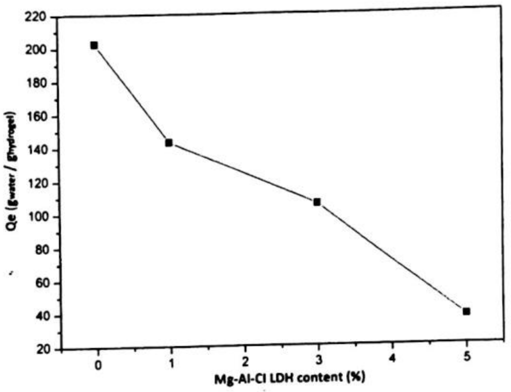

Figure 7. The effect of the content of Mg–Al–Cl LDH on the water absorbency of nanocomposite hydrogels

Conclusion

A series of nanocomposite hydrogels containing Mg–Al–Cl LDH [poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs] were synthesized by free radical chain polymerization of NaAA and HEA in Mg–Al–Cl LDH suspension. FTIR analysis showed that the nanocomposite hydrogels were successfully obtained. Furthermore, XRD analysis of the samples showed that Mg–Al–Cl LDH layers were exfoliated in the hydrogel structure. According to the SEM images, NH-3LDH has has a fiber-like structure, non-porous surface morphology and its shape is significantly different from that of the Mg–Al–Cl LDH and H. Swelling studies showed that swelling capasity of the nanocomposite hydrogels decreased 30%, 48% and 82% with increasing amount of Mg–Al–Cl LDH from 1 to 5 wt%, respectively. It is then concluded that the poly(NaAA-co-HEA)/ Mg-Al-Cl LDHs synthesized in this study may be used as an alternative water absorbent.

Acknowledgments The present work was supported by the Research Fund of Istanbul University; Project Numbers 6940 and 15841.

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