Variable morphologies of poly(vinyl acetate)–montmorillonite nanocomposites obtained by emulsion polymerization in the presence of poly(vinyl pyrrolidone)

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Abstract: Nanocomposites containing poly(vinyl acetate) and montmorillonite (MMT) were prepared using a one-batch emulsion polymerization recipe, assisted by poly (vinylpyrrolidone). The relative clay concentration with respect to the other reaction partners influences drastically the morphological units in the end-products. For low [MMT], well-defined, spherical PVAc particles are formed. At the other extreme, for high [MMT], production of polymeric, water-swollen aggregates is favored. Depending on the MMT/PVP ratio, the clay will be dispersed in the final polymer matrix in variable forms, from individual platelets to agglomerates of reformed tactoids.

Introduction

The field of layered inorganic-organic nanocomposites has grown in a fast tempo in the last two decades. In the quest for new materials with tunable properties, researchers’ attention was caught by various options to manipulate the morphology in the end-products if one uses clay in the starting recipe [1-4]. Naturally, in this case, the dispersion state of the clay becomes very important. At low clay content, exfoliated nanocomposites could be prepared. In such composites, a continuous, more or less thick polymer matrix separates individual clay platelets. As the inorganic load becomes higher, flocculated and / or intercalated hybrids can be eventually formed.

To achieve any of these three morphologies, one can use the 2:1 layered silicates: montmorillonite, hectorite and saponite. Montmorillonite (MMT) is a hydrated alumina-silicate clay composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The silicate layers of MMT are planar, stiff, ~ 10 Å in thickness, about 2000 Å in length. In nature, the MMT clays do not occur as isolated individual units but as crystalline structures (also known as tactoids) formed by aggregation [3, 5-8].
In this paper, we explore the possibility to obtain polymer-MMT hybrids using an one-batch recipe, with growing of the polymeric phase via a radicalic (emulsion) polymerization, after dispersion of the MMT tactoids in water. The starting monomer is vinyl acetate (VAc) and the reaction is assisted by a water-soluble, polar polymer: PVP - poly (vinylpyrrolidone).

The pigment-dispersing ability and specific polymer – inorganic interactions generated a significant number of publications focused on the adsorption of poly (vinylpyrrolidone) onto clay minerals [10-20] and other oxides [21-24]. Also, due to its good biocompatibility, PVP proved to be a successful blood plasma extender [25]. In other therapeutic applications, PVP is added to oral drugs as excipient [26]. Spray-dried products, obtained from various formulation, some based on a recipe with emulsion polymerized PVAc [27], are widely used as well.

Our study could be seen as an attempt to have a closer look into the different morphologies that can be generated in the end-products if the additive (in this case a clay) is temperature resistant, water-insoluble and could arrange itself in lamellar phases.

**Results and Discussion**

**PVP-clay mixtures**

One of the most used techniques to investigate clay-polymer interactions is XRD, since it provides a look into the extent of platelets crystalline-like ordering and, for clay-organic mixtures, a clue as to organic incorporation by the $d$(001) basal spacing.

![XRD patterns for clay/PVP mixtures (different weight ratios).](image)

**Fig. 1.** XRD patterns for clay/PVP mixtures (different weight ratios).

For the dry NaMMT, the peaks at 12.5 Å and 4.00 Å correspond to (001), respective (110,020) reflections (see Fig. 1).
The lack of diffraction peaks in samples with PVP and low cloisite content indicates the dispersion of tactoids as single-units and the fact that there is enough excess PVP between individual clay platelets as to prevent reformation of crystalline-like arrangements. As the NaMMT / PVP is increased, a weak peak at ~ 35.1 Å becomes visible in the XRD data. For even higher inorganic / polymer ratios, a stronger diffraction at ~ 28.3 Å is measured.

Similar trends of the XRD patterns were reported also in [20]. In their study, Blum and Eberl were interested in the absorption of PVP onto smectites and investigated many samples, with low- and high-charge of the platelets [20]. The shifts in the XRD peaks were explained based on a simple structure, with stacking of 12.5 Å clay crystals (10 Å - 2:1 silicate layer + 2.5 Å due to hydration of the surface) with either one or two PVP layers (see Fig. 7 in [20]). Our NaMMT behaves similar to the Kinney – sample in [20], a high-charged smectite. Considering the 35.1 Å peak associated with a double polymer layer sandwiched between platelets, we can calculate an average of 11.3 Å per PVP-layer thickness, which is in good agreement with 11 Å calculated by Blum and Eberl [20]. More important is the conclusion reached by these researchers, namely that: “The insensitivity of the absolute mass of PVP sorbed on the chain length indicates the PVP chains are lying parallel to the silicate surface, so that the area covered per polymer is approximately proportional to the polymer length. The large area covered by each PVP polymer, coupled with the apparent lack of sensitivity of PVP sorption to the details of surface chemistry, layer charge or solution pH, suggest the interaction between adjacent PVP chains is a major factor in the formation of the surface layer. However, there is no indication of the addition of more than an ~11 Å thick layer of PVP to the surface, suggesting that the surface also plays an important role in the formation of the PVP layer, and that this is not a surface-precipitation-type process.”

The XRD peaks at 28.3 Å and 35.1 Å (Fig.1) also suggest the formation of two different types of structures: ‘intercalated’, respective, ‘intercalated-and-flocculated’ in the PVP-cloisite dried mixtures.

The changes in the basal spacing are a clear indication that the organic has been incorporated within the interlayers during clay’s reformation of the crystalline-like arrangements. DSC and TGA give more evidence for this organic uptake.

Polymer contacts with the clay are sensitive to the local polarity and specific interactions. Differences in the chain mobility would be expressed in differences in the glass transition, as measured with differential scanning calorimetry (DSC).

**Tab. 1.** Summary of the DTG results on NaMMT – PVP mixtures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>T(°C) maximum degradation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVP</td>
<td>458</td>
</tr>
<tr>
<td>M-0.2</td>
<td>460</td>
</tr>
<tr>
<td>M-0.4</td>
<td>466</td>
</tr>
<tr>
<td>M-1.0</td>
<td>468</td>
</tr>
<tr>
<td>M-2.0</td>
<td>472</td>
</tr>
</tbody>
</table>
For very low content in NaMMT (like in the mixture \textit{M-0.2}), the DSC curve is almost identical with a DSC-recording on pure PVP. The process is characterized by a lot of relaxations which can be attributed to different glass transition of amorphous PVP depending on a variable molecular weight as seen in TGA-DTG analyses. The glass transition of the pure PVP at $M_w = 40000$ is about 150°C where a fast relaxation of the macromolecular structure was registered on the DSC curves (Fig.2). However the DSC curves were repeated several times by cooling the samples and the reanalysed and the existence of different molecular weight was again evident by the presence of a lot of relaxation processes. All the transitions are however influenced by the clay content, all the transitions are shifted towards higher temperature, which is a clear effect of the reduced mobility of the macromolecular chains.

Another observation from the DSC curves refers to the increasing of the bonded water with the clay content. All the studied systems showed a starting endothermic process after 100°C which can be attributed to the bonded water. The process is shifted towards higher temperatures as the amount of clay increases in the materials (Fig.2).

![DSC heating curves for clay/PVP mixtures.](image)

**Fig. 2.** DSC heating curves for clay/PVP mixtures.

The thermal stability of PVP with clay, determined by TGA as weight loss during a programmed heating, was found to increase with the cloisite content (Table 1). The TGA curve for pure PVP shows that the maximum degradation rate is attained at around 458°C (Fig.3a). When temperature increases beyond ambient level, the polymer loses first the hydration water (at T<100°C). Even after the long drying time used in preparations, one cannot remove completely this physically bonded water.
The total amount of it is around 9% (Fig. 3a), which is in agreement with earlier published data [28], reporting a similar value (70°C) as for the hydration of the PVP chains around 10%.

Fig. 3. Thermogravimetrical TGA (full lines) and derivative DTG curves (dotted lines) for pure PVP-40T (a) and for the clay/PVP mixture M-2.0 (b).

Also, the commercial PVP-40T could contain small fractions of chains with lower-than-average and, respective, higher-than-average molecular weight. In the derivative DTG curve (Fig. 3a) these small fractions generate two contributions: at 382°C and, respective, 560°C, on the two sides of the maximal degradation temperature (458°C). These macromolecules could interact selective with the clay.

Inspecting the DTG curves for the PVP-clay mixtures, we find again a gradual increase in thermal stability with the growth in inorganic content, but the two contributions present on the sides' maxima are not so evident anymore. This could mean that the interaction is not as selective as was presumed. However for M-2.0 (see Fig. 3b), the DTG curve in the temperature range 400°C to 550°C is still a convolution of two contributions. The bonded PVP is more stable and its contribution has a maximum at 472°C.
Hybrids (containing PVAc)

During the preparation of hybrids, both the clay and the growing PVAc particles will compete for the PVP. In the emulsion polymerization without NaMMT, PVP will act as a stabilizing agent for the PVAc particles and the end-product will be a PVAc latex with well-dispersed particles, covered by PVP chains. Due to PVP’s good solubility in water, one would expect the stabilizing layer created by this polymer to be like a polymer-brush. The hydrodynamic diameter of these particles (measured with DLS) was found to be around 180 nm (Fig.4). Water removal during film drying, even at the slow rate used in the present work, generates the contraction of the matrix which implies tension in the film and the so-created morphology does not preserve the spherical shape of the PVAc particles. Instead, ellipsoidal shapes are seen in the scanning electron microscopy (SEM) images – see Fig.5a. After fracturing the films because of contraction and the hardness differences between phases the ellipsoidal shapes are induced.

Adding NaMMT in the preparations induces a distribution of the PVP between: (i) the bonded-state, where this polymer is adsorbed onto the cloisite platelets and (ii) the free-state. The last one plays an important role for the emulsion polymerization of PVAc, since the amount of free-PVP decides the amount of polymer that can be stabilized at the water interface. The less the content in free-PVP, the bigger the resulting spheres (Fig.4).

![Hydrodynamic diameter vs cloisite/PVP ratio](image)

**Fig. 4.** Average diameter for the PVAc particles, measured with dynamic light scaterring (DLS).

Moreover, the morphology in the fractures of the hybrid films (as inspected with SEM) shows important modifications, clearly depending on the amount of Na-MMT used in the initial formulations. While for hybrid H-0.1 one can easily recognize the spherical PVAc particles and small reformed clay tactoids (see the middle of Fig.5b), the fracture of H-0.2 has a reduced population of spheres and a rather extended region without obvious PVAc particles (see Fig.5c). The morphology in the film at high loads of cloisite (like in H-0.5, Fig.5d) has no evidence of spheres; instead, rather large tactoid agglomerates stick to a smooth polymer matrix. After fracturing, the surface big agglomerates are present like the one focused in the Fig.5d, which generates...
bigger domains of the preferential deformation. These big aggregates were predictable if we check the DLS results (see Fig.4 at high content of clay). Since all the films have an identical fabrication history, the differences in the SEM images could only be explained by a variation in the film-building units.

![Fig. 5. Scanning electron microscopy micrographs for the hybrids: H-0, without clay (a) and H-0.1 (b), H-0.2 (c), H-0.5 (d), all in fractures.](image)

Another interesting observation is the fact that, at low or medium cloisite/PVP ratios, a spherical shape imprint of the PVAc latex particles is preserved also in the dried state. These findings point towards the presence of individual or very small agglomerations of cloisite lamellae in the PVP stabilizing layer. Using transmission electron microscopy, one can see the clay platelets surrounding the PVAc particles (Fig.6a-b).

The shift in the emulsion polymerization equilibrium can be spotted also from kinetics data. Based on the VAc conversions at different moments from the beginning of the polymerization, we were able to calculate the reaction rate and found that it has a dependence on the amount of Na-MMT in the recipe. At high enough MMT
concentrations, the growing oligomeric PVAc radicals can be affected by degenerative transfer reactions with the mineral crystals edges [29], hence decreasing the reaction rates. Another explication of the reaction rates decreasing at high concentration of clay, could be also the physical barrier effect of the clay present in the media.

**Fig. 6.** Transmission electron microscopy images for the hybrids: H-0.2 (a) and H-0.3 (b). The arrows indicate 'exfoliated' and the brackets: 'flocculated and intercalated' structures.
**Fig. 7.** The maximal reaction rate of the VAc-polymerization in the presence of added Na-MMT.

**Fig. 8.** Thermogravimmetrical TGA (full lines) and derivative DTG curves (dotted lines) for a PVAc latex prepared only with PVP, like in recipe: H-0 (a) and for the nanocomposite H-0.5 (b).
Tab. 2. Summary of the DTG results on hybrids.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>T(°C) maximum degradation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-0.0</td>
<td>360</td>
</tr>
<tr>
<td>H-0.1</td>
<td>360</td>
</tr>
<tr>
<td>H-0.2</td>
<td>360</td>
</tr>
<tr>
<td>H-0.3</td>
<td>360</td>
</tr>
<tr>
<td>H-0.5</td>
<td>367</td>
</tr>
</tbody>
</table>

The existence of structural differences in the nanocomposites is well reflected in their thermal properties (see Figs. 8 and 9 and Table 2). In the presence of MMT, the polymers thermal degradation is retarded. Both, the PVAc contribution (see the DTG curve in Fig. 8b, temperature range < 300°C) and the PVP contribution (ibidem, temperature range between 300°-500°C) are shifted compared with the hybrid without clay (Fig. 8a).

An even more obvious effect of different morphologies is seen in the DSC curves (Fig. 9). For the PVAc latex with PVP and no clay, the DSC curve shows a $T_g$ (PVAc) = 52°C, much higher than the normal glass transition ($\approx 27.5°C$) of PVAc prepared with low molecular surfactant [30]. After the melting of PVAc (endothermic peak at 58°C) the DSC curve has all the elements already seen for pure PVP (see the comments for Fig. 2).

Fig. 9 DSC heating curves for hybrids.
For low [MMT], the DSC curve of the hybrids does not have major modifications. However, for the highest clay/PVP ratio (=0.5) used in the present study, one finds two important modifications: (i) an additional glass transition step at around 27°C and (ii) an endothermic process which starts around 100°C. As discussed already, this second effect is attributed to the bonded water (see also in Fig.2). The appearance of a secondary glass transition indicates that the PVAc polymerization has generated shorter polymeric chains, which are not protected by PVP against temperature-induced conformational changes. The evident transition (at 27°C) which appears at high clay content is in good correlation with the induced morphology observed in SEM section (Fig.5d). These observations can be explained by the precipitant emulsion polymerization theory for VAc. As the surfactant is “consumed” in the interaction with the clay the systems do not preserve enough free surfactant to assure the latex stability (see also in Fig. 4) and that is why a second phase of “pure” PVAc appears which has a T_g unaffected by the PVP or clay interaction.

Based on all the above-presented data obtained with several experimental techniques, in the wet phase (DLS) and dried films (SEM, TGA, DSC and XRD), one can advance a coherent scenario that explains all the experimental findings.

In normal emulsion polymerization of vinyl acetate with PVP, at the end of the reaction, a good dispersion of spherical particles is obtained. These particles show a rather narrow size distribution and have an average hydrodynamic diameter \( \approx 180 \) nm. Casting films from these PVAc latexes will result in a solid with a rather regular structure, where the PVAc particles are deformed to ellipsoidal (i.e., acicular) shapes and are embedded in a PVP matrix (see Fig.5a).

If increased amounts of Na-MMT are added in the formulations, the strong affinity of the PVP for the clay platelets drives the equilibrium during the radical polymerization into significant deviations from the result obtained without clay.

Due to clay-PVP initial coupling, there is less PVP left in the aqueous phase (hence the DSC, SEM and DLS results on mixtures, Fig. 2, 5 and 4). This turns the balance during the polymerization towards formation of larger latex particles or even PVAc spheres with a high water/polymer ratio. These last entities are more close to super-swollen polymer aggregates than to classical, dense polymeric spheres. Such entities will have larger diameters (see the DLS result for formulation H-0.3) and will shrink and fuse very easily when dried (see SEM image in Fig.5c, H-0.2).

In the extreme case when (almost) all PVP chains are used in the interaction with cloisite, the PVAc polymerization will proceed as a ‘stabilizer-free’ reaction. Since the VAc monomer has a relative high solubility in water: \( \sim 2 \% \), the polymerization will start directly in the aqueous phase. Further, after the initial oligomers have been grown beyond a critical length, they collapse in aggregates. When the dimensions of these aggregates exceed the buoyancy limit, they phase separate (as seen for the formulation H-0.5, see Fig. 4). Since there is no stabilization layer in films cast from H-0.5, the PVAc chains can interpenetrate and the final morphology in the dried state comprises more or less reformed NaMMT-tactoids in a polymer, smooth matrix (see Fig. 5d).

Conclusions

In the present study, polymer-clay nanocomposites were synthesized by a simple emulsion polymerization technique, using smectic clay modified by interaction with PVP. By modifying the MMT / PVP ratio, one can incline the reaction equilibrium in
different directions. As a result, in the final dispersions, the morphological units could belong to a variety of forms, spread between: well-defined, spherical VAc particles covered with PVP-protective layers at one extreme (i) and, at the other extreme, a mixture of PVAc, water-swollen aggregates and PVP-clay complexes (ii). At intermediate clay concentrations, combinations will be found. In dried films, the final structure is a reminiscence of the morphological units obtained at the end of the radical reaction.

**Experimental**

**Materials**

Sodium-montmorillonite (Cloisite Na-MMT) was generously donated by Southern Clay Products, Inc., USA and do not contain any modification agent from the provider specifications. Vinyl acetate (VAc, Chimopar - Romania) was purified by rectification Poly(vinylpyrrolidone) - PVP-40T, with average $M_w=40000$, was provided by Sigma-Aldrich. This polymer and the initiator of the VAc radicalic polymerization: the ammonium persulphate (from LOBA-Feinchemie), were used without further purification.

**Formulations**

When clay-organic recipes were prepared, different amounts of Na-MMT were first mixed with water and equilibrated at room temperature, under stirring, for 1 h., before adding the PVP (as 10 % solution in water). The *so-obtained* dispersions were kept under stirring for another 5 h.

**Tab. 3.** List of all the samples investigated and stability (in time) if left undisturbed after preparation.

<table>
<thead>
<tr>
<th>Series</th>
<th>Index of the formulation</th>
<th>VAc monomer (g)</th>
<th>Clay / PVP (ratio based on wt.)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mixtures</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-0.2</td>
<td></td>
<td>0</td>
<td>0.2</td>
<td>Depending on the clay amount, a yellow precipitate forms in 2-4 days</td>
</tr>
<tr>
<td>M-0.4</td>
<td></td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>M-1.0</td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>M-2.0</td>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td><strong>Hybrids</strong></td>
<td></td>
<td>20</td>
<td>--</td>
<td>Stable for over 1 year</td>
</tr>
<tr>
<td>H-0.0</td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>H-0.1</td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>H-0.2</td>
<td></td>
<td></td>
<td>0.3</td>
<td>Very slow precipitation after 3 months</td>
</tr>
<tr>
<td>H-0.3</td>
<td></td>
<td></td>
<td>0.5</td>
<td>Phase separation already after 1 week</td>
</tr>
<tr>
<td>H-0.5</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
For complete formulations, the next step was to increase the temperature at 65°C, add a fixed amount of monomer (VAc, 20 g) and initiator (0.25 g APS). For kinetics determinations, small aliquots were taken and analysed every 15 min., during the entire reaction time (6 h).

After preparation, aliquots were taken from all the wet phases, deposited on poly(ethylene) sheets and dried at room temperature (25°C), under a mild nitrogen stream, for 2 weeks, followed by 24 h. drying under vacuum. Before measurements in the resulting dried state, the poly(ethylene) substrate was peeled off.

NOTE: In the text, the mixtures are indexed with M and the complete nanocomposites with H, followed by the clay/PVP ratio, according to Table 3.

Techniques

Monomer conversion (during polymerization) was calculated based on gravimetric measurements of the PVAc phase, after water elimination and then the reaction rates were evaluated.

Size distributions and hydrodynamic diameters for particles in the final PVAc latex dispersions were determined by dynamic light scattering (DLS), using a NICOMP 270 equipment.

Thermogravimetric analysis (TGA) was carried out at a heating rate of 20°C min⁻¹ in air using a Du Pont 2000 instrument. Same instrument was used for differential scanning calorimetry (DSC), at a heat flow rate of 10°C min⁻¹.

A DRON-20 X-ray diffractometer, with horizontal goniometer, scintillation counter and a Cu Kα (λ = 1,5418 Å) radiation source was used for X-ray diffraction (XRD) studies, in the Bragg-Brentano reflexion geometry.

For SEM analyses the films obtained after water removal, were mechanically fractured and after coverage with a thin (20 nm, sputtered) gold layer, the fractured surfaces of the dried polymer-clay composites were observed by scanning electron microscopy (SEM), using a JEOL-5610 equipment operated with a high-tension voltage of 20 kV.

The transmission microscopy images were recorded using an EM 201C Philips – TEM, on thin sections (50-80 nm) obtained from the specimens by cutting with a diamond knife (Leica ultramicrotome) after cooling the films at liquid nitrogen temperature.

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References