

Aqueous Colloidal Dispersion of Conducting Polymers Promoted by Platelet-Like Clays and their Film Photoluminescence Properties

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Abstract

Conducting polymers (CPs) have a generally poor solubility in organic mediums and even worse in water and require a structural derivation before processing for practical applications. We report here a simple process by pulverizing coil-like CPs with platelet-like clays such as Mica to achieve a physically mixed hybrid with a fine colloidal dispersion in water. The unique dispersion phenomenon is unprecedented in literature and attribute to a physically mutual exclusion phenomenon through which the two materials' inherent non-covalent bonding interaction and resultant aggregation is minimized. For the CPs, their π - π stacking force is possibly interfered through the clay geometric interference while the clay surface charge is playing a role for promoting the CP dispersion. After screening the clays with different sizes and ionic species, it was found that the clay dispersion efficiency is influenced by size and aspect-ratio of the plate-like dimension. The finely dispersed colloidal suspension can be sprayed into CP-clay films which were subsequently demonstrated their photophysical characteristics by analyzing their ultraviolet-visible (UV-vis) and photoluminescence (PL) properties. One of PPV-clay film exhibited a spectrum at $\lambda_{\text{max.abs}}=580\text{nm}$ for UV absorption and $\lambda_{\text{max.em}}=605\text{nm}$ for PL. A blue shift phenomenon was observed for the Mica promoted CP dispersion.

Introduction Conducting polymers (CPs) are well-documented for their wide applications.¹⁻⁴ However, their sluggish solubility in organic mediums and water has largely limited for further advances in different areas of applications. Structural variations including the attachment of alkoxy and flexible side chains via synthetic routes are the common methods for preparing soluble CPs in organic solvent.^{1,2} Recently, water-soluble CPs with anionic groups on the alkyl side-chain has been reported particularly for biomedical uses.⁵ Previously, we had showed that aggregation of carbon nanotube can be mitigated by the presence of clay.⁶ Herein, we report a convenient method of dispersing CPs in water by mixing with platelet-like clay through a physically pulverization. Various clay species with different size, aspect-ratio, were screened and their physical properties were investigated by using UV-vis and PL.

Experimental Section Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (PPV, Mw 51000) was purchased from Aldrich Chemical Co. The synthetic fluorinated mica (Mica) and synthetic smectite (SWN) were obtained from CO-OP Chemical Co. Sodium montmorillonite (MMT) was supplied from Nanocor Co. The anionic clays have an average plate dimensions of *ca.* $300\times 300\times 1\text{nm}^3$ (Mica), $100\times 100\times 1\text{nm}^3$ (MMT) and $80\times 80\times 1\text{nm}^3$ (SWN). With similar plate structure (*ca.* $200\times 200\times 1\text{nm}^3$) but different cationic character, the layered double hydroxide (LDH) $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3\cdot 4\text{H}_2\text{O}$ was prepared. The PPV-Mica hybrid was prepared by ground PPV with Mica at weight ratio of Mica/PPV=1/3 to 2/1. After ground, PPV-Mica hybrid dispersed in water.

Results and Discussion I. Dispersion of CP-Clay in Water By grinding PPV with Mica, the PPV-Mica hybrid became dispersible in water (**Figure 1a**). Controlled experiments showed the pristine PPV were not dispersible in water but forming severe aggregates. The efficacy for the PPV dispersion depends on the relative amount of the Mica presence. The hybrid generated a fine slurry and can be differentiated by naked eyes as a red dispersion (1/1–2/1) from red solid precipitates (1/3–1/2). By using ultraviolet exposure (**Figure 1b**), PPV-Mica

solution showed orange emission due to PPV has been dispersed well in water and excited by ultraviolet exposure. In order to understand the nature of PPV-Mica interaction, MMT, SWN and LDH were further examined (**Figure 1c**). Both PPV-Mica and PPV-MMT solutions showed deep red appearance with a homogeneous dispersion, however, PPV-SWN and PPV-LDH solutions revealed light red with large-aggregated suspension. The dispersion, further analyzed by UV-vis spectrometer, showed that Mica is most effective for dispersing PPV (**Figure 2a**). Besides the effect of geometric shape and aspect ratio, the clay surface charges may play another role for influencing the CP dispersion in water. In **Figure 2b**, the PPV dispersion can be correlated to the weight ratio of PPV/Mica and the absorbance becomes more intensive with the increasing amount of Mica addition. In **Figure 2c,d** it is showed by the TEM images that the dispersion of PPV-Mica hybrid is uniform distribution and the particle size of Mica at 300–1000nm.

II. Optical Performance of CP-Mica Film

The photophysical characteristics of PPV-Mica film has a spectrum at $\lambda_{\max.\text{abs}}=580\text{nm}$ and $\lambda_{\max.\text{em}}=605\text{nm}$ (**Figure 3a**). The film was exposed to UV lamp (365nm) and showed noticeably orange emission (**Figure 3a insert**). The orange appearance is exactly correlated to the PL observations.

III. Explanation for the Dispersion Behavior of CP-Clay

Both UV-vis and TEM revealed the dispersion of CP by the influence of the clay presence. As illustrated by an illustration in **Figure 3b**, the initial grinding of two distinctly different shapes of nanomaterials, coil-like CPs and platelet-like Mica, reduced the original CP van der Waals force and π - π stacking attraction. The CP entanglement force may be mitigated or blocked by the neighboring Mica platelets.

Conclusion By simply grinding CPs with clays, the CP-clay mixture exhibited a fine dispersion in water. The Mica with high aspect-ratio and cationic charges is preferred for the formation of colloidal dispersion. The rationale for the unique dispersion behavior is provided for explaining the CP-clay mutual interactions. The fine dispersion of CPs by the simple Mica colloidal process provides a convenient method and broadens their applications.

References

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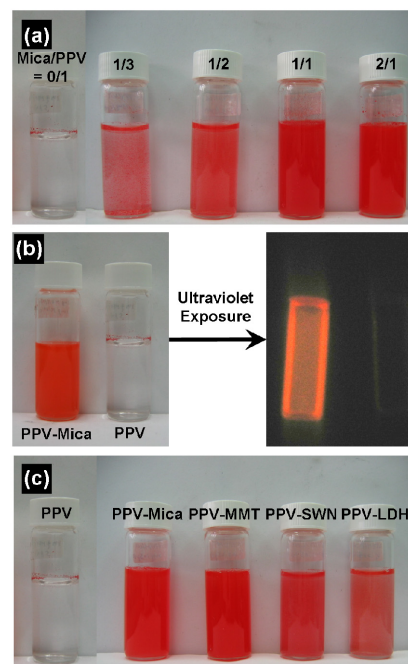


Figure 1. Dispersion of PPV-Mica.

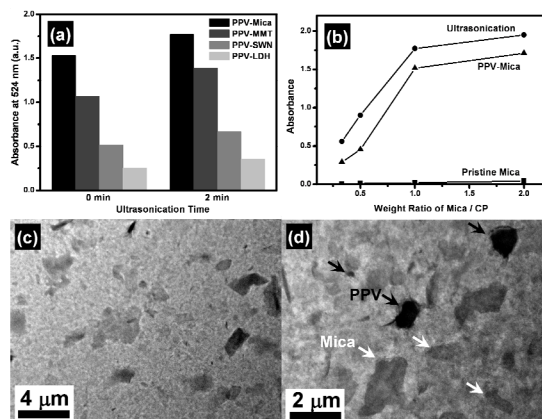


Figure 2. UV-vis and TEM of PPV-clay hybrid

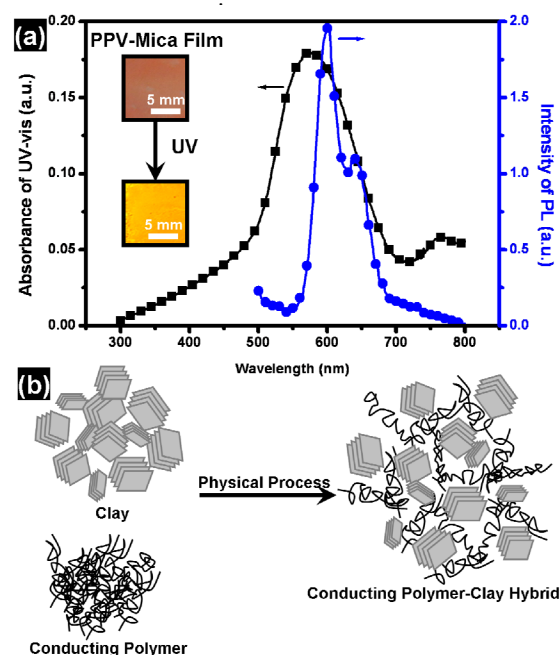


Figure 3. UV and PL of the PPV-Mica hybrid