

OPTICAL FILMS BASED ON POLY(*P*-PHENYLENE VINYLENE) (PPV) AND ITS NANOCOMPOSITES

Duangporn Saramas¹, David C. Martin² and Rathanawan Magaraphan¹

¹The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

²Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, USA

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Abstract. Nanocomposites of poly(*p*-phenylene vinylene) (PPV) were studied. The natural sodium-montmorillonite was cation exchanged with bis(hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride. Content of modified montmorillonite had varied from 30-60 wt% in pure PPV. These polymer/layered silicate nanocomposites were synthesized and consisted of different organically-modified clays, proven by TGA, WAXD, FTIR, and TEM. Barrier property and color tunability improved with increasing organophilic clay content. The rate of photoluminescence decay in polymer-clay nanocomposites drastically reduced compared to that of pristine polymer. The results showed important implications for enhanced lifetime of polymer-clay nanocomposites based optoelectronic devices.

1. INTRODUCTION

The development of light-emitting diodes (LEDs) based on conjugated polymers has been received a great deal of attention since the discovery in 1990 by Friend *et al.* at Cambridge University [1]. Poly(*p*-phenylene vinylene) (PPV) is the first conjugated polymer for electroluminescence emission and remains as the most popular conjugated polymer class for this application. The use of conjugated polymers as active materials has a number of advantages, including their versatility for fabrication, flexibility, low cost, low operating voltage, and the ease with color tuning of light emission [2-4]. Nevertheless, polymeric light-emitting devices exhibit short lifetime in an oxygen atmosphere. Most of efforts have been concentrated on improving the stability of the devices. Therefore, new techniques for solving LEDs into long term stability against oxygen are needed.

Smectite clays and related silicates are usually used as a filler in polymer nanocomposites due to

their reinforcing property and economy reason. Montmorillonite, used in this work, is one of smectite clay minerals normally applied to polymeric matrix nanocomposites. Due to the intercalation chemistry of the silicate layers, polymer-clay nanocomposites can exhibit dramatically improved properties such as barrier, mechanical, optical, and thermal properties. For LEDs application, the color tuning is one of the important advantages of organic over inorganic materials. The length of the conjugation which sets certain characteristics of the molecules can be adjusted by smectite clays. Moreover, the constraint brought by the nanocomposites structure to the polymer chains is the essential factor contributing to the decrease of oxygen permeability. Polymer-clay nanocomposites appear to be a very promising class of polymer for electroluminescence devices. In this study, improvement of organic LEDs by introduction of organically modified montmorillonite into PPV is discussed.

Corresponding authors: Duangporn Saramas, e-mail: Saramas@chula.com and Rathanawan Magaraphan, e-mail: Rathanawan.k@chula.ac.th

2. EXPERIMENTAL SECTIONS

2.1. Materials

Sodium montmorillonite (Kunipia-F) with cation exchange capacity (CEC) of 119 meq/100 g was provided by Kunimine Industrial Co., Ltd., Japan. Bis (hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride was kindly supplied by Unilever Thai Holdings Co., Ltd. *p*-xylylene bis(tetrahydrothiophenium) chloride was purchased from Aldrich Co., Ltd.

2.2. Methodology

The preparation of organically modified montmorillonite with bis(hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride was done by ion exchange reaction [5]. The precursor polymer was synthesized from *p*-xylylene bis(tetrahydrothiophenium) chloride by the method of Burn *et al.* [6].

A dispersion of organophilic montmorillonite in butanol was stirred vigorously using magnetic stirrer for 48 hours. Next, the solution was sonicated for 6 hours. Poly [*p*-xylylenebis (tetrahydrothiopheniumchloride)] solution was blended with organophilic clay solution and mixed together. Contents of modified montmorillonite were varied from 30-60 wt% in pure PPV. After mixing, the solution was stirred for 18 hours. Since the photoluminescence intensity of PPV films spin coated on glass decreased with increasing conversion temperature [7], the low conversion temperature at 110 °C was chosen.

2.3. Characterization

The FTIR spectra in the range of 4000–400 cm⁻¹ were obtained on an Equinox 55 BRUKER spectrometer with 32 scans at a resolution of 2 cm⁻¹. The results of Wide Angle X-ray Diffraction (WAXD) experiments used to confirm the organization of the clay layers in polymer-clay nanocomposites. WAXD spectra were performed at room temperature by a Rigaku Model D/MAX 2000 diffractometer. The Cu K-alpha ($\lambda=1.54 \text{ \AA}$) radiation source was operated at 40 kV/30mA. The percent of ion exchange was determined by an atomic absorption spectrometer Varian SpectrAA-300 that acetylene was used as fuel and air was used as supported gas. The hollow cathode lamps used were sodium cathode lamps for sodium ion with 5 mA lamp current. Ion solution standard 1000 ppm was prepared according to the analytical method of Varian. The wavelength at 589.0 nm was

used to determine the absorbance of sodium ion. Thermogravimetric analysis technique was used to determine thermal stability and water absorption. Using a Dupont 2950 thermogravimetric analyzer, characterization was performed by heating about 10 mg of each sample at the heating rate 10 °C/min under the nitrogen atmosphere. The mass change with increasing temperature was monitored and recorded. The photoluminescence spectra were measured by Stellarnet spectrometer. The SpectraWiz[®] operating software is included with the Stellarnet miniature fiber optic spectrometer system. Polymer-clay nanocomposites were excited with monochromatic light at 410 nm from a laser diode (Power Technology, maximum optical power at 25 milliwatts). Typical optical power measured at the output of the fiber-optic delivery system is 10 milliwatts. The change of photoluminescence intensity of PPV-clay nanocomposites as the function of time were investigated at maximum peak while exciting with the strong monochromatic light.

3. RESULTS AND DISCUSSION

The chemical characteristics of both the organic and inorganic materials can be studied by IR spectra analysis. Fig. 1 (a) shows FTIR spectra of sodium-montmorillonite (Na-MMT) compared with (b) bis (hydrogenated tallow) dimethyl ammonium chloride (OH) and (c) bis (hydrogenated tallow) dimethyl ammonium chloride-montmorillonite (OH-MMT). The pristine clay, Na-MMT, exhibited its unique characteristic peaks at 3620, 1040, 720, 520, and 466 cm⁻¹ which can be assigned orderly to O-H stretching, Si-O stretching, N-H out of plane bending, Al-O stretching, and Si-O bending. For modifying agents, OH, showed important absorption peaks of O-H stretching, C-H stretching of methyl group, C-H stretching of methylene group, and C-H stretching

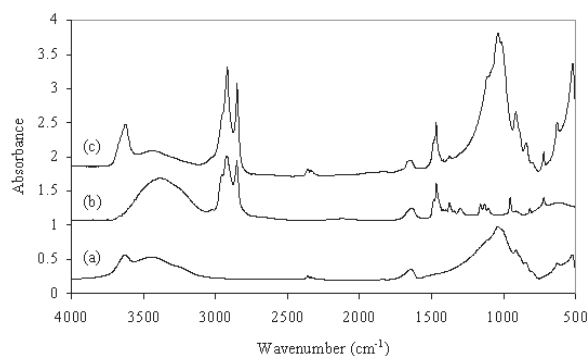


Fig.1. FTIR spectra of (a) Na-MMT, (b) OH, and (c) OH-MMT.

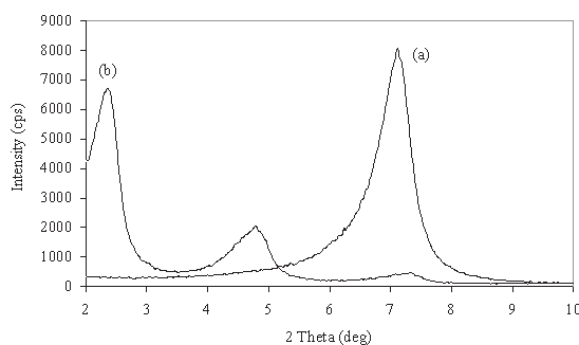


Fig.2. WAXD patterns of (a) OH and (b) OH-MMT.

of ammonium ion at 3620, 2950, 2850, and 1430 cm^{-1} , respectively. Clearly seen from this figure, FTIR spectrum of OH-MMT shows the specific absorption characteristics of both inorganic and organic components with respect to aluminosilicate layers and the alkylammonium molecules.

The strong supported evidence for the incorporation of modifying agent into montmorillonite structure was obtained from WAXD. The X-ray diffraction spectra of Na-MMT and organically modified montmorillonite or OH-MMT in the region from $2\theta = 2^\circ$ to $2\theta = 10^\circ$ are demonstrated in Fig. 2 (a) and (b). From this figure, each curve had d_{001} spacing at $2\theta = 7.20^\circ$ and 2.32° , respectively. Peak position of OH-MMT was transitioned to lower 2θ angles relative to that of Na-MMT. This indicates that the distances between silicate layers are expanded significantly due to the incorporation of modifying agent into the montmorillonite structure. The interlayer distances were calculated from peak position of basal spacing. Therefore, the interlayer spacing of Na-MMT found in this work is 12.17 Å. After treatment via ion-exchange reaction, the interlayer spacing of OH-MMT is 37.08 Å.

As well as WAXD, thermogravimetric analysis is applied to confirm the incorporation of modifying agent into montmorillonite structure. TGA thermograms for Na-MMT, OH, and OH-MMT are given in Fig. 3. The decomposition temperature (T_d) was obtained from the derivative TGA thermogram. As evident from Fig. 3, T_d of modifying agent, OH, was found approximately 180 °C while T_d of Na-MMT was around 655 °C. It is observed that improvement in thermal stability of modifying agent resided between silicate layers could be substantiated by the thermogram of OH-MMT which shows T_d at 328 °C. The reason for the improvement in T_d of modifying agent

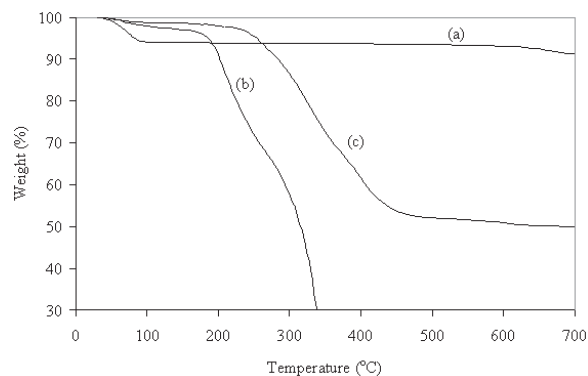


Fig.3. TGA thermograms of (a) Na-MMT, (b) OH, and (c) OH-MMT.

was resulted from the ionic force between alkylammonium ion and negative charge of montmorillonite. The purity of the organophilic-montmorillonite was determined by measuring a recovery percentage of sodium ions in an acidic solution. The percentage of ions exchange from Na-MMT in the process of preparation of organically-clay was determined by the air acetylene flame AAS. Consequently, the percentage of sodium ions exchange was equal to 96.16%.

Table 1. FTIR absorption bands assignment of poly(*p*-phenylenevinylene).

Frequencies (cm^{-1})	Assignments
3105	Aromatic C-H stretching
3024	Trans-vinylene C-H stretching
2950	C-H stretching from remnant saturated aliphatic groups
1594	C-C ring stretching
1519	
1421	
1336	
1267	C-H in-plane bending
1176	
1102	
964	Trans-vinylene C-H out of plane bending
837	Phenylene ring C-H out of plane bending
555	Phenylene out of plane ring bending

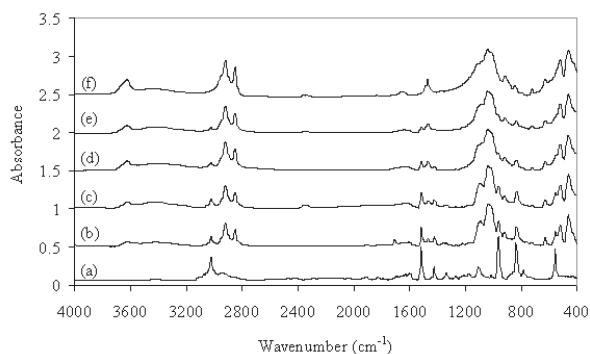


Fig. 4. FTIR spectra of (a) PPV, PPV/OH-MMT (b) 30 wt %, (c) 40 wt %, (d) 50 wt %, (e) 60 wt %, and (f) OH-MMT.

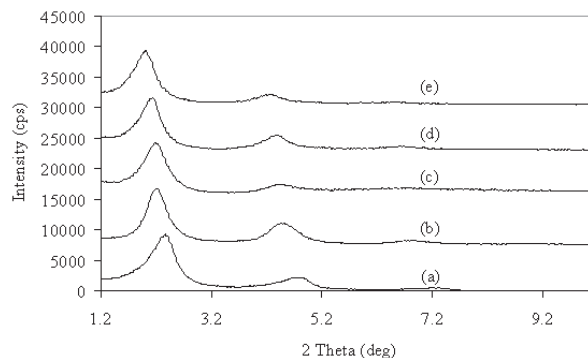


Fig. 5. WAXD patterns of (a) OH-MMT, PPV/OH-MMT (b) 30 wt %, (c) 40 wt %, (d) 50 wt %, and (e) 60 wt %.

Characterization of PPV/OH-MMT Nanocomposites. IR spectroscopy has been proved to be a useful technique to study the molecular and electronic structure of PPV. The mechanism of reaction was reported by Lenz *et al.* [8]. Frequencies of the IR-active modes in PPV are concluded in Table 1 [9]. After that, conversion to PPV was done by heating to 200 °C for 16 hours in vacuum oven to remove all of the water, organic sulfides and HCl. The resultant, homogeneous and densed, films were brownish yellow in color.

FTIR spectra of PPV-clay nanocomposites as shown in Fig. 4 exhibit the presence of characteristic absorption due to both the organic and the specific filler components. Clearly seen from this figure, absorptions of these peaks increase with increasing clay loading. WAXD results of various contents of modified montmorillonite are demonstrated

in Fig. 5. These data explain the relationship between the peak shift to lower 2θ angle correlates with the higher OH-MMT loading. This revealed the presence of silicate layers existed in an intercalated form which is a particular type of the clay nanocomposites [10]. Not only structural characterization of polymer layered silicate nanocomposites has centered around X-ray diffraction, but the observation has also revealed by Transmission Electron Microscopy (TEM). Fig. 6 shows a TEM bright-field image of an organically modified layered silicate 40 wt% intercalated with PPV.

Further evidence is observed in the evolution of PL spectra as shown in Fig. 7. The PPV emitted green light with an emission maximum around 524 nm. The PL emission peaks move towards longer wavelengths as increasing clay contents. The PPV-clay 30 and 40 wt% nanocomposites emit a maxi-

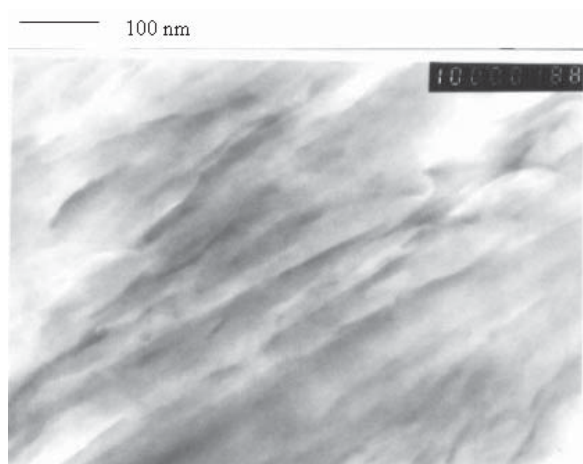


Fig. 6. TEM of PPV/OH-MMT 40 wt %.

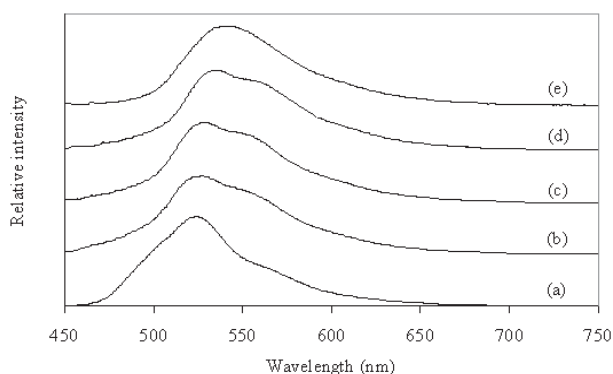


Fig. 7. Photoluminescence spectra of (a) PPV, (b) PPV-clay 30 wt %, (c) 40 wt %, (d) 50 wt %, and (e) 60 wt %.

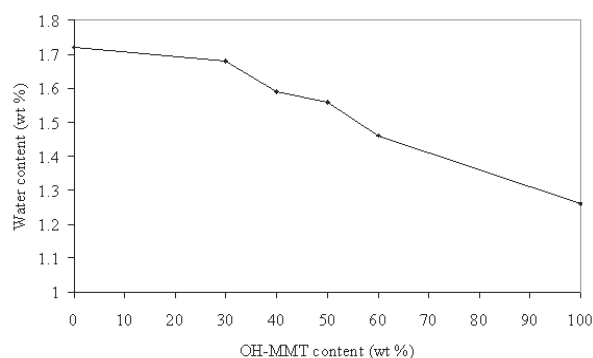


Fig. 8. Effect of organophilic-clay on water absorption of PPV.

mum peak at 527.5 nm with a shoulder at 550.5 nm and a maximum peak at 529.5 with a shoulder at 553 nm, respectively. Next, Yellow-green light emission maximum was observed from PPV-clay 50 wt% nanocomposites with an emission maximum at 536 nm with a shoulder at 562 nm. In addition, the PPV-clay 60 wt% nanocomposite emits a maximum peak at 542.5 nm without shoulder. The increasing of conjugation chain length in the intercalated polymer shows a shift of luminescence peak wavelength due to chain planarization [11-12].

Thermogravimetric analysis was used for study on water absorption of polymer and polymer-clay nanocomposites. Weight loss of PPV-clay nanocomposites are much reduced, illustrated in Fig. 8. Generally, the water absorption of PPV is very high because the water molecules can easily diffuse to form H-bonding along that polymer chains. The figure suggests that the polymer is originally associated with a relatively higher moisture content and thus higher weight loss due to the removal of water at elevated temperature. Moisture can be a source of oxygen supply for further photooxidation and thus reduce the stability of light emission. The reduction of diffusing water molecules is due to the stacking layer of polymer-clay nanocomposites that can act as a barrier to water diffusion into polymer. The impressive decrease of permeability was attributed to the clay layers to increase the tortuosity of the path for gas and water to diffuse into the nanocomposites [13-16].

As no polymer is capable of withstanding prolonged exposure to solar radiation, stabilization of polymers is extremely important. A great deal of light inducing damage to polymers is due to photo-oxidation reaction [17-18]. In order to examine the

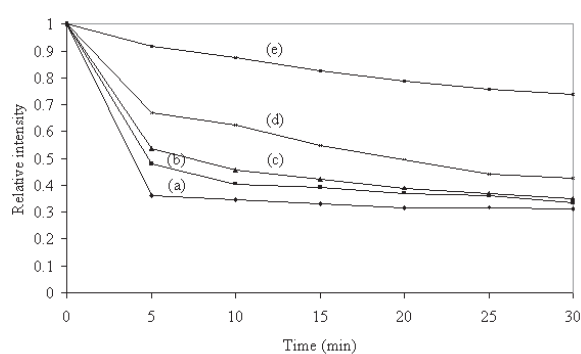


Fig. 9. The irradiation time dependence of photoluminescence intensity of (a) PPV, PPV/OH-MMT (b) 30 wt %, (c) 40 wt %, (d) 50 wt %, and (e) 60 wt %.

effect of radiation, the dependence of clay content on photoluminescence intensity was also investigated. Fig. 9 exhibits the PL decay of PPV observed at various clay contents. The interesting feature is that the pure PPV shows the fastest decay during the same period compared with its clay nanocomposites. Moreover, the result showed that the higher content of clay, the slower decay of photoluminescence intensity. This is also corresponded to the reduced moisture absorption. Due to the reduction of the reactive sites with oxygen, photo-oxidation of polymer-clay nanocomposites was significantly reduced [12]. It is concluded that the lifetime of light-emitting devices is improved by polymer-clay nanocomposites.

4. CONCLUSIONS

The successful preparation of organically modified montmorillonite with bis(hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride was done by ion exchange reaction. The TGA results of organophilic-clay demonstrated some interaction between modifying agent and silicate layers. In addition, AAS and WAXD techniques approved that most of Na^+ ions were exchanged and the modifying agent was intercalated into silicate layers. Furthermore, FTIR can verify the incorporation of modifying agent into the structure of clay.

PPV/layered silicate nanocomposites where organically modified montmorillonite was dispersed at the molecular level has been synthesized via solution and thermal elimination of the sulfonium group from poly(xylylene tetrahydrothiophenium chloride)-clay nanocomposites. All of organic-inorganic hybrid light-emitting nanocomposites in this study can be classified as intercalated type con-

firmed by WAXD and TEM. The FTIR spectra of the nanocomposites exhibited the presence of characteristic absorption due to both the organic and specific filler components.

The characteristic brought by the nanocomposites structure brought about improvement in barrier property, color tunability, and environmental stability. Water absorption of polymer/layered silicate nanocomposites was reduced as compared to pure polymer owing to increasing the tortuosity of the path. Increasing intercalation level showed a shift of photoluminescence peak wavelength toward lower energy which led to an increase in the effective conjugation length. Moreover, the dramatic improvement of environmental stability was given by the intercalated structure on polymer-clay nanocomposites. The photoluminescence intensity of the nanocomposites decreased more slowly with irradiating time than that of the pristine polymer.

In conclusion, the addition of organically modified clay nanoparticles to light-emitting devices based on PPV was a great class of very promising new materials of color tunability and environmental stability for optoelectronic applications.

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