Microscopy as a tool to control predicted morphology and/or dispersion of a binary and ternary compounds in polymeric particles and fibre.

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The synthesis and manufacture of microparticles and functional polymeric fibres have attracted considerable attention due to the combination of the properties of an inorganic compound with those of the polymeric system. To gain various properties, the binary or ternary blend enhances in an advantageous way, and more specially the ability of the polymer to form coating or to embed them. The latter could prevent their aggregation in liquid and therefore improving their chemical stability. One the other hand, one the major factors affecting the thermo-physicochemical properties of the resulting system is the morphology, which can be predicted from thermodynamical parameters of each compounds. One the main challenges in this active research fields is the study, more especially the control, of the morphology processes during the manufacture of functional materials. Thus, the use of transmission and scanning electron microscopy (TEM and SEM) is necessary to control the morphology of these systems to achieve desirable functional properties.

Keywords Scanning electron microscopy, transmission electron microscopy, microencapsulation, melt spinning process, multifunctional materials

1. Introduction

The understanding of the influence of surface free energy and cohesion parameters on polymeric material interactions is a great help to the formulation, since it allows determining the system morphology without any experiment. Surface energy determination by means of contact angle has been frequently used to investigate the surfaces materials properties such as adhesion. This kind of measurement reflects the thermodynamics of a liquid/solid interaction, and surface energies are most of time estimated using the geometric approach of Owens-Wendt. It takes in account the dispersive and polar component of surface energy, based on Young-Dupré’s equation [1] in Eq. (1):

\[-\gamma_{SV} + \gamma_{SL} + \gamma_{LV} \cos \theta = 0\]  

(1)

Where \(\theta\) is the equilibrium contact angle, measures between the tangents to the liquid-vapor and solid-liquid interfaces within the liquid phase, under the action of the three interfacial forces, i.e. solid-vapor (\(\gamma_{SV}\)) (mN.m\(^{-1}\) or mJ.m\(^{-2}\)), solid-liquid (\(\gamma_{SL}\)) (mN.m\(^{-1}\) or mJ.m\(^{-2}\)), and liquid-vapor (\(\gamma_{LV}\)) (mN.m\(^{-1}\) or mJ.m\(^{-2}\)) tensions. The relationship between the contact angle (\(\theta\)) of the liquid phase deposited onto a solid phase is derived from the general Fowkes’ expression [2] which considers the polar and dispersive contributions for both solid and liquid designated as \(\gamma_S\) and \(\gamma_L\), with a superscript ‘d’ or ‘p’ for the dispersive and polar contribution, respectively, in Eq. (2).

\[\gamma_L(1 + \cos \theta) = 2(\gamma_L^d \gamma_S^d)^{1/2} + 2(\gamma_L^p \gamma_S^p)^{1/2}\]  

(2)

Thus, from equation (2) for two different test liquids it is possible to determine the surface energy of the solid phase (\(\gamma_S\)) as the sum of two components: a dispersive component, \((\gamma_S^d)\) attributable to London attraction, and a specific (or polar) component, \((\gamma_S^p)\) owing to all other types of polar interactions such as hydrogen bonding. In order to determine the interfacial tension between different polymers, Young’s equation can be used by treating one of the polymers as a solid substrate and the other as a liquid. The interfacial energy can be evaluated from the surface energy of the components. However, in some cases, it is difficult to determine the contact angle between polymers. Thus, to solve it, Wu’s equation [3] is used, which is a harmonic mean approximation for both the dispersion and polar components and avoids the need for a contact angle, in Eq. (3).

\[\gamma_{SL} = \gamma_S + \gamma_L - 4 \frac{\gamma_L^d \gamma_S^d}{\gamma_L^d + \gamma_S^d} - 4 \frac{\gamma_L^p \gamma_S^p}{\gamma_L^p + \gamma_S^p}\]  

(3)

On the one hand, classical thermodynamics is often used to predict the location of a filler at the interface of two immiscible polymers can be obtained from theoretical predictions given by the wetting coefficient. In the equilibrium state, it can be predicted by the miniimization of the interfacial energy; and according to Young’s equation, the
evaluation of the wetting coefficient, \( \omega_{A-B} \) in Eq. (4) introduced by Sumita et al. [4] allows determination of the equilibrium position of the filler.

\[
\omega_{A-B} = \frac{\gamma_{\text{filler-B}} - \gamma_{\text{filler-A}}}{\gamma_{A-B}}
\]  

(4)

Where \( \gamma_{\text{filler-B}} \), \( \gamma_{\text{filler-A}} \) and \( \gamma_{A-B} \) are the interfacial energies between filler and polymer B, between filler and polymer A and between polymer A and polymer B, respectively. When, the wetting coefficient is either higher than 1 or lower than -1, the filler will preferentially be located in polymer A and polymer B, respectively. And, if the wetting coefficient is between -1 and 1, the filler will be located at the interface between the two polymers.

On the other hand, during an encapsulation process, the adsorption of polymer on the dispersed core phase is a key step. Thus, spreading coefficient can be used to predict the encapsulation of one polymer phase within another. For a typical emulsion polymerization system comprised mainly of polymer (phase ‘k’), solvent or immiscible liquid (phase ‘j’) and active substance, (phase ‘i’) the surface free energy change that occurs on spreading one phase over another can be expressed as follows in Eq. (5)[5]:

\[
S_i = -\Delta G_i = \gamma_{jk} + \gamma_{ij} \]

(5)

Where \( \gamma_{jk} \) is the interfacial tension between the phases j and k and designating phase i to be that for which \( \gamma_{ij} > \gamma_{jk} \), then \( S_i < 0 \). Therefore, the three spreading coefficients (\( S_i \), \( S_j \) and \( S_k \)) describe the equilibrium state of a three-phase system. And, thus there are only three sets of values, i.e. \( S_i < 0 \), \( S_j < 0 \) and \( S_k > 0 \), \( S_i < 0 \), \( S_j > 0 \) and \( S_k < 0 \), \( S_i > 0 \), \( S_j < 0 \) and \( S_k > 0 \). When, the first conditions are satisfied, a core-shell morphology was adopted, for the other cases partial engulfment or two separate droplets for \( S_j < 0 \) or \( S_j > 0 \), respectively was obtained.

Microscopy (SEM, TEM) is a well-established basic method to observe the morphology of the material surface, as well as the localization of filler in a polymer blend, and the relationships between them. In this chapter, we will present how from the study of the thermodynamical approach used to conceptualize two different kinds of system, i.e. microencapsulation and melt spinning processes, microscopy is a powerful tool to control the desired morphologies. Using predictive equations derived from surface free energies and cohesion parameters, values of interfacial tension, spreading coefficient, wetting coefficient were used to describe interactions across the interfaces, and thus to establish predicted morphology of the systems. Based on SEM and TEM observations of samples at various manufacturing parameters, mechanisms of structure evaluation were proposed to show that microscopy is a powerful tool to assist microfabrication and dispersion.

2. Processes description

For the last ten years, the market and the needs for technical or smart textiles have been constantly growing, that leads to more technical developments and innovations of advanced textiles for new functionalities. In the same way, the formulation and understanding of polymeric surfaces have progressed tremendously to obtain systems with well-defined functionality.

2.1 Microencapsulation

Microencapsulation refers to the formation of polymeric particles with a range of diameters from nanometers to millimeters, and which exhibits several kinds of morphologies, in which the mains are so called microcapsules and microspheres. Microspheres consist of polymeric network structure in which an active substance is enclosed, whereas in microcapsules or core/shell structures exhibit a reservoir structure, i.e. the core substance is surrounded by a polymeric layer. Although, there are more than 200 microencapsulation methods described in scientific literature and patent, most of them include three basic steps, i.e. enclosure of core component, formation of the microparticles, and hardening of it. These methods are generally divided or classified in three main groups, which are based on the mechanisms of microparticle formation, such as mechanical, chemical and physico-chemical processes. The choice of a method rather than another is based on the cost of processing, the use of organic solvents for health and environment considerations. Polymer-solvent interactions occurring in the microencapsulation process have probably the stronger effect on morphology and properties of the resulted particles. Thus, each encapsulation step is affected by the solvency of the oil phase, and therefore to form a distinct membrane or shell, the solvent used should favour the precipitation of the polymer at the early stage of the reaction, and also allow the continuing diffusion of the monomers through the existing membrane to allow growing it. Gander et al. [6] have shown that the morphology of the microparticles depended on the
polymer solvent system. One method predicting the solubility of a solute in a solvent is to compare their solubility parameters. Thus, a good solvent for a solute such as a polymer has a solubility parameter close to that of the solute and Hildebrand or partial Hansen solubility parameters (δt, δd, δp, δh) can to be used for predicting polymer/solvent properties.

2.2 Extrusion and fiber spinning

Implementation by melting ways of polymers consists to raise the temperature of the polymer beyond its melting point. Polymeric material is introduced in solid form in a heated sleeve having one or several screws for bringing the polymer in molten state by increasing temperatures and shear rate. The extrusion followed by a melt spinning step provides multifilaments for technical applications that meet the current demand of the textile market. In fact, during the extrusion step, makes it possible to functionalize polymers by using immiscible polymers blends or by introducing fillers to amend the initial properties of the system. Previous study already published an example of modified multifilaments during extrusion step has highlighted the importance of obtained morphology and dispersion for the final properties [7]. This morphology is determined by the physico-chemical properties of polymers such as viscosity ratio, blend composition (weight fraction), interfacial tension between the both polymers and between polymers and fillers, etc; and by the process parameters such as the elasticity ratio (depending on the residence time in the extruder), and the mixing intensity (shear).

3. Biphasic mixture

3.1. Microencapsulation of n-hexadecane by an in situ polymerization

Two kinds of microparticles containing n-hexadecane for the first one, and n-hexadecane and hydrated salt for the second one, were synthesized by in situ polymerization from partial etherified melamine-formaldehyde resins. The ability of amino resins for self condensation around the core material droplet is linked to its surface activity and is an enrichment of resin molecules within the interface. The concentration of reactive resin molecules in the boundary layer is enhanced by hydrophilic/hydrophobic interactions of the partial methylolated melamine. Thus, the resin condensation proceeds much faster in the boundary layer than in the volume phase, allowing the formation of tougher capsule walls. The condensation of the melamine-formaldehyde resin is greatly influenced by the pH value, which contribute to increase the interfacial tension between the continuous medium and the amino pre-condensate polymer until to reach a value lower than this of n-hexadecane/continuous medium allowing the synthesis of a core/shell structure as depicted in Fig. 1 [8].

![Figure 1](image)

The microencapsulation of active two immiscible active substances, i.e. hydrated salt and n-hexadecane, from a water in oil in water emulsion with an amino resin, depends not only on the synthesis reaction steps, but also on the establishment of a stable double emulsion. Thus, the thermodynamic factors determine the equilibrium morphology of the final particles, whereas the kinetic factors determine the ease with which such thermodynamically morphology can be obtained. The characteristics of each phase involved in this process allow to predict a partial entrapment of the active substance which can be correlated to an acorn structure or an uncompleted encapsulation (Table 1). The morphological control of the microparticles by SEM analysis allows checking the polymeric shell formation, which induces the obtention of spherical and porous particle even if the surface state seems to be relatively smooth. Nevertheless, the presence of holes and dimples (like craters) at their surface denotes the release of water and or hydrated salt from the inner side to the surrounding medium during the polymerization process or during the solidification of the paraffin after...
polymerization, since the contraction of the core materials is greater than of the shell producing deformation in the weakest part of the capsules in Fig. 2. In this condition, the predicted morphology is confirmed by SEM analysis.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Interfaces</th>
<th>Interfacial tension (mN.m⁻¹)</th>
<th>Spreading coefficient (mN.m⁻¹)</th>
<th>Predicted engulfment</th>
</tr>
</thead>
<tbody>
<tr>
<td>batch n°1</td>
<td>hydrated salt/n-hexadecane</td>
<td>8.0</td>
<td>&lt;0</td>
<td>full</td>
</tr>
<tr>
<td></td>
<td>hydrated salt/continuous phase</td>
<td>---</td>
<td>&lt;0</td>
<td>partial</td>
</tr>
<tr>
<td></td>
<td>n-hexadecane/continuous phase</td>
<td>4.2</td>
<td>&lt;0</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Characteristics of different interfaces present in the two microencapsulation mediums during the emulsion steps.

Figure 2 SEM images of microparticles containing a binary mixture of immiscible active substance as the core.

3.2 Melt spinning process of biphasic polymer blends: Polyamide12/Polycaprolactone and Polypropylene/Polycaprolactone

Several morphologies can result from a blend of two immiscible polymers. To describe them, the spatial distribution of components, the size, shape and form factor, phase composition, the nature of the interfaces, etc, are used. The knowledge of morphology plays an important rule, since it conditions the resulted properties of the structure at the macroscopic scale. The morphology can be divided in three main categories, in which the spherical allows obtaining a better resistance to impact and shock resistance, the fibrillar enhances the elastic properties and/or the barrier effect, and the co-continuous allows a combination of the characteristics of each polymer, such as conduction properties. Taking in account the specify of each process parameters which induce either droplets breaking or coalescence, the generalization of the predicted morphology remains a challenge as shown in the literature. The first semi-empirical approaches, to describe the predicted morphology of a biphasic blend, are based on the viscosity ratio of both polymers. They lead the phase inversion point which corresponds to a co-continuous structure [9, 10]. Willemse et al. shown that models based on the viscosity ratio can not exhaustively describe the experimental results obtained on different systems [11, 12]. They have developed a model-concept based on the shape and size of dispersed droplets, as presented in Eq. (6).

\[
\frac{1}{\phi_{\text{max}}} = 1.38 + 0.0213\left(\frac{\Gamma \eta_m R_0}{\gamma}\right)^{1.2}
\]

Where \(\phi_{\text{max}}\) is the volume fraction of the minority phase (vol.%), \(\eta_m\) is the viscosity of the matrix (Pa.s), \(\Gamma\) is shear rate(s⁻¹), \(R_0\) is the diameter of the sphere of the dispersed phase (m) and \(\gamma\) is interfacial tension (mN.m⁻¹).

Two immiscible polymer blends were carried out under identical extrusion conditions, i.e. the first one is Polyamide12/Polycaprolactone and the second one is Polypropylene/Polycaprolactone (PA12/PCL and PP/PCL). PP and PA12 not having very different viscosity at the extrusion temperature of 200°C and if we considered the Willemse’s model, the interfacial tension between those two polymers is a determinant point of the morphology of blends. The surface energy of each raw material is deduced from the contact angle realized at room temperature with applying correction factors to correspond to the extrusion temperature [3, 13]. Values are summarized in Table 2 and the calculated interfacial tensions using the harmonic and geometric means of each of the polymers in the blend are tabulated in Table 3. The interfacial tension of PP/PCL is higher than that of PA12/PCL. A low interfacial tension leads
to an increase of the contact surface between the phases, which favours the macromolecular chains interpenetration. Thus, for PP/PCL blend, taking into account that the PCL is the dispersed phase (or minor phase), a low amount is required in the PA12/PCL blend to reach the co-continuous phases.

Table 2 Calculated surface energies and its components (dispersive and polar) at 200°C of PCL, PP and PA12. Surface energy and its components of CNT at room temperature issued from literature data.

<table>
<thead>
<tr>
<th></th>
<th>Surface energy (mN.m⁻¹)</th>
<th>Dispersive component (mN.m⁻¹)</th>
<th>Polar component (mN.m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>27</td>
<td>23.7</td>
<td>3.4</td>
</tr>
<tr>
<td>PP</td>
<td>20.7</td>
<td>20.6</td>
<td>0.1</td>
</tr>
<tr>
<td>PA12</td>
<td>24.4</td>
<td>21.3</td>
<td>3.1</td>
</tr>
<tr>
<td>CNT [14]</td>
<td>27.8</td>
<td>17.6</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table 3. Interfacial energies between different components of blend (polymer-polymer or polymer-CNT) at 200°C using harmonic and geometric mean equations.

<table>
<thead>
<tr>
<th>Interfacial energy (mN.m⁻¹) (Harmonic mean)</th>
<th>Interfacial energy (mN.m⁻¹) (Geometric mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{PP-PCL}$</td>
<td>3.4</td>
</tr>
<tr>
<td>$\gamma_{PA12-PCL}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$\gamma_{PP-CNT}$</td>
<td>10.3</td>
</tr>
<tr>
<td>$\gamma_{PA12-CNT}$</td>
<td>4.1</td>
</tr>
<tr>
<td>$\gamma_{PCL-CNT}$</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 3 illustrates the morphology obtained by SEM analyses of the two blends in 70/30 (wt/wt) composition. The observed morphologies are in correlation with those predicted from the Eq. (6). For the PP/PCL blend in Fig. 3-a), the introduction of 30 wt.% of PCL induces a dispersed phase in PP, corresponding to a high interfacial tension. Furthermore, the presence of PCL inclusions (10 µm), under elongated form, allows stipulating that an increase of PCL leads to the co-continuous structure. The presence of high loading content in the dispersed phase in the system minimizes the interfacial energy by decreasing the contact surface between the two materials. For the PA12/PCL system, in Fig. 3-b), PCL spherical inclusions are observed in the PA12 matrix, and the nodule size (0.5 to 1.5 µm) is smaller in the blend PP / PCL for a same loading content. The low interfacial tension between the two polymers provides a more important interpenetration due to an increase of the contact surface and thereby well dispersed inclusions with narrow size distribution. Thus, from a certain amount of PCL in the system, the co-continuous phase is reached as predicted by the model (Eq. (6)).
4. Triphasic mixture

4.1 Microencapsulation with a double layer shell

Microcapsules with a double-layered shell containing acid dyes were prepared using an original two step process. A double emulsion based on an encapsulation process was developed and allowed the entrapment of the dye. The first step, a hot melt process, involves the dispersion of the aqueous dye solution in a melting carnauba wax. Then, the second step consists in the formation of a thermoplastic outer shell by coacervation method. The outer wall is made of a thermoplastic polymer such as polystyrene or polyethylene.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Solubility parameters (MPa$^{1/2}$)</th>
<th>Surface tension (mN.m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_d$</td>
<td>$\delta_p$</td>
</tr>
<tr>
<td>batch n°2-2</td>
<td>polystyrene</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>carnauba wax</td>
<td>16.6</td>
</tr>
<tr>
<td>batch n°2-3</td>
<td>polyethylene</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Table 4 Hansen solubility parameters and calculated surface tensions by the Owens-Wendt method.

Table 5 Predicting polymer solubility.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$R_0$</th>
<th>$\Delta\delta(s-p)$</th>
<th>RED</th>
<th>Note</th>
<th>Predicted morphology</th>
<th>State and surface appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>batch n°2-2</td>
<td>12.8</td>
<td>11.8</td>
<td>0.93</td>
<td>swelling</td>
<td>core/shell</td>
<td>Rough surface with a raspberry-like morphology</td>
</tr>
<tr>
<td>batch n°2-3</td>
<td>6.0</td>
<td>2.8</td>
<td>0.46</td>
<td>solubility</td>
<td>matrix</td>
<td>Well defined, spherical, smooth surface</td>
</tr>
</tbody>
</table>

Scanning micrographs of the microspheres loaded with acid dye revealed various shapes and particle sizes in the range of 1–5 $\mu$m, in Fig. 4. It seems that the shape and the morphology of the microparticles are deeply influenced by the choice of the external polymeric shell. Thus, with a PE shell, the microparticles are well defined and have a spherical, smooth surface. During the coating with PS, the particles tend to aggregate before hardening. The resultant microparticles have rough surface with a raspberry-like morphology. The difference between these two morphologies can be attributed to the miscibility of carnauba wax with PE according to the solubility parameters (15.8–17.1 J$^{1/2}$/cm$^{3/2}$ and 16.8 J$^{1/2}$/cm$^{3/2}$ for PE and carnauba wax respectively) in organic solvent at high temperature. Thus, during the shell formation, PE and carnauba wax are mixed together to form an interpenetrated network, in Table 4. Whereas, the physico-chemical parameters of the PS coacervation phase (17.4–19.0 J$^{1/2}$/cm$^{3/2}$) do not allow the formation of an ideal binary mixture of these two compounds. These results are in accordance with those predicted in Table 5 [15].

Figure 4 SEM images of acid dye/wax/polystyrene (A), acid dye/wax/polyethylene (B & C), microspheres at a magnification of 2000 and 4000.

4.2 Multinuclear microparticles formation

A microencapsulation method, in which a paraffin medium and small sub-micron spheres were encapsulated by an amino resin has been realized. This process is based on several emulsion mixings following Torza and Mason’s approach, in which we combined the characteristics of a coacervation with a conventional interfacial reaction and an in situ polymerization followed by a water in oil in water emulsion. The inner phase of the microcapsules consisted of a mixture of paraffin and microspheres of poly(vinyl) alcohol/hydrated salt cross linked by methylene diisocyanate.
Table 6 Characteristics of different interfaces present in the microencapsulation medium in the emulsion step.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Interfaces</th>
<th>Interfacial tension (mN.m⁻¹)</th>
<th>Spreading coefficient (mN.m⁻¹)</th>
<th>Predicted engulfment</th>
</tr>
</thead>
<tbody>
<tr>
<td>n°1-3</td>
<td>microparticles/n-hexadecane</td>
<td>11.0</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>microparticles/continuous phase</td>
<td>26.8</td>
<td>-20.0</td>
<td>total</td>
</tr>
<tr>
<td></td>
<td>n-hexadecane/continuous phase</td>
<td>4.2</td>
<td>-33.6</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 SEM images of broken multinuclear particles, outer shell (A) and inner side (B).

Figure 5 shows the resulting hybrid structure with the presence of small spheres with a mean diameter less than 1 µm in a bigger sphere. The external aspect of the particles shows an irregular and granular shell. Furthermore, the outer inner shell seems to be constituted of microparticles linked together by the amino resin. The spreading coefficient is affected with time as the microcapsules harden, i.e., as the crosslinking reactions of melamine resin occur in the continuous phase. The polymer solution concentrations change, altering the effective surface and interfacial tensions. An indirect estimation of the final configuration can be made from the interfacial tension, in Table 6. Furthermore, the polarities of microparticles and amino resin and their polar components are close and much higher than that of n-hexadecane. On the other hand, on the basis of the data from the Table 6, n-hexadecane has much affinity with the microparticles, and these latter can remain at the interface until the formation of the resin shell. Thus, the microparticles tend to locate at the interface between n-hexadecane and amino resin, and either are linked in the inner shell or dispersed in the paraffinic medium as predicted [16].

4.3 Localization of carbon nanotubes (CNT) in two immiscible polymer blends.

CNT was introduced to bring electrical conductivity of multifilaments in the two blends previously studied (PP/PCL and PA12/PCL). Blends were extruded in two consecutive steps, i.e. in the first one, the CNT were incorporated into the PCL with a loading content of 4 wt.% (for mixing with PP) or 6 wt.% (for mixing with PA12) and are homogeneously dispersed using twin screw extruder; in a second step, this filled PCL is mixed with PP or PA12 pellets to obtain the biphasic blends at 60/40 weights ratio. According to the location of the filler, i.e. in a single polymer phase, at the interface or in the two polymers, different properties may be obtained. The wetting coefficients (Eq. (4)) are used to predict the phase for which the CNT will have the most affinity. However, CNT, due to their polarity (Table 2), tend to migrate to the more polar polymer. The PP has a polar component close to zero, whereas the PA12 which has a significant polar component (3.1 mN.m⁻¹), which promotes the mobility of CNT in PA12 phase.

Table 7 Wetting coefficients of blends as calculated using harmonic and geometric mean equations and conclusions about localization of CNT.

<table>
<thead>
<tr>
<th>Wetting coefficient (Harmonic mean)</th>
<th>Wetting coefficient (Geometric mean)</th>
<th>Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_{PCL-PP} ) = 1.74</td>
<td>( \omega_{PCL-PA12} ) = -1.58</td>
<td>CNT in PCL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CNT in PA12</td>
</tr>
</tbody>
</table>

The TEM observations, in Fig. 6, confirm calculated wetting coefficients for the spatial localization of CNT. Thus, TEM analyze, in Fig. 6-a), for the PP/PCL blend, shows that the CNT are mainly located in the PCL, which is in accordance with the calculation of the wetting coefficient with \( \omega_{PCL-PP} > 1 \) (Table 7). PA12/PCL blend, CNT are dispersed in the two phases, as shown in Fig.6-b). The wetting coefficient \( \omega_{PCL-PA12} < 1 \) predicts that the CNT are located in the PA12 phase. Implementation and especially the initial conditions of dispersion of the fillers are responsible for this difference in distribution for blend. Indeed, CNT are first introduced into the PCL phase in a first extrusion; CNT migrate in the PA12 during the second one [17].
Figure 6 Location of CNT by TEM analysis on PP/PCL+4wt% CNT rod a) and b) PA12/PCL+6wt% CNT rod in proportion 60/40 (w/w). CNT are selectively located in the PCL phase in PP/PCL, and they are located both in PCL and PA12 phases in PA12/PCL.

5. Conclusion

The quality of the dispersion of one compound in the system is intrinsically linked to the interfacial tension between the polymeric system and the filler, which depends mainly on the surface state, the strength of the interaction and also on the size of the interface. Thus, during the manufacture new surfaces and interfaces are created and the system tends towards morphology with a minimum total free energy. SEM and TEM analyses are a powerful tool to observe and check the predicted morphology for various systems. Thus, whatever the system considered, microcapsules as well as polymeric blends, microscopy is a powerful tool to control the desired morphologies conceptualized from thermodynamical approach.

References