

# Intercalative Redox Polymerization and Characterization of Poly(*N*-vinyl-2-pyrrolidinone) in the Gallery of Vermiculite: A Novel Inorganic–Organic Hybrid Material

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**ABSTRACT:** In this article we present the synthesis of poly(*N*-vinyl-2-pyrrolidinone) (PNVP)–vermiculite hybrid material and its characterization by various spectroscopic techniques, X-ray diffraction (XRD), and thermal analysis. The polymer was synthesized by intercalative redox polymerization of the monomer at 110°C, using copper (II) ion-exchanged vermiculite. XRD analysis following intercalative polymerization indicates the presence of two prominent peaks with corresponding *d* (002) spacing of 14.3 (intercalated) and 9.9 (not intercalated) Å, suggesting the formation of a partially intercalated hybrid material. Electron spin resonance studies of the intercalated material show values of “*g*” different from that of the Cu (II)-ion-exchanged vermiculite, indicating that polymer formed in the gallery of vermiculite complexes with the unreacted Cu (II). Thermogravimetric analysis indicates the amount of polymer in the gallery spacing to be ≈20 mass %, which is confirmed by I<sub>2</sub> labeling of the PNVP in the nanocomposite, followed by UV spectroscopy. The IR absorption peaks corresponding to PNVP, along with the XRD and thermal analysis data confirms that the gallery expansion is due to the formation of a partially intercalated inorganic-organic hybrid material. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1825–1830, 2000

**Key words:** hybrid material; nanocomposite; template synthesis; redox polymerization; vermiculite; gallery polymerization

## INTRODUCTION

Much work has been focussed on the synthesis of nanoscopic materials in the past decade owing to its significant contribution to technological applications. Nanostructures are assemblies of bonded atoms that have dimensions in the range of 1 to 10<sup>2</sup> nm. Developing techniques for synthesizing and characterizing ultralarge molecules and molecular assemblies–nanostructures<sup>1</sup> is one of the

grand challenges now facing chemistry. One drive for nanostructures in electronic systems has been toward small, fast devices and high-density information storage. One of the latest areas, which has gained importance in the recent years, deals with the development of methods for synthesizing various nanoscopic materials within the pores/channels/layers/galleries of various mesoporous materials.<sup>2,3</sup> This kind of activity is motivated by the realization that the nanoscale materials exhibit properties that are distinct from those of either of the pure component phases and even distinct from those of the related macro or micro composites. For example, they have improved strength and modulus,<sup>4</sup> decreased thermal expansion coefficient,<sup>5</sup> and enhanced or decreased electrical conductivity compared with the bulk polymer.<sup>6</sup>

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In several of the nanocomposites studied, the host materials are inorganic, rigidly connected lattices that contain layers/channels with sub-nanometer dimensions. They can therefore expand only slightly, without breaking strong bonds, upon nanocomposite formation. These inorganic hosts include a variety of layered compounds and three-dimensional matrices such as zeolites,<sup>7-9</sup> MCM-41,<sup>10,11</sup> montmorillonite,<sup>12,13</sup> ferric oxy chloride,<sup>14</sup> zirconium dioxide,<sup>15</sup> vanadium pentaoxide,<sup>16</sup> ruthenium chloride,<sup>17</sup> layered phosphates,<sup>18,19</sup> silica,<sup>20</sup> clays,<sup>21-23</sup> polycarbonates,<sup>24</sup> molybdenum trioxide,<sup>25</sup> titanium sulphides,<sup>26</sup> organically modified silicates<sup>12,27-29</sup> and other mica-type silicates.<sup>21,22,30</sup>

Polymeric guests having linear and rigid backbones can fit into the available pore dimensions of the hosts. These polymers include polyaniline,<sup>7,10,11,14,16-18,21,22,25</sup> polypyrrole,<sup>8,20,23</sup> and polythiophene.<sup>9</sup> Other nonconducting polymers such as polystyrene,<sup>12,27,28</sup> poly(*N*-vinylcarbazole),<sup>13</sup> poly(*N*-vinyl-2-pyrrolidinone),<sup>30</sup> poly(ethyleneoxide)<sup>6,24</sup> have been incorporated as well. Traditionally, intercalation involves insertion of the monomer followed by radical polymerization<sup>10</sup> as well as aerial oxidation (*in situ* polymerization).<sup>16-20</sup> Other methods include melt polymer intercalation,<sup>27-29</sup> exfoliation-adsorption,<sup>26</sup> template synthesis,<sup>24</sup> and direct intercalation from solution phase.<sup>30</sup>

One of the inorganic hosts of interest in the preparation of nanocomposites has been the silicate family, and in particular, mica-type silicates.<sup>13,22</sup> Mica-type silicates possess the same structural characteristics as other silicate minerals such as talc.<sup>31</sup> Their crystal structure consists of two-dimensional layers formed by the fusion of two silicate tetrahedral sheets. This shares the edge with an octahedral sheet of aluminum. These sheets are stacked one above another and this leads to layered structure and the interlayer spaces are occupied by cations that balance the charge deficiency that is generated due to replacement of certain silicon atoms of the tetrahedron by some aluminum atoms. These ions are hydrated. In this study, vermiculite, a mica-type silicate has been used to synthesize hybrids with nanophase dimensions. Vermiculite is a 2:1 layer silicate with the general formula,  $M_x(\text{Mg})_3[\text{Al}_x\text{Si}_{4-x}\text{O}_{10}](\text{OH})_2$  where  $M$  is the exchangeable divalent cation. The layer charge is close to that of mica but the interlayer cations are magnesium ions. It is present in nature as large crystals and in the natural samples magnesium cations lie in the plane midway

between adjacent layers with one plane of water molecule on either side with a basal spacing of 14.3 Å. The most important characteristics of these silicates are that the magnesium ions can be exchanged by other cations and in the case of sodium, two well-defined hydrates exist. The two-layer hydrates have a spacing of 14.8 Å and the one-layer hydrate has a spacing of 11.8 Å. Typical cation exchange capacity encountered is approximately 100 milliequivalents per 100 g of silicates. Completely dehydrated samples give a basal spacing of 10 Å, similar to that of mica. Fully calcined vermiculite has a water absorption capacity of 200–500 g per g of vermiculite depending on the particle size.

The motivation behind the current work was to prepare vermiculite-poly(*N*-vinyl-2-pyrrolidinone) (PNVP) nanocomposite and characterize it. To this end, *N*-vinyl-2-pyrrolidinone was polymerized in the gallery of vermiculite by redox polymerization using Cu(II) ion exchanged vermiculite. Cu(II) initiated polymerization of aniline in the gallery of fluorohectorite has been reported earlier.<sup>22</sup> The novelty of this work arises from the fact that (1) polymer intercalation in the gallery of vermiculite; (2) redox polymerization in the gallery using ion exchanged silicates; and (3) polymerization of NVP in the gallery to obtain the nanocomposite has not been reported so far, although a recent communication describing direct intercalation of PNVP in kaolinite has appeared.<sup>30</sup> The nanocomposite is expected to absorb water, organics, as well as a mixture of organics in water and function selectively in metal ion adsorption, based on the properties exhibited by the individual components. In addition, the nanocomposite should offer a specific advantage, namely accessibility to individual phases which is absent in the case of the micro and the macro composite.

## EXPERIMENTAL

### Materials

Calcined vermiculite was a generous gift from Femnor Minerals, Chennai, India and was heat-treated at 100°C for 24 h before use. *N*-vinyl-2-pyrrolidinone (Acros Organics, Belgium) was vacuum distilled over anhydrous calcium chloride. *p*-xylene (S. D. Fine Chemicals, Chennai, India) was dried over anhydrous calcium chloride distilled and stored over 4 Å molecular sieves. Copper (II) chloride (S. D. Fine Chemicals) was used

without further purification. PNVP (BDH) was used as received. Acetone and methanol (Qualigens) were used as received.

### Methods

Powder X-ray measurements were performed using a Seifert XRD P3000 with Ge curved crystal monochromator Cu-K $\alpha_1$  radiations of wavelength 1.504 Å. Thermal analyses [thermogravimetric (TGA) and differential scanning calorimetry (DSC)] were performed using DuPont's 2950 Thermal Analysis System, between ambient and 700°C at a heating rate of 10°C per min under nitrogen atmosphere. IR spectrum (KBr) was recorded using a Shimadzu IR 470 spectrometer. Electron spin resonance (ESR) measurements were performed using a Varian E -112 X/Q band spectrometer operating at 9 GHz with a 100-kHz modulation. All the experiments were performed at X band. Mate ARL 3410, inductively coupled plasma (ICP) analyzer with mini torch was used for metal analysis. UV measurements were performed using a UV-240 Shimadzu spectrophotometer.

### Preparation of Copper (II) Vermiculite [Cu (II)-V]

To 0.1 g of vermiculite, dried at 100°C for 24 h, was added to 100 mL of 1 M copper (II) chloride solution. The mixture was boiled at 100°C for 48 h. The solution was then cooled, filtered, and rinsed with water until the filtrate was no longer blue in color. The residue was finally rinsed with acetone and dried at 100°C for a few hours before use.

### ICP Analysis of Cu(II)-Vermiculite

Two hundred fifty milliliters of 1 M Cu(II) chloride was prepared and boiled with 100 mg of vermiculite. Appropriately diluted original solution and the filtrate obtained following the exchange reaction were analyzed by inductively coupled plasma spectrometry. The Cu(II) concentration was 351.2 ppm before the exchange and 332.9 ppm after exchange suggesting that the Cu(II) exchange capacity of the vermiculite used is 0.76 milliequivalents per g of vermiculite.

### Redox Polymerization of *N*-vinyl-2-pyrrolidinone

To 0.1 g of Cu(II)-V suspended in *p*-xylene medium was added 2 mL of *N*-vinyl-2-pyrrolidinone. The mixture was heated at 120°C with constant

stirring for 24 h. It was allowed to cool to room temperature, filtered, and rinsed with methanol to remove any adsorbed polymer. The residue was finally rinsed with acetone and dried at 75°C for a few hours before use.

### Preparation of Iodine Complex with PNVP and the Estimation of PNVP in the Nanocomposite

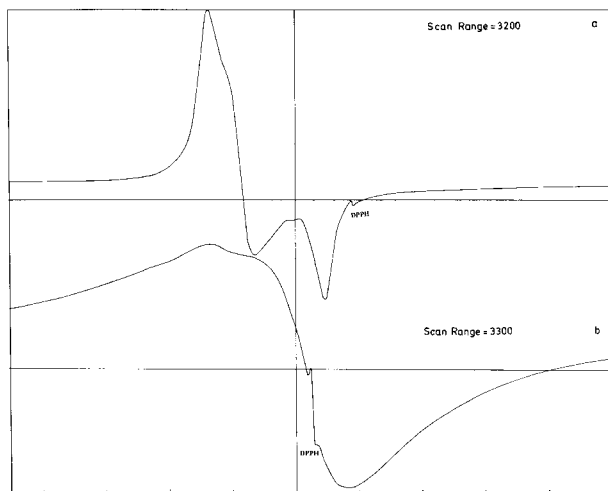
To 300 mL of carbon tetrachloride, 44 mg of iodine was added and this was allowed to stir at room temperature for 10 min. Its absorbance at 521 nm was recorded. To this solution, PNVP was added in increasing amounts after suitable intervals and the absorbance was rerecorded, continuously. A calibration graph of absorbance versus the amount of PNVP was obtained from this experiment. The absorbance of the polymer in the hybrid material was obtained by adding 48.4 mg of the nanocomposite to a solution consisting of CCl<sub>4</sub> (300 mL) and I<sub>2</sub> (44 mg) and the absorbance was found to be 0.548. From the calibration graph, the amount of PNVP in the hybrid material was evaluated.

### Recovery of the Polymer from the Hybrid Material for UV Spectrophotometry

The hybrid material containing the polymer was dissolved using concentrated sulphuric acid to destroy the silicate matrix. The excess acid was neutralized using sodium hydroxide, to neutral pH. The aqueous layer was rinsed with chloroform to remove any organic soluble impurities. Its UV spectrum was recorded.

## RESULTS AND DISCUSSION

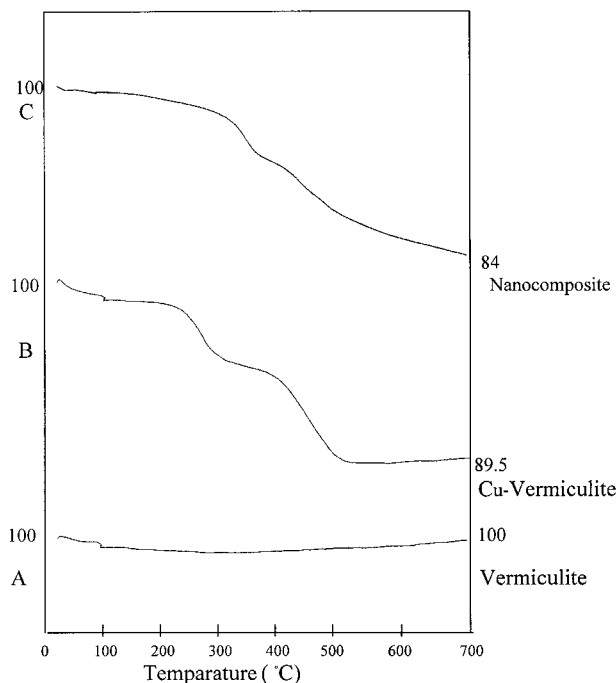
We envisaged that replacing divalent cations (Mg<sup>2+</sup>) in the gallery of vermiculite with Cu(II) could bring about the redox polymerization of *N*-vinyl-2-pyrrolidinone analogous to results reported earlier for the polymerization of aniline in the fluorohectorite gallery.<sup>22</sup> To this end, the divalent cations in the gallery were replaced by Cu(II) as reported in Experimental. ICP analysis following Cu(II) exchange indicated that we have introduced 0.76 milliequivalents of Cu(II) per g of vermiculite (which is less than the maximum expected value of 1). To confirm Cu(II) substitution, ESR was performed. The ESR spectrum is shown in Figure 1, trace a. It shows the resonance components for both  $g_{\parallel}$  and  $g_{\perp}$  observed for Cu(II) ion



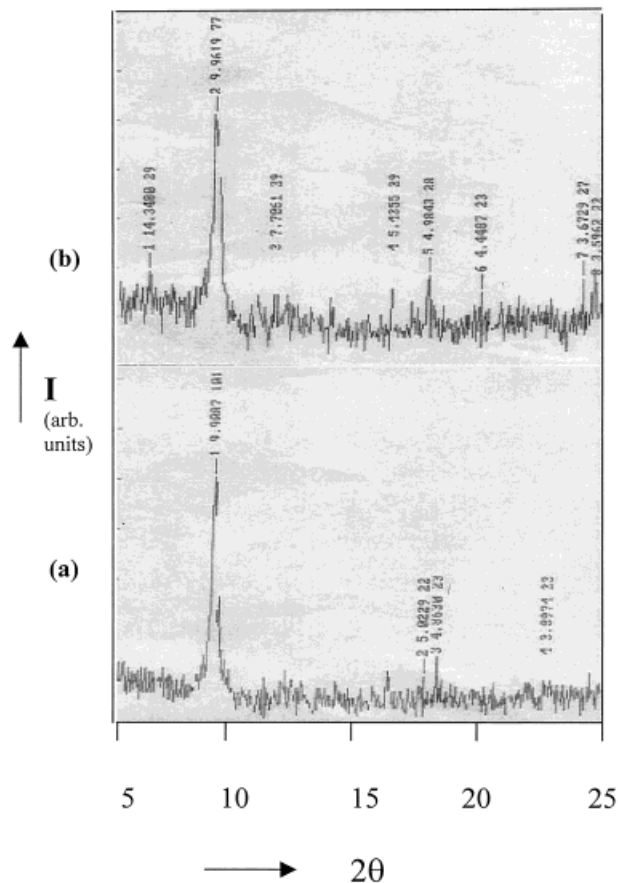
**Figure 1** ESR spectrum of Cu(II)-vermiculite (trace a) and the nanocomposite (trace b).

under the conditions in which three layers of water occupy the gallery.<sup>32</sup> The  $g$  value for Cu(II)-V was calculated to be 3.224, 2.741, and 2.168. ESR thus confirms the presence of copper in the gallery of vermiculite.

The TGA of vermiculite is shown in Figure 2, trace A. The mass loss in the range from ambient to 100°C is 16  $\mu\text{g}$  and from 100 to 200°C is 6  $\mu\text{g}$



**Figure 2** TGA of vermiculite (trace A), Cu(II)-V (trace B), and the nanocomposite (trace C).



**Figure 3** XRD of vermiculite (trace a) and the nanocomposite (trace b).

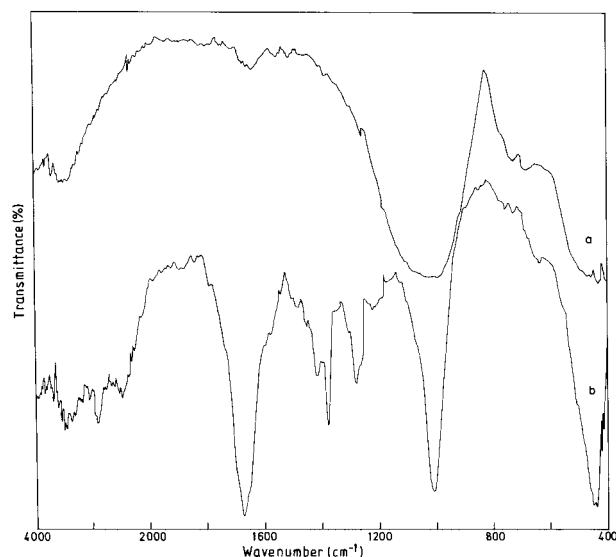
out of a sample size of 6.176 mg, suggesting that very little amount of water molecules are present in between the silicate layers. In the case of Cu(II)-V, the significant mass losses are in the range 200 to 300°C (approximately 3 mass %) and 350 to 500°C (approximately 6 mass %). We attribute this to the water of hydration in Cu(II)-vermiculite (shown in Fig. 2, trace B) and the water molecules must have entered the gallery during the ion exchange process.

Following the redox polymerization in the gallery of Cu(II)-V the XRD analysis indicates the presence of a new peak corresponding to a  $d$  spacing value of 14.3 Å; the peak corresponding to a  $d$  spacing value of 9.9 Å due to unmodified, calcined, vermiculite is observed as well, over and above the change due to intercalative polymerization. This is shown in Figure 3, traces a and b. The observed expanded dimension along the stacking direction ( $d = 4.4$  Å) suggests the formation of the intercalated nanocomposite due to partial expansion of the gallery spacing.<sup>17,29,33</sup> The observed

increase of 4.4 Å is consistent with the picture that the polymer chains are oriented parallel to the silicate layer. We attribute this to the fact that smectites (montmorillonite, vermiculite, hectorite) have lower charge density compared with the fluorohectorites and when the monolayer of the polymer is placed parallel to the axis, the interaction between the silicate layer and lone pair of electrons on the nitrogen as well as the  $\pi$  cloud on the carbonyl is maximized.<sup>34</sup>

The thermogravimetric analysis of the nanocomposite (Fig. 2 trace C) was performed to establish the presence of the intercalated polymer, quantitate the amount of the polymer in the gallery, as well as to study any change in thermal degradation behavior upon intercalation. The TGA of the nanocomposite indicates two major mass loss peaks; one between 250 to 350°C and the other between 350 to 700°C. This is attributed to the thermal degradation of the intercalated polymer consistent with the observed thermal degradation of the homopolymer of PNVP (data not shown). It is to be noted that the weight loss peaks due to the water of hydration in Cu(II)-V disappear on intercalation, suggesting that the metal ion could be one of the possible centers for initiating the intercalative polymerization. The mass loss rate for the intercalated polymer is smaller than that of the unintercalated polymer, particularly above 400°C, suggesting that the host functions to slow down/inhibit the thermal degradation of the polymer. We have observed this with other intercalated polymers such as poly(2-vinylpyridine), poly(4-vinylpyridine), and polyaniline intercalated in the gallery of vermiculite. From the TGA data, we infer that the wt % of the polymer intercalated to be approximately 20%. The DSC of the nanocomposite (data not shown) shows a broad endotherm beginning from 160°C and is essentially featureless.

Polymerization in the gallery was also confirmed by IR spectroscopy. In the case of vermiculite, the prominent peaks due to Si—OH stretching and Si—O stretching appear at 3700  $\text{cm}^{-1}$  and 1020  $\text{cm}^{-1}$ , as shown in Figure 4, trace a. In the case of the nanocomposite, prominent peaks due to PNVP are seen at 3088  $\text{cm}^{-1}$  (aromatic C—H), 2928  $\text{cm}^{-1}$  (aliphatic C—H), 1673  $\text{cm}^{-1}$  (C=O) in addition to the peaks of vermiculite, as shown in Figure 4, trace b. It is also seen that the peaks in the nanocomposites due to Si—O and Si—OH stretches appear much sharper than the peaks of pure vermiculite. This can be correlated to the replacement of loosely held water mole-



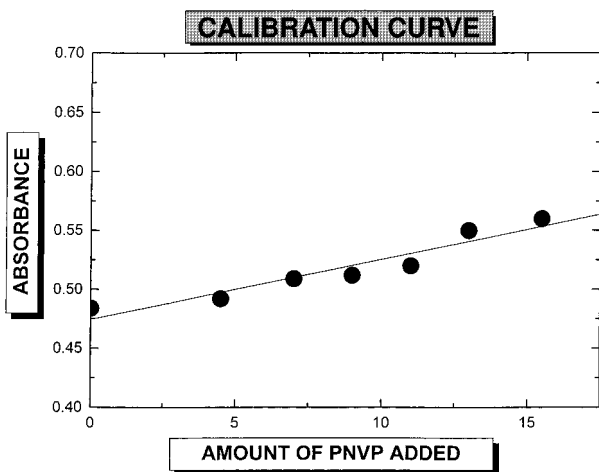
**Figure 4** IR spectrum of vermiculite (trace a) and the nanocomposite (trace b).

cules in the gallery by the polymer and thereby reducing the capability to form extensive hydrogen bonding. The ESR spectra of the PNVP-vermiculite nanocomposite is shown in Figure 1, trace b. It is seen that the nanocomposite has some amount of unreacted copper which complexes with the polymer formed in the vermiculite gallery, as evident from the different "g" values obtained. The "g" values were calculated to be 2.8585, 2.5222, 2.0418, and 1.8324.

The UV spectra of the intercalated material (data not shown) were recorded to confirm the presence of PNVP in the gallery (the details are presented in Experimental). The  $n-\pi^*$  transition observed with the polymer from the nanocomposite at 198 nm, matches exactly with that from the reference polymer sample. This confirms that the intercalated polymer is PNVP. A calibration curve was drawn with the absorbance versus amount of PNVP data, as shown in Figure 5. The absorbance value for the nanocomposite was found to be 0.548, which indicates that 29.5 mass % of the polymer is present in 100 mg of vermiculite, a value greater than the 20 mass % observed by means of TGA. We attribute this to the error associated with the serial (continuous) dilution technique used in this method and estimate the error to be approximately 5%.

## CONCLUSION

Exchangeable magnesium cations present in the gallery of vermiculite is exchanged successfully



**Figure 5** UV absorbance versus the amount of PNVP added.

with Cu(II) ions. The exchange capacity is found to be 0.76 milliequivalents per g of vermiculite. Cu(II) present in the gallery is used to polymerize NVP by redox *in situ* polymerization. XRD, TGA, UV, and IR measurements confirm the formation of the polymer-vermiculite nanocomposite with partial intercalation. Further, the XRD analysis indicates parallel orientation of the polymer chain to the silicate layer upon intercalation. The amount of polymer intercalated is found to be 20% of the net weight of vermiculite. With the special property of vermiculite to absorb water and that of PNVP to absorb water and organic solvents, this inorganic-organic hybrid material should find use as a novel water-treatment material.

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