## Preparation and Evaluation of Composites from Montmorillonite and Some Heterocyclic Polymers. II. A Nanocomposite from *N*-Vinylcarbazole and Ferric Chloride-Impregnated Montmorillonite Polymerization System

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ABSTRACT: The polymerization of N-vinylcarbazole in the presence of FeCl<sub>3</sub>-impregnated montmorillonite resulted in the formation of a poly(N-vinylcarbazole)-montmorillonite composite. XRD analysis of the composite revealed no expansion for  $d_{001}$  spacing, in sharp contrast to that for the same composite prepared in the absence of FeCl<sub>3</sub>. This indicated that the poly(N-vinylcarbazole) was not intercalated in the montmorillonite lamellae but was glued to it in the same way as was polypyrrole in colloidal silica, zirconia, or tin oxide nanocomposite systems. TEM analysis revealed the particle size of the composite to be in the range 30-40 nm. The dc conductivity of the poly(N-vinylcarbazole)-montmorillonite composite was in the range  $(3-5) \times 10^{-5}$  S/cm depending upon the FeCl<sub>3</sub> loading of montmorillonite. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2971–2976, 1999

**Key words:** nanocomposite; montmorillonite; ferric chloride; poly(*N*-vinylcarbazole); conductivity

## **INTRODUCTION**

Nanostructured materials from polymer-clay interaction have drawn considerable research attention in view of the many improved bulk properties of these materials relative to the base polymer. The various preparative methods so far used include (a) direct polymerization of monomer-impregnated clay in the presence of a free-radical catalyst; (b) direct adsorption of the linear polymer onto clay; (c) grafting of polymer onto clay via coupling agents; (d) copolymerization of vinyl monomers with vinyl monomer-montmorillonite (MMT) intercalates; and (e) reactions of derivat-

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Journal of Applied Polymer Science, Vol. 73, 2971–2976 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/142971-06 ized polymers bearing positively charged "onium" moieties with aqueous swollen clay.<sup>1</sup>

Speciality monomers such as pyrrole (PY) and aniline (ANI) were very recently used in conductive nanocomposite dispersion preparations by adding these water-soluble monomers to an aqueous suspension of colloidal silica,  $tin(IV) \text{ oxide},^{2-4}$ and zirconium dioxide<sup>5</sup> in the presence of FeCl<sub>3.</sub> The precipitating polymers were believed to be "glued"<sup>2,3</sup> to the surface of the colloidal particles.

The absence of the *N*-heterocyclic polymers in the long list of polymers so far used in nanocomposite preparations with MMT is conspicuous. In this series, poly(N-vinylcarbazole) (PNVC) is a well-studied polymer of outstanding thermal and photophysical properties<sup>6,7</sup> and, consequently, nanocomposites of PNVC with MMT or other inorganic oxides might lead to materials with interesting properties.

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With this expectation, we undertook the preparation and evaluation of nanocomposites of PNVC with MMT or colloidal silica. In part I of this series, we reported that MMT alone was capable of initiating NVC polymerization directly without any cocatalyst and that a part of the resultant PNVC was retained by the MMT layer as a nanocomposite intercalate.<sup>8</sup> We also reported elsewhere<sup>9</sup> a novel procedure of preparing a conductive dispersion of PNVC-silica using ferric chloride-impregnated silica as a catalyst for NVC polymerization.

In course of this work, the idea occurred to us that the combination of MMT with ferric chloride—itself a potential Lewis acid catalyst for NVC polymerization as well as an efficient dopant for PNVC—might reinforce the catalytic effeciency of MMT toward nanocomposite formation from PNVC and vis-à-vis improve its bulk conductivity. Accordingly, we studied the NVC-ferric chloride-impregnated MMT polymerization system and now highlight in this article some distinctive features in the formation of the PNVC-MMT nanocomposite system compared to the same prepared in the absence of ferric chloride.

## **EXPERIMENTAL**

#### **Materials**

N-Vinylcarbazole (BASF, Germany) was recrystallized from predistilled n-hexane and stored in the dark. Montmorillonite, K-10 (Aldrich, Milawaukee, WI) was used as received. All other chemicals and reagents were of A.R. grades and used after necessary purification by a standard procedure.

#### **Preparation of Catalyst**

 $\rm FeCl_3$ -impregnated MMT powder was prepared by a thorough mixing of an acetone solution of anhydrous  $\rm FeCl_3$  (of known weight) with powdery MMT followed by solvent evaporation under reduced pressure at 50°C.<sup>10</sup>

#### **Polymerization**

The polymerization was carried out by stirring a 5-mL benzene solution of NVC of the desired concentration in a known weight of  $FeCl_3$ -impregnated MMT powder as a heterogeneous catalyst at 50°C in a stoppered Pyrex tube. After a definite polymerization time, the total contents of the re-

action vessel were precipitated in methanol and the precipitate was quantitatively filtered, repeatedly washed with methanol to remove all  $FeCl_3$ , and, finally, washed with boiling methanol to remove any unreacted monomer<sup>11</sup> and dried at 60°C for 7 h.

#### Isolation of the Composite

The precipitated mass, thus isolated in the above procedure, was extracted with benzene through continuous stirring for 30 min. The total contents of the tube were centrifuged and the centrifugate was separated from the residue. The procedure was repeated for various lengths of time, until the extracts did not give any precipitate with methanol. This procedure was expected to dissolve out all surface-adsorbed PNVC.

After subsequent drying of the benzene-extracted mass, an increase in the weight of the catalyst was realized which varied under different conditions. This mass, after various physicochemical characterizations, was confirmed to contain PNVC glued to the MMT layer, forming a nanocomposite and not removable by benzene extraction as observed in other comparable systems so far reported.<sup>1–3</sup>

# Characterization and Property Evaluation of the Composite

FTIR spectra were taken on a Perkin–Elmer Model 883 instrument. XRD analyses were performed on a PHILIPS X-ray diffractrometer Cu LFF 40 kV, 20 mA, with wave lengths 1.54060 and 1.54438. The surface morphologies of MMT and the PNVC–MMT composite were examined by taking scanning electron micrographs on a Hitachi S415A instrument. The particle size of the PNVC–MMT composite was determined by transmission electron microscopy using a Hitachi 600 instrument. dc conductivity measurements were conducted with a Keithley 617 solid-state electrometer using a cell containing a guard ring and stainless-steel electrodes.

## **RESULTS AND DISCUSSION**

#### **General Features of Polymerization**

In the NVC–MMT polymerization system reported earlier,<sup>8</sup> we proposed that the initiation was cationic, occurring through interaction of NVC with Brõnsted acid sites originating through

Entry. No.	Weight of MMT (g)	$\begin{array}{c} \text{Weight of FeCl}_3 \\ (g) \end{array}$	% Conversion to PNVC <sup>a,b</sup>	% Polymer Present in Composite/g <sup>b</sup>
1	0.100		73.6	10.0
2	0.102	0.007	86.0	12.9
3	0.102	0.015	94.0	19.5
4	0.100	0.029	95.6	18.6
5	0.100	0.050	$\sim 100$	с

 Table I
 Loading of PNVC in PNVC-MMT Composite

<sup>a</sup> In each case, polymerization was conducted at 50 °C for 1 h with 0.1M NVC in benzene and the total volume of the reaction system was 5 mL.

<sup>b</sup> Data represent average of three sets of experiments.

<sup>c</sup> Polymer gelled out in the medium as a separate layer and no loading of PNVC occurred in the MMT layers.

the dissociation of the interlayer water molecules coordinated to the exchangeable cations in MMT.<sup>1</sup> Futhermore, in contact with NVC, MMT underwent a typical color change from a light gray to a bluish green shade. We interpreted this<sup>8</sup> as being due to an electron-transfer initiation between the N-lone pair and 3d metal centers present as oxides in MMT.<sup>1</sup> In the present system, since FeCl<sub>3</sub> was a potential Lewis acid initiator for NVC, a substantial yield of PNVC was reasonably expected. However, the relevant point in this context was whether MMT alone also participated in the initiation process. This point will be duly addressed to while discussing the XRD data below.

Table I summarizes some quantitative polymerization data on the NVC-FeCl<sub>3</sub>-MMT system. Comparison of entry 1 in Table I with the other entries clearly endorsed the expectation that the FeCl<sub>3</sub>-impregnated MMT would lead to a larger overall yield as well as to PNVC loading in the composite. As the  $FeCl_3$  loading in the initial feed increased, the PNVC loading in the composite tended to increase. However, beyond a certain FeCl<sub>3</sub> loading, PNVC loading in the composite started to decrease. Most interestingly, at higher FeCl<sub>3</sub> loading (entry 5, Table I), the total PNVC gelled out, and under this condition, the benzeneextracted MMT was found to contain no PNVC. In the light of this observation, it appeared that the observed tendency of the PNVC loading to decrese (entry 4, Table I) despite the overall PNVC yield being higher was an indication of the onset of partial gelation of PNVC at the FeCl<sub>3</sub> amount used in the MMT impregnation.

## Nature of PNVC Loading in the PNVC–FeCl<sub>3</sub>–MMT Composite System

In our preceding publication on the NVC–MMT polymerization system,<sup>8</sup> it was established that a

part of the total PNVC produced in the system existed as a MMT-intercalated PNVC, and the rest, as surface-adsorbed PNVC readily washable by solvent extraction. As evidence, we observed that the XRD spectrum of the PNVC–MMT composite revealed a peak at 14.6 Å usually characteristic of the expansion of the  $d_{001}$  reflection of MMT-based intercalates<sup>1</sup> and another at 9.8–9.9 Å due to unintercalated MMT.<sup>12</sup> Most interestingly, in the PNVC–FeCl<sub>3</sub>–MMT composite system, the XRD spectrum revealed no peak at 14.6 Å but the one at 9.8 Å remained intact. This observation therefore ruled out any intercalation of PNVC in the PNVC–MMT composite.

Conceptually, the observed loading of the precipitating PNVC on the MMT particles reflected a situation essentially similar to the PPY/PANI-FeCl<sub>3</sub>-colloidal silica nanocomposite systems studied in detail by Armes et al.<sup>2,3,13</sup> and also reported in the PPY-FeCl<sub>3</sub>-ZrO<sub>2</sub> system.<sup>5</sup> Relevantly, we recently reported<sup>9</sup> a very similar effect in NVC-FeCl<sub>3</sub>-colloidal silica polymerization/ nanocomposite formation systems where PNVC remained glued to the oxide particles following methanol precipitation of the polymer. A tentative mechanism for the observed stabilization of adsorbed PNVC on the MMT particles could involve electrostatic attraction between the PNVC polycations and the characteristic negative oxide layer charge on the lamellar surface of MMT.<sup>1,12</sup> A suggestion of this nature was also proposed by Armes et al.<sup>13</sup> to explain the formation of stable colloids in PANI/PPY-silica/water nanocomposite systems. The absence of any PNVC-intercalated MMT in the NVC-FeCl<sub>3</sub>-MMT composite was explained by the fact that FeCl<sub>3</sub> was a much faster Lewis acid initiator for NVC polymerization compared to Brönsted acids in MMT and, consequently, the NVC moieties would hardly find any



Figure 1 SEM photographs for (a) MMT and (b) the PNVC–MMT composite.

chance to enter the MMT lamellae for polymerization therein, before which they would be initiated by the  $\rm FeCl_3$  moieties existing along with the MMT particles.

#### IR Characteristics of the PNVC-MMT Composite

A comparison of the IR spectra of MMT, the PN-VC–MMT composite, and PNVC readily endorsed the presence of PNVC in the composite. Peaks common to PNVC and the PNVC–MMT composite that appeared in the FTIR spectrum were 2930 cm<sup>-1</sup> (aromatic C—H assymmetric stretching),1630 cm<sup>-1</sup> (C=C stretching of vinyledene groups), 1600 cm<sup>-1</sup> (ring vibration of NVC moieties), 746 cm<sup>-1</sup> ()CH<sub>2</sub> rocking vibration ), and 725cm<sup>-1</sup> (ring deformation of the substituted aromatic structure).<sup>14</sup> For the PPY–MMT nancomposite, Christopher and Lerner<sup>15</sup> reported three principal peaks for MMT at 1040, 590, and 480 cm<sup>-1</sup> which were also present in the the PNVC–MMT nancomposite FTIR spectra.

#### **Scanning Electron Microscopic Analysis**

A comparative analysis of the SEM photographs for MMT [Fig. 1(a)] and the PNVC–MMT composite [Fig. 1(b)] revealed the preponderence of nonuniform aggregates of particles of mixed-up shapes and sizes for MMT. By contrast, the PNVC– MMT composite SEM exhibited a tendency to form predominantly spherical particles with denser packing.

### **Transmission Electron Microscopic Analysis**

Figures 2(a,b) represent two TEM photographs of the PNVC-MMT nanocomposite prepared in two different experiments. The TEM photograph of MMT powder [Fig. 2(c)] indicated a stringlike particle morphology in distinct contrast to the grossly spherical morphology exhibited by the PNVC-loaded MMT particles. The characteristic change over of the particle morphology was recently observed by us in PPY–MMT<sup>16</sup> and PANI– MMT<sup>17</sup> nanocomposite systems. The typical morphology of these MMT-based polymer systems was reminiscent of the raspberry morphology of PPY/PANI oxide-based nanocomposite systems studied by Armes et al.,<sup>2,3,13</sup> wherein the oxide particles would be present not only on the particle surface but also distributed throughout the interior of the particles. Visually, Figures 2(a,b) revealed that the distribution of the polymer particles in the microaggregate (darker regions) in-





Figure 2 TEM photographs for PNVC–MMT composites of (a,b) two independent preparations and (c) for MMT.

Material	Conductivity (S/cm)	Reference
1. Unmodified PNVC	$10^{-12}$ to $10^{-16}$	[7,18]
Modified PNVC		-, -
2. PNVC–PPY blend	$3.3 imes 10^{-6}$	[19]
3. PNVC–PPY composite	$5.0 imes10^{-2}$	[20]
4. PNVC–PPY ( $FeCl_3/Aq$ )	$(2.2  ext{ to } 3.5)  imes 10^{-3}$	[22]
5. PNVC–Carbon black composite	1.0 - 1.2	[23]
6. PNVC–MMT nanocomposite (no FeCl <sub>3</sub> )	$\sim 10^{-6}$	[8]
7. PNVC–silica nanocomposite	$1.4 imes 10^{-5}$	[9]
8. PNVC–FeCl <sub>3</sub> –MMT nanocomposite	$3.1 imes 10^{-5}(0.0074)^{ m a}$	This study
, I	$5.2 imes 10^{-5}(0.0289)^{ m a}$	·

 Table II
 dc Conductivity of PNVC-Based Composites

<sup>a</sup> Values in parentheses indicate FeCl<sub>3</sub> loading of MMT (Table I).

volving MMT (lighter regions) was nonuniform. The average particle diameter as calculated from the TEM photographs was in the range of 30-40 nm, confirming the formation of nanostructured composite particles.

### **Conductivity Characteristics**

Table II presents the dc conductivity values of  $PNVC-FeCl_3-MMT$  composites along with the same for unmodified PNVC and some PNVC-based materials. Significantly, the PNVC-MMT nanocomposites exhibited appreciably enhanced dc conductivities (10<sup>7</sup>- to 10<sup>11</sup>-fold) relative to unmodified PNVC. Such an improvement in conductivity on nanocomposite formation was clearly established in the PPY-zirconia nanocomposite<sup>5</sup> system and was consistent with the formation of stronger polymer grains in intimate association with the clay particles which should be expected to facilitate conduction.<sup>5</sup>

The conductivity of the PNVC-MMT nanocomposite prepared without any FeCl<sub>3</sub> (entry 6, Table II) was appreciably lower than that in the presence of FeCl<sub>3</sub> (entries 8 and 9, Table II). Further, a three-and-half-fold increase in the FeCl<sub>3</sub> loading of MMT enhanced the conductivity of the composite by about 1.7-fold. Thus, these trends in the conductivity data were consistent with the expected doping effect of FeCl<sub>3</sub>. In a previous work on the NVC-FeCl<sub>3</sub>-toluene-water system,<sup>23</sup> we observed the conductivity of the PNVC to continue increasing up to a certain FeCl<sub>3</sub>/NVC weight ratio, falling thereafter with further increase in the FeCl<sub>3</sub> concentration in the system. It would have been of interest to study the nature of the (conductivity-FeCl<sub>3</sub> loading in the MMT) variation for the present system. Unfortunately,

the onset of gelation of PNVC at a higher  $FeCl_3$  impregnation level became a deterrent factor.

#### Water Dispersibility of PNVC-MMT Composites

To check whether the PNVC-MMT composite could be obtained in a stable aqueous dispersion, the composite was added to an aqueous solution of poly(vinyl pyrrolidone) (PVP), a polymeric stabilizer,<sup>24</sup> and the system was sonicated for 5 h. The resulting suspension was initially stable for a few hours, but on standing, the dispersion gradually became unstable. Relevantly, PPY-MMT<sup>16</sup> and PANI-MMT<sup>17</sup> nanocomposites were able to produce stable aqueous suspensions under similar conditions. The reason for this difference in behavior among PNVC, PPY, and PANI is obscure at the moment, but we feel that the water compatibility of the concerned monomers (pyrrole and aniline-water soluble, NVC-water insoluble) might be one of the factors. Incidentally, we were able to prepare a stable aqueous dispersion of a PNVC-silica nanocomposite under similar conditions.<sup>9</sup> This possibly could be due to the higher dispersibility of colloidal silica in water relative to MMT acting as a more efficient particulate dispersant for the precipitating polymer.

#### CONCLUSIONS

The polymerization of NVC by ferric chloride-impregnated MMT resulted in the formation of a PNVC–MMT nanocomposite, where the PNVC was not intercalated in the MMT lamellae. The composite exhibited a bulk conductivity which was almost  $10^7$ - to  $10^{11}$ -fold higher than the same for unmodified PNVC and could be improved further through the doping action of ferric chloride.

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