Synthesis and Characterization of Poly(N-Ethyl Aniline) / Talc Composite Materials

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Summary

A new substituted polyaniline/layered talc conductive composite material were synthesized chemically using ammonium persulfate as oxidizing agent in aqueous HCl medium. The oxidant type, N-ethyl aniline to oxidant mole ratio and N-ethyl aniline concentration on the PNEAn content and conductivity of the composite were investigated as the effect of the polymerization conditions. Optimum reaction conditions were outlined as NEAn/oxidant ratio 1 and 0.2 M NEAn monomer concentration with $(NH_4)_2S_2O_8$ on the poly(N-ethyl aniline) yield and conductivity. The conductive composites were characterized by two probe technique for surface resistance and thermo gravimetric analysis (TGA) techniques.

The increased thermal stability of the composite compared to that of pure polymer was obtained by the thermogravimetric analysis method.

Keywords: Talc, N-Ethyl Aniline, conducting polymer, composite

Introduction

With the ease of synthesis, environmental stability and simple acid/base doping/dedoping polyaniline (PANI) is a promising conducting polymer (He et al., 2012). PANI and its derivatives have attracted great attention in various science and engineering fields in consequence of their numerous applications as in electrochromic devices, batteries, magnetic, electrical and optical areas (Jeyakumari et al., 2010; Lin and Yang, 2004).

Synthesizing of conductive polymer composites with inorganic materials such as layered silicates has received great interest lately. By the use of conductive polymers with inorganic materials, nanocomposites with high electrical conductivity, thermal stability, mechanical properties could be prepared (Çetinkaya et al., 2007). Wu et al. studied the intercalated polyaniline/clay nanocomposite prepared by the in-situ polymerization method of anilinium and intercalated synthetic mica clay. The resulted polymer nanocomposites were characterized by WAXD, FT-IR, UV-Vis, TEM, SEM, AFM and conductivity meter and the conductivity increased with polyaniline content (Wu et al., 2007). Gök et al. (2004) prepared poly(2-flouroaniline) (P2FAn), poly(2-chloroaniline) (P2ClAn), poly(2-bromoaniline) (P2BrAn) and poly(2-iodoaniline)(P2IAn) were prepared chemically with using $K_2Cr_2O_7$, $(NH_4)_2S_2O_8$ and $FeCl_3.6H_2O$ oxidants. FT-IR, UV-Vis, DSC, TGA and conductivity meter were used in the characterization of the polymers and the P_2ClAn give the highest conductivity among them.

Talc is a tri-octahedral 2:1 layer silicate mineral and it has a nature of endurance to heat, electricity and acids. Talc also characterized by three octahedral Mg positions per four tetrahedral Si positions (Zhou et al., 2007).

In this study, conductive poly(N-ethyl aniline) (PNEAn) /talc composites were resulted from the chemical polymerization of N-ethyl aniline using ammonium persulfate in the presence of talc particles in aqueous media. The effects of polymerization conditions such as type of oxidant, oxidant to monomer mole ratios and monomer concentrations on the conductivity and polymer amount of the prepared conducting composites were investigated. The prepared poly (N-ethyl aniline)/talc composite material was characterized by TGA technique.

Materials and Methods

Talc with the chemical composition of 61.00&SiO_2, 32.00&MgO, 0.10&Al_2O_3, 0.40&Fe_2O_3, 0.20&CaO, particle size smaller than 38 μm, were obtained from Esan/Eczacıbaşı Raw Materials Industry, Inc. N-Ethyl aniline (N-EAn) (Merck) was distilled by vacuum distillation. HCI (Merck), ($(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, $KMnO_4$, $FeCl_3.6H_2O$, KIO_3, K_2CrO_4 and $K_2S_2O_8$ (Merck) were used as supplied.

PNEAn/Talc composites were prepared by in situ chemical polymerization of N-ethyl aniline using ammonium persulfate $(NH_4)_2S_2O_8$ as an oxidant in the presence of talc particles. 17 mL aqueous 1.0 M HCl solution was added onto certain amount (1.0 g ± 0.01 g) of talc into the polymerization tube and mixed for 15 min, and suitable amount of N-ethyl aniline was added into the suspension formed. The polymerization was started by adding 3 ml of aqueous acidic $(NH_4)_2S_2O_8$ solution as drop by drop over it. The composite powder was separated from the mixture by centrifugation. To get rid of unreacted monomer and oxidant the product was washed with distilled water and methanol. To gain back the dopant which was lost from the composite during washing processes 1.0 M HCl solution was used. At the end the composite was dried by at 50 ^oC for 12 h under vacuum and weighed.

The percentage of PNEAn in the composite was calculated gravimetrically as shown below:

$$\text{PNEAn}\,(\%) = \frac{W - W_O}{W_O} \times 100$$

where W is the weight of PNEAn/talc composite material and Wo is the weight of talc particles.

Under 80 kN pressure for about 5 min conducting polymer samples were performed as pellets. And also with the help of Keithley 6517A Model electrometer, the resistance of composite samples was carried out by two-probe technique.

The thermogravimetric analyses were examined by Shimadzu TA50 model thermal analyzer by 10°C min^{-1} under nitrogen atmosphere (Anaklı and Çetinkaya, 2010).

Results and discussion

Oxidant type

By using 7 different oxidants ($(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, $KMnO_4$, $FeCl_3.6H_2O$, KIO_3, K_2CrO_4 and $K_2S_2O_8$), in Table 1 the influence of oxidant type on PNEAn content and conductivity of composites were given.

From Table 1, despite the composite having the highest PNEAn content (25.22%) was achieved with KIO_3, the highest conductivity was get by (7.31×10^{-8} S cm^{-1}) $(NH_4)_2S_2O_8$. Our main goal in the study is to obtain high conductive composites, so the following experiments were prepared by $(NH_4)_2S_2O_8$ oxidant.

Fig. 1 shows the PNEAn contents and conductivities of the composites obtained by changing $(NH_4)_2S_2O_8$/NEAn mole ratio in the range of 0.125–2.0. The conductivity of composite increased up to 1.0 mole ratio of oxidant to monomer and decreased at higher ratios. We prepare the composites on the basis of conductivity, the most suitable values were obtained with 14.21& PNEAn content and at the 1.0 $(NH_4)_2S_2O_8$/NEAn mole ratio.

The PNEAn content and conductivity of the composite increased gradually up to 0.2 M NEAn concentration, above this value conductivity of the composite showed a sharp decrease but the PNEAn content of the composite did not change too much. PNEAn content and conductivity of the composite showed the best values at 14.21% and 4.35×10^{-7} Scm^{-1}, respectively (Fig. 2).

Thermogravimetric analysis

In Fig. 3, the thermograms of doped PNEAn, pure talc and PNEAn/talc composite containing 14.21% PNEAn are shown. Compared with those of pure talc and PNEAn, the thermal stability of composite was between them in the 20 and 900°C temperature range. While the composite decompose at 368°C and losed 15% its weight, pure talc and PNEAn decompose 780°C and 353°C and losed about 5.11% and 98.5% their weights, respectively. As can be seen from the results thermal stability of the composite increased equated to polymer PNEAn.

Conclusions

In this work, conductive PNEAn/talc composite could be obtained by chemical polymerization by using substituted aniline N-ethyl aniline and talc particles. The polymerization conditions played an important role

Table 1. Difference in the PNEAn content and conductivity of PNEAn/talc composite with the type of oxidant

Tabela 1. Różnica w zawartości PNEAn i przewodności kompozytu PNEAn/talk w zależności od rodzaju utleniacza

Type of oxidant	NEAn/Oxidant (mol/mol)	PNEAn (%)	Conductivity (S/cm)
K_2CrO_4	3	4.35	2.57×10^{-9}
$KMnO_4$	5	0.95	–
$(NH_4)_2S_2O_8$	**2**	**8.86**	**7.31×10^{-8}**
$FeCl_3.6H_2O$	1	1.65	–
$K_2Cr_2O_7$	6	7.09	2.05×10^{-9}
KIO_3	6	25.22	3.64×10^{-8}
$K_2S_2O_8$	2	3.75	–

on the PNEAn content and the conductivity of the composite. 0.2 M NEAn and 1.0 $(NH_4)_2S_2O_8$/NEAn mole ratio for 2 h at 20°C are the optimum conditions for the composite having the highest conductivity.

It was found that with talc particles thermal stability of the composite increased compared with HCl doped PNEAn.

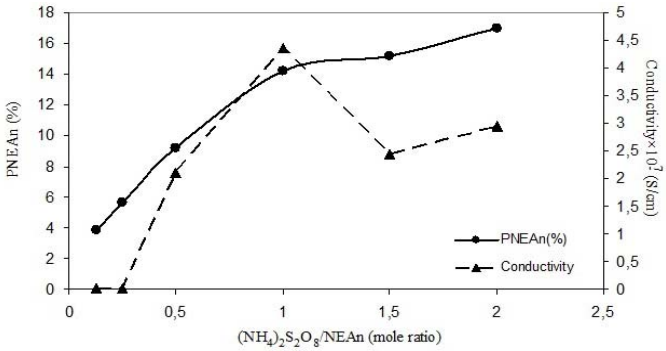

Fig. 1. The change of $(NH_4)_2S_2O_8$/NEAn mole ratio on PNEAn content and conductivity of PNEAn/talc composite. [HCI]: 1,0 M; [NEAn]: 0.2 M; temperature: 20°C; polymerization time: 2 h

Rys. 1. Zmiana stosunku molowego $(NH_4)_2S_2O_8$/NEAn na zawartość PNEAn oraz przewodność kompozytu PNEAn/talk. . [HCI]: 1,0 M; [NEAn]: 0.2 M; temperatura: 20°C; czas polimeryzacji: 2 h

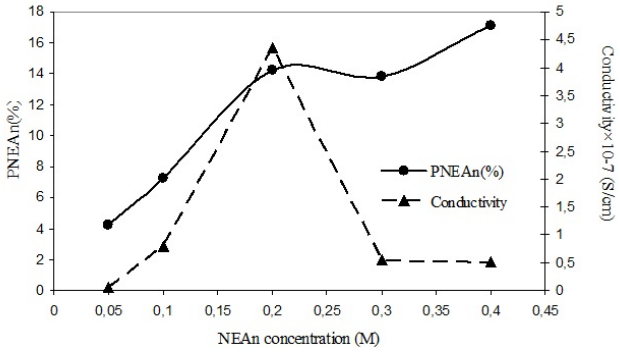

Fig. 2. The effect of NEAn concentration on the PNEAn content and conductivity of PNEAn/talc composite [HCI]: 1.0 M; $[K_2CrO_4]$: 0.2 M; temperature: 20°C; polymerization time: 2 h

Rys. 2. Wpływ stężenia NEAn na zawartość PNEAn oraz przewodność kompozytu PNEAn/talk. [HCI]: 1.0 M; $[K_2CrO_4]$: 0.2 M; temperatura: 20°C; czas polimeryzacji: 2 h

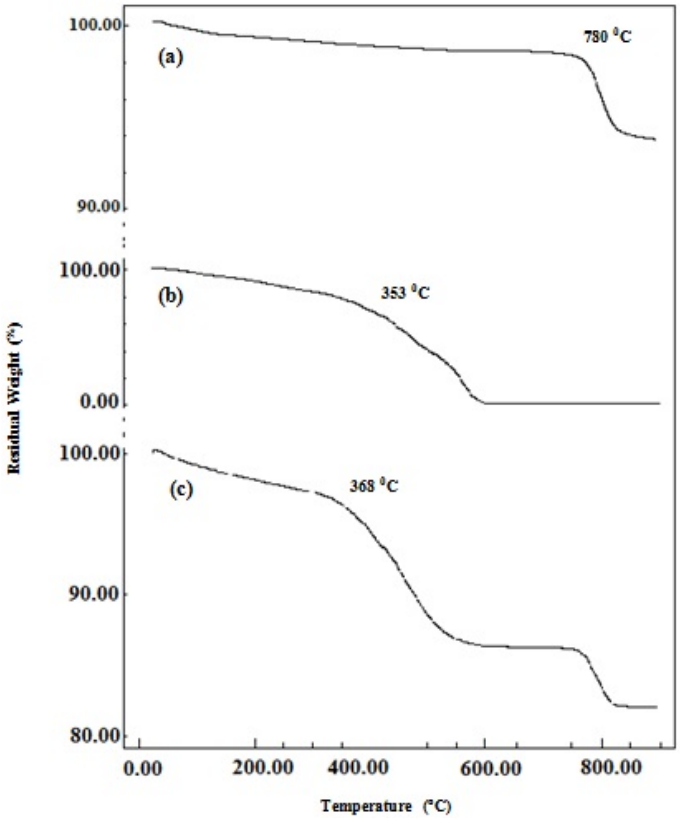

Fig. 3. Thermograms of (a) pure talc, (b) HCl doped PNEAn and (c) PNEAn/talc composite containing 14.21% PNEAn

Rys. 3. Termogramy (a) czystego talku, (b) PNEAn z domieszką HCL oraz (c) kompozytu PNEAn/talk zawierającego 14,21% PNEAn

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Synteza i charakterystyka Poli(N-etylo aniliny) / Talk

Nowy przewodzący materiał kompozytowy podstawiony polianiliną/warstwowany talkiem zsyntetyzowano chemicznie przy użyciu nadtlenodisiarczanu amonu jako czynnika utleniającego w wodnym kwasie chlorowodorowym. Badano rodzaj utleniacza, anilinę N-etylową do stosunku molowego utleniacza oraz stężenie aniliny N-etylowej w PNEAn [Poly(N-ethyl aniline)] oraz przewodność kompozytu co jednocześnie było skutkiem warunków polimeryzacji. Optymalnymi warunkami jakie określono dla reakcji to NEAn/utleniacz w stosunku 1 oraz 0,2M stężenie monomeru NEAn wraz z $(NH_4)_2S_2O_8$ na polianilinie N-etylowej. Kompozyty przewodzące zostały scharakteryzowane przez badanie oporu powierzchni oraz analizę termograwimetryczną (TGA).
Zwiększona stabilność termiczna kompozytu została porównana do tej z czystego polimeru została określona przez metodę termograwimetryczną.

Słowa kluczowe: talk, N-etylo anilina, polimer przewodzący, kompozyt