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Montmorillonit / HEC ve Sepiyolit / HEC Nanokompozitlerinin Termal Özelliklerinin Karşılaştırılması

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Anahtar kelimeler
Montmorillonit;
Sepiyolit; HEC;
Nanokompozit;
Termal özellikler.

Özet

Bu çalışmada hidroksietil seliloz (HEC) polimerinin yapısal ve termal özellikleri üzerine Na-Montmorillonit (NaMMT) yada Sepiolit (Sp) kil ilavelerinin etkilerini inceleyebilmek için kil-polimer nanokompozitleri hazırlanmıştır. Polimerik filmler HEC polimerinin sulu çözeltisi ile killerin sulu dispersiyonlarının birleştirilmesi esasına dayanan çözeltilerin birleştirilmesi yöntemi ile hazırlanmıştır. Suda çözülebilen polimer matrikslerinde çözeltilerin birleştirilmesi yöntemi polimerin kararlılığı, killerin kolayca dağılabilmesi bakımından kullanışlı bir yöntemdir. Hazırlanan nanokompoziteler Fourier Transform infrered (FT/IR) ve geçirimli elektron mikroskopisi (TEM) yöntemleri ile karakterize edilmiş, termal özellikleri termogravimetrik analiz (TGA) ve taramalı diferansiyel kalorimetri (DSC) yöntemleri ile araştırılmıştır.

Thermal Comparison of Montmorillonite / HEC and Sepiolite / HEC nanocomposites

Keywords
Montmorillonite;
Sepiolite; HEC;
Nanocomposites;
Thermal properties.

Abstract

In this study, clay-polymer nanocomposite films were prepared to examine the effects of the addition of clay minerals on the structural and thermal properties of Hydroxyethyl Cellulose (HEC). Polymeric films were prepared by "solution casting method" which is also known as the method of mixing solutions based on the mixing of aqueous dispersion of HEC polymer with aqueous solution of clays. The method of mixing solutes in water-soluble polymer matrices is a useful method in that the stability of the polymer is improved and the clays can be easily dispersed. The structure of nanocomposites characterized by FT/IR and TEM analysis. The structure of nanocomposites have been characterized by Fourier Transform İnfrared spectroscopy (FT/IR) and Transmission Electron Microscopy (TEM) analysis. Their thermal properties have been determined by Thermogravimetric (TGA) and Differential Scanning Calorimetric (DSC) methods.

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1. Introduction

Nanofillers in polymers improve the properties of polymers. In 1950's clay-polymer composites are started to synthesized to reinforce the properties of polymers especially with the small amount of clay mineral additions. Nanocomposites are created by distributing an inorganic material (clay) in an organic matrix (polymer). Clay particles have naturally nanometer sizes around 1nm to 100nm in one dimension and they are good fillers because of their high dispersibility, low costs, high adsorption, and swelling capacity (Alexandre & Dubois, 2000; Amarelis, Carrado, Bergaya, Clay Minerals Society., & Groupe français des argiles., 2007; Bergaya, Theng, & Lagaly, 2006; S. Gul, Kausar, Muhammad, & Jabeen, 2016; Pinnavaia & Beall, 2000; Suprakas Sinha Ray, 2013; S. S. Ray & Okamoto, 2003; Utracki, 2004)

Clays are natural materials and they can be used for many different industrial applications according to their different physical and chemical structures.

Montmorillonite is a hydrated sodium, calcium, aluminum, magnesium, silicate hydroxide. It is a clay mineral which is a member of 2:1 layered phyllosilicate. Crystal structure consists of layers made up of two tetrahedral sheets and one octahedral sheet. Layer thickness of montmorillonite is around 1nm. Hence, it is topologically 2-dimensional nanofiller. It has high swelling capacity (increases greatly in volume when it absorbs water). Montmorillonite is used as a drilling mud as soil additive, as preventer for leakage of fluids. It is also used as a plug for water wells because of its swelling property and as an absorptive of heavy metals in medicine and pharmacology. As a layered silicate it is an attractive filler due to its high surface area. It can generate big interfacial contacts with the polymer phase (Bergaya et al., 2006).

Sepiolite is a hydrated magnesium silicate. It is a clay mineral, formed by hydroxylation of particles of conglomerated stones, which are complex of Magnesium and Silisium, in deep metamorphosis layers of earth with hydrothermal effects. Sepiolite has fibrous form, so it is topologically 1-dimensional nano filler. The first chemical analysis was made on the Sepiolite in the form of Eskişehir meerschaum in the second period of 18th century. Their most significant property is the high thermal strength (Alvarez, 1984; Galan, 1996; Jones, 1988; Lv, Liu, & Rao, 2017; Nagy, 1955).

The interaction of polymers and clay particles depends on the ionic or non-ionic character of polymers. Hydroxyethyl cellulose (HEC) is a cationic, water-soluble polymer, an amorphous cellulose derivative which has an HEC backbone with small amounts of long alkyl chains. It has high molar mass and toughness, stable chemical structure, biodegradability, compatibility, gelling, thickening, stabilizer, emulsifier and dispersive effects. It is widely used in cleaning solutions, cosmetics, agriculture, building materials, paints, drilling oils and other household products. Long fibrous building material give a strong nature to cellulose derivatives. HEC, like the other cationic polymers can interact electrostatically with charged surface of clay particles. (Alan & Isci, 2014; Bergaya et al., 2006; E. Isci & Turutoglu, 2011; S. Isci, Gunister, Ece, & Gungor, 2004).

In this study, thermal properties of Na-Montmorillonite/HEC and Sepiolite/HEC nanocomposites were prepared by solution casting method to compare the thermal properties. Sepiolite is known as a good thermally stable clay, montmorillonite is known with layered structure. Although sepiolite has large surface areas, montmorillonite can create much more surface area than sepiolite because of the delamination of the layers in polymer matrix. Hence, the comparison of the clay minerals in polymer nanocomposite is indeed the comparison of the surface area and the structure of the clay minerals in polymer matrix.

2.1. Materials

Na-montmorillonite (NaMMT)-was supplied by Bensan Co., Enez, Turkey. The Sepiolite (Sp) sample was collected from Eskişehir-Margi, Turkey. X-ray diffraction-XRD, Philips PW 1040, Infrared-FTIR Jasco Model 5300, were used to determine the clay mineral types.

XRD diagram of montmorillonite was given at Figure 1. According to the diagram, the dominant clay mineral for montmorillonite with minor amounts of illite and kaolinite.

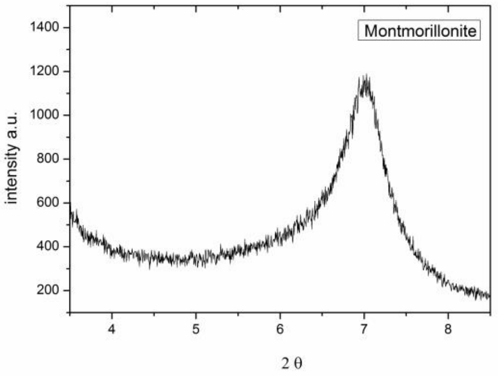


Figure 1 : XRD diagram of Na-Montmorillonite

The sepiolite (Sp) was also characterized by X-ray diffraction and the diagram was given at Figure 2.

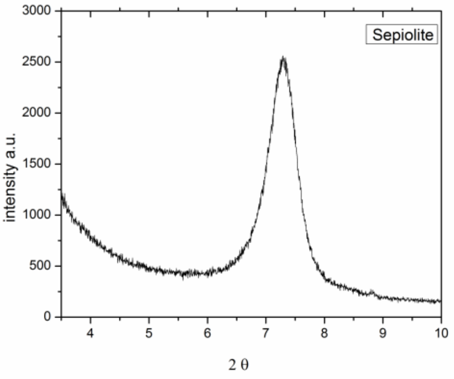


Figure 2 : XRD diagram of Sepiolite

The chemical compositions of the clay minerals were determined by atomic adsorption spectroscopy and the results were given at Table 1.

Table 1. Chemical contents of clay minerals

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
NaMMT	58.8	18.73	3.71	3.34	2.62	3.36	2.7	0.49
Sp	61.03	0.83	0.1	0.55	2.25	0.01	0.01	0.01

HEC were purchased from Sigma–Aldrich Co. and used without further purifications. The chemical structure representation of HEC was given at Figure 3.

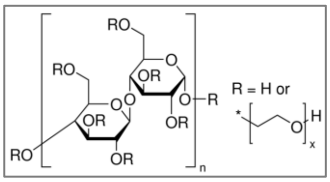


Figure 3 : Chemical structure representation of HEC

2.2. Preparation of dispersions

Solution casting method is used to prepare nanocomposite films. It is probably the most common method for preparing clay/polymer nanocomposite. Three major steps were followed to disperse the nanoparticles in the polymer solution.

Firstly; clays were dispersed separately in distilled water by under vigorous stirring for 24 h and then sonicated for 15 min. Secondly, the clay dispersion was mixed with the previously prepared aqueous HEC solution by heating and stirring for 5 minutes and degassed in ultrasonic bath. These mixtures were casted on silicone plates and dried at 40 ⁰C in an oven. Finally, the films were peeled off from the plates.

2.1. Methods

FTIR analyses were performed between 400-4000 cm-1 on Perkin Elmer Spectrum 100 FTIR spectrophotometer using clay-polymer nanocomposite films with a concentration of 1% and recorded as a function of wave number in absorbance mode.

TEM, Transmission electron microscopy, analyses were performed with FEI Tecnai G2 Bio (TWIN) at 120 kV.

TGA, thermogravimetric analysis, was performed at Perkin Elmer Diamond in a temperature range 200 ⁰C-2000 ⁰C with rate of 50 ⁰C/min and at a frequency of 1 Hz.

The thermal behaviors of nanocomposites were also determined by using Differential Scanning Calorimetry method at Perkin Elmer Diamond. DSC was performed at a temperature range of 25 ⁰C and 600 ⁰C with heating rate of 10 ⁰C/min under Nitrogen atmosphere.

3. Results

3.1. Structural Characterization of Nanocomposites

Generally, nanocomposites characterized by XRD by following the characteristic XRD peaks. The disappearance of the characteristic X-ray peaks of clay in the polymer matrix means that the delamination of clay layers. However, the sepiolite conserved its fibrous structure in the polymer matrix without delamination, so the characteristic XRD peaks stay always the same position in the XRD diagram. Because of that, the prepared nanocomposites were characterized by FTIR method. FTIR spectras of clay minerals, HEC and nanocomposites were given at Figure 4.

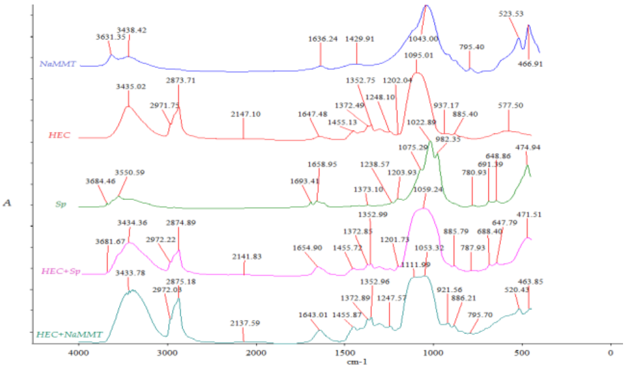


Figure 4. FTIR spectra of NaMMT, HEC, Sp, HEC+SP, and HEC+NaMMT

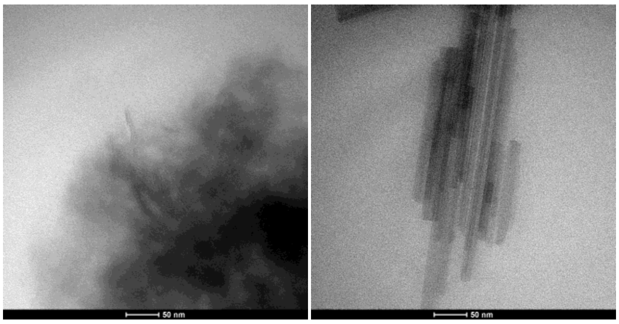
The IR spectra of NaMMT has water absorption bands near 1630 and 3400–3700 cm-1 in the scattering region. The SiO_4 and Al_2O_3 bands are between 400 and 710 cm-1 (Frost & Rintoul, 1996; Loh, 1973). The AlMgOH bending appeared as peak at 795cm-1 and the structural OH bound to octahedral cations bending bands appeared between 840 and 925 cm-1 (Bergaya et al., 2006; Isci S, 2006).

The main characteristic bands of Sepiolite at 3684 cm^{-1}, 3550 cm^{-1}, 1693 cm^{-1}, and 1658 cm^{-1}, 1204 cm^{-1}, and 1022 cm^{-1}, 780 cm^{-1}, 691cm^{-1}, and 648 cm^{-1}, are ascribed to bending of Mg-OH, -OH stretching, OH bending, Si-O-Si bands, bending of Mg-Fe-OH and Mg-OH bending, respectively (Alan & Isci, 2014; S. Isci, 2015; Serna & Vanscoyoc, 1979).

The main peaks of HEC; the strong absorption peak at 3435 cm^{-1} shows of the presence of hydroxyl groups (-OH), besides of the absorption peaks at 2971 cm^{-1} and 2873 cm^{-1} are saturated alkyl ($-CH_3-$, $-CH_2-$), and the absorption peak at 900–1200 cm^{-1} are ether linkage peaks (C-O-C) (Wang & Ye, 2010) .

Addition of Sepiolite and Na-Montmorillonite to HEC changed mostly the –OH peaks due to the hydrogen bonding between HEC and clays. Besides, the characteristic peaks of clays appeared at the nanocomposites slightly increasing with increasing of the solid content of clays in HEC (Figure 4).

TEM analysis and the pictures showed the state of clay dispersion in the polymer matrix. Image a and b in Figure 5 show that Mt, is mainly present in the composite as primary particles with observable intercalation and exfoliation together. The fibrous structure of the Sp particles clearly was seen in the Figure 5b. The distribution of the clay particles in the polymer phase is an effective and important parameter on the properties of the prepared nanocomposites. (Amarelis et al., 2007; Pinnavaia & Beall, 2000; Suprakas Sinha Ray, 2013; S. S. Ray & Okamoto, 2003; Utracki, 2004).



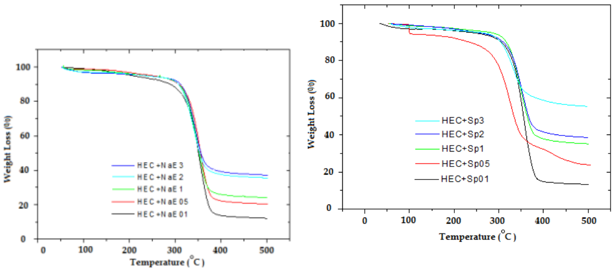
(a) (b)

Figure 5. TEM pictures of a) NaMMT/HEC and b) Sp/HEC

3.2. Thermal Characterization of Nanocomposites

Addition of both Sepiolite and Na-Montmorillonite to polymer significantly increased the thermal stability of HEC. As the concentration of clay increased, thermal stability also increased.

The residue of the nanocomposites at high temperatures, were found very higher than pristine HEC. The value increased from 10% to 60 % for 3wt% Sp addition and also increased from 10% to 40% for 3wt% NaMMT addition as compared to neat polymer. The TGA graphs were given at Figure 6 a and b. The different clay structures resulted in the different amount of residues of the nanocomposites. Sepiolite has much more stable structure and can keep the water molecules in its fibrous structure at high temperatures comparing to montmorillonite, so is has more residues in the nanocomposites meaning that more stable at high temperatures.



(a) (b)

Figure 6. TGA weight loss graphs for a) HEC+NaMMT and b) HEC+Sp

The thermal behavior of nanocomposite films was also determined by using Differential Scanning Calorimetry method. The results were given at Table 2 and Table 3 for NaMMT/HEC and Sp/HEC nanocomposites respectively.

Table 2. DSC results of NaMMT/ HEC

NaMMT % in HEC	**Tg(°C)**	**To(°C)**	**Tm(°C)**	**Tf(°C)**	ΔT(Tf-To)
0	-	46,7	103	161	114,3

0.1	42,3	93,8	118,4	183	87,2
0.5	44,7	98,5	121,8	185	86,5
1	45,6	74	113,6	159	85
2	50,2	72	115,9	165	93
3	59	47,9	107,4	168	120,1

Table 3. DSC results of + Sp/ HEC

Sp % in HEC	Tg(°C)	To(°C)	Tm(°C)	Tf(°C)	ΔT(Tf-To)
0	-	46,7	103	161	114,3
0.1	-	45,6	106,7	159	113,4
0.5	-	47,3	105,5	154	106,7
1	-	44,2	103	153	108,8
2	-	46,7	106,8	159	112,3
3	-	47,4	105,7	163	115,6

HEC shows a chemically disordered liquid crystal polymer behavior when its aqueous solution is very concentrated. HEC can be characterized by a low Tg, a long biphasic region and a broad mesophase to isotropic phase transition peak because of the size distribution of partially crystalline phase in amorphous phase (Bheda, Fellers, & White, 1980a, 1980b; V. E. Gul, Khanchich, & Savchenko, 1996; Wang & Ye, 2010). In this study, HEC was not used in very concentrated form for film casting, so glass transition temperature can not be determined precisely for pure polymer. However, NaMMT addition to polymer results partially concentrated regions in matrix and make it possible to investigate a definite glass transition temperature. The Tg values obtained for NaMMT addition started from 42,3°C and increased to 59°C. When concentration of montmorillonite increase, the crystallinity of nanocomposite also increases due to the intercalation ability and crystallized structure of montmorillonite. Also the the delamination of NaMMT layers increased the surface area so the increased number of the hydroxyl groups in the nanocomposites which caused to Tg values(Alexandre & Dubois, 2000; Chang & An, 2002; Qian, Lindsay, Macosko, & Stein, 2011; Suprakas Sinha Ray, 2013). Hence, T_g values are getting higher and shifting right towards endothermic transition peak. It shows that the addition of NaMMT increased the thermal stability of HEC. The increasing value of Tg values for NaMMT addition were given at Figure 7.

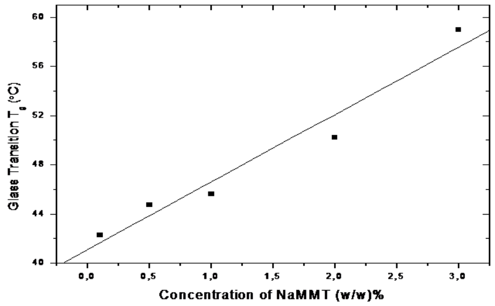


Figure 7. Glass transition temperature for different NaMMT concentration

In the Table 2 and 3, T_o represent the initial temperature of melting, T_m melting temperature and T_f final temperature of melting process. Each clay addition retarded the melting temperature of HEC. However, the significant changes were observed for NaMMT addition. The T_o values for NaMMT addition increased almost to 40°C higher values while only 2-3°C higher values for Sp addition. As the same, T_m and T_f values of NaMMT increased to almost 15°C higher in values in contrast to decreased values of Sp addition. Obviously, when the values of the melting temperatures compared according to the clay types, NaMMT addition was much more successful than Sp addition. The delamination of NaMMT increased surface area of the clay mineral, which caused to more bonding with surfaces and polymer, resulted in increasing the thermal stability of HEC.

The width of phase transition peak in DSC thermographs, which can be seen at ΔT(Tf-To) values, is getting narrow with increasing clay concentration. This value is related with crystallinity of the polymer matrix. NaMMT addition gives some ordered structure to the composite.

values of NaMMT were determined less than Sp. However, after a specific concentration, high polymer concentration of polymer generates too much cross linking reactions in interlayer space of montmorillonite, so clay particles break down, clay platelets disperse isotropically through in matrix (like exfoliation). Each NaMMT layer behaves like a individual crystal particle which caused to increase the ΔT values as much as Sp addition. The changes of phase transition range for clay mineral addition were given at Figure 8. The delamination of NaMMT layers caused a big difference on the phase transition of the nanocomposites while Sp addition is more or less stable during the phase transition.

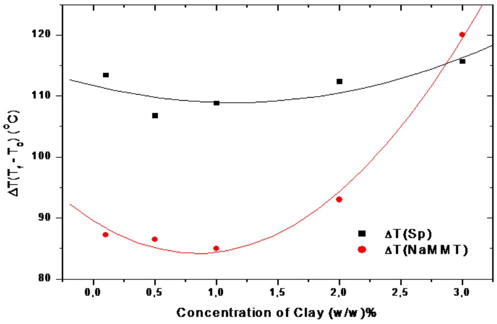


Figure 8. Temperature range for phase transition

4. Conclusion

Addition of clay particles dramatically affected the thermal properties of HEC nanocomposites. The layered structure of montmorillonite increased the glass transition and melting temperatures of the polymer by supplying more surface area and ordered structure in the matrix. The fibrous structure of sepiolite increased the thermal stability because of the conservative fibrous which were not delaminated in polymer. The both clay particles can be dispersed well in HEC and can be chosen according to application.

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