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Microstructure–conductivity relationship in conducting polypyrrole/epoxy composites

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Abstract

Four dispersing methods were used to disperse increasing amounts of Polypyrrole (PPy), synthesized either via dispersion (PPy_d) or suspension polymerization (PPy_s), in an insulating epoxy matrix in order to make it electrically conductive. As shown in SEM micrographs and by the physical characteristics, PPy_d particles exhibit higher density and smaller particle size than PPy_s. In addition, optical micrographs of the blends show that PPy_d form compact agglomerates and PPy_s aerated clusters. It is deduced from conductivity measurements, that energy intensive methods or larger particle size (PPy_s) provide low percolation threshold. Indeed, energy intensive methods, by breaking the PPy_d agglomerates, favour the formation of conductive network of fine particles and therefore lower the PPy concentration at percolation. Similarly, larger PPy_s particles are arranged in clusters allowing a more homogeneous distribution of PPy particles in the resin and a smaller percolation threshold. The microstructure of the blends are observed by TEM.

Keywords: Electrically conductive composite; Percolation threshold; Filler distribution

1. Introduction

This study is part of our on-going research project to develop a high performance composite material with electrically conductive properties.

For years, composite materials consisting of fibrous reinforcement within a polymeric matrix were widespread and widely used by the aircraft manufacturers. Indeed, the interaction of their constituents gives them overall mechanical and physical properties satisfying stiffness, mass and temperature requirements. Nevertheless, as the matrices used in these composites are good electrical insulators they cannot deal with the problem of electrostatic charges elimination usually encountered in the aircraft wings, vertical fin, flaps, etc. For several years aircraft manufacturers have solved the problem of lightning strike protection by introducing a metallic braid lightning conductor and a network of aluminum wires in the various parts of the aircraft made of composite materials. However, these metallic structures are difficult to process and to handle. Therefore, an alternative solution can be to improve the electrical conductivity of the polymeric matrix itself. Since the matrices usually used in high performance composites meet all the specifications required in the aeronautic industry it would be of great interest to keep them and give them good electrical properties.

There are several ways to make a polymeric matrix electrically conductive [1]. Classically, the insulating polymers are filled either with carbon black [2,3] or with metallic particles [4], leading to an extrinsically conductive polymer in which the fillers ensure the electrical conduction. However, these high density fillers, whose specific mass is, respectively, about 1.8 and 2.8 (for aluminum) induce a significant increase in the matrix specific mass, which is usually lying between 1.1 and 1.4. Thus, the solution considered in this report is to fill this matrix used in high performance composite materials with an intrinsic conductive polymer. Yet, because of their structure these polymers, electrically conductive by themselves without any fillers, are very brittle and cannot carry any mechanical load. In addition, they are difficult to process and to manufacture [1]. Nevertheless, intrinsic conductive polymer can exhibit a conductivity close to that of copper i.e. 10^3 S/cm [5] combined with a low specific mass (1.2–1.7) and therefore represent an interesting conductive filler. However, the

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composites obtained from the dispersion of particles of electrically conductive polymers into an insulating polymeric matrix, do not provide conductivity as high as those obtained with metallic or carbon black fillers. Effectively, an epoxy filled with carbon black [2,3] can exhibit a conductivity value of 0.4 S/cm for a black content as low as 2% by volume while epoxies filled with particles of electrically conductive polymers generally offer lower conductivity values. Nevertheless, they are sufficient to meet the specifications required for our application.

To prepare composites of insulating matrix filled with an intrinsic conductive polymer, two principle methods were developed [6]. The composite can either be a blend or an interpenetrating polymer network. The latter are made by synthesizing the conducting polymer inside the host polymer using chemical [7–9] as well as electrochemical [10–12] methods of polymerization. Some authors [13] have also developed a copolymerization method leading to a conductive polymer grafted onto the insulating matrix. However, limitations exist regarding the practical applications of polymer composite prepared by these methods. Indeed, uniform thin films of the host polymer are necessary to allow the solvent to open channels throughout the thickness and swell the whole matrix in which the polymerization will take place. As a consequence, these composites are difficult to prepare on a large scale [6]. The second way to synthesize composites are blends. They are either prepared by mixing liquid prepolymer of the matrix with the conducting polymer powder followed by the thermal cure of the system [2,11,14] or by the chemical polymerization of the conducting polymer onto insulating polymer particles which are then compression moulded [15–17]. Although these methods lead to a less conductive composite compared with the interpenetrating polymer network [11], the preparation of the polymer blends has the advantage of shorter reaction time and easier large scale production of uniform blends. This latter method suits better the fabrication of large thick pieces and therefore meets the requirements of our application.

Polymer composites prepared as a mixture of a conjugated conducting phase and classical non-conducting phase normally show a significant jump in the electrical conductivity at a certain critical concentration of the conducting polymer called percolation threshold. The electrical percolation phenomenon was studied thoroughly during the previous two decades. Several statistical, thermodynamic, geometrical and structure-oriented percolation models were developed for the prediction of the percolation concentration or conductivity of filled systems. A good overview of existing models, their applicability and limitations, is presented and discussed by Lux [18] in a recent report. In fact, most of the time the systems do not fulfill the assumptions of the models and the percolation threshold rarely meets the value of 0.16 volume fraction of conducting filler predicted by the classical percolation theory [19,20] for a three-dimensional system. Depending on their nature, matrix and filler can or cannot create strong interactions which has an influence on the fillers distribution in the blends. For example, many workers [10,12] have observed the formation of H-bonds between functional groups of the constituents. These kind of interactions enable a better dispersion of the filler and account for a lower percolation threshold often observed in the polymer mixture. Indeed, both the chemical composition and the processing method [3] can lead to significant variations of the system properties and a new model has often to be designed. In this regard each polymer blend is unique. Therefore, an attempt to elaborate a universal model describing all systems or giving quantitative interpretation of the conductivity values in the polymer mixtures will face serious difficulties.

The aim of this study is to make a trifunctionnal epoxy resin normally used by the aircraft industry, as a matrix in structural carbon/epoxy composites, electrically conductive. For this, epoxy prepolymer of the matrix will be mixed together with polypyrrole (PPy) which is, because of its high electrical conductivity, good environmental stability and easy synthesis [21,22], the most suited intrinsic conducting polymer. As the initial mechanical properties of the epoxy matrix must be preserved, the fabrication of these electrically conductive composites has to be optimized i.e. the system must show the jump of conductivity at the smallest amount of conductive filler. Therefore, PPy was synthesized via two different polymerization routes and the dispersion of the PPy in the matrix was performed by four different dispersing methods. Conductivity measurements as well as SEM, MET and optical micrographs performed on the various kinds of samples have shown the influence of the filler morphology and the dispersing method on the percolation threshold position and the filler distribution in the matrix.

2. Experimental

2.1. Materials

For this study a bicomponent epoxy system commercialized by Hexcel composites was used as a polymeric matrix. It consists of a liquid bisphenol A epoxy resin prepolymer (LY564, density of 1.2 g/cm^3) containing a reactive diluent and a cycloaliphatic amine hardener (HY2954, density of 0.94 g/cm^3) which are mixed together according to the manufacturers specifications.

The intrinsically conductive polymer, polypyrrole (PPy), was synthesized via two different routes: either in colloidal form via dispersion polymerization [23,24] (PPy_d) or via suspension polymerization (PPy_s). The unique difference between these two syntheses is the presence of a steric stabilizer PVA [poly(vinylalcohol)] in the dispersion polymerization route.

As already described in a previous report [25], the PPy synthesis conditions are the following: 3.53 ml pyrrole monomer (Aldrich 98%) are added to a 500 ml aqueous solution of an aromatic acid (*p*-toluenesulfonic acid monohydrate 98%, Janssen Chimica), with an oxidizing agent ammonium persulfate ($(NH_4)_2S_2O_8$ Janssen Chimica) and in the case of the dispersion polymerization, a steric stabilizer [poly(vinylalcohol) 96% hydrolyzed (PVA 96, Janssen Chimica)]. The oxidizing agent causes the formation of positive charges in the polymer chain and their displacement will result in the conduction phenomena. Doping anions which achieve the electrical neutrality of the polymer are present along the carbon backbone. They result from the decomposition of the oxidizing agent, but they can be replaced by others anions provided by components introduced in the reaction media. For example, the dissolution of the aromatic acid in the reaction media will provide aromatic anions which impart a better stability to the polymer [26].

In order to obtain a highly conjugated PPy structure, the reaction is allowed to proceed between 5°C and 7°C and at a pH lower than 3. At the end of the reaction, the solution is filtered and washed successively with water, ethanol and acetone. The obtained product is dried under vacuum (0.09 MPa) at room temperature in presence of desiccant salts. Finally, in order to obtain a fine powder and break the agglomerates, the crude black PPy powder has to be crushed in a mortar.

2.2. Preparation of the blends

Three dispersion methods (wing mixer, turax, ultrasonic probe) were used to mix increasing amounts of colloidal PPy_d (synthesized via dispersion polymerization) with the epoxy matrix prepolymer (resin/hardener ratio = constant) leading to three sets of samples. A fourth set was obtained by using the PPy_s powder (synthesized via suspension polymerization) as a filler in blends prepared by manual stirring. The dispersion methods are detailed hereafter.

2.3. Method 1: wing mixer

Various amounts of PPy_d (lying between 5% and 20% by mass) are added to a mixture of the prepolymer LY564 with the hardener HY2954 and are stirred during 5 min at 400 rpm with the wing mixer. Then, the blends, thus, obtained are degassed under vacuum (20 mbar).

2.4. Method 2: turax

The main problem encountered in the use of this method is that it can induce (because of high mixing speeds used) a temperature increase in the mixture. Consequently, in order to prevent any curing reaction between the LY564 prepolymer and the HY2954 hardener, the PPy_d (between 5% and 17% by mass) powder is added to the LY564 prepolymer only. This mixture is stirred for 2 mn at 10 000 rpm with the turax mixer. Then, after cooling, the HY2954 hardener is incorporated in this first mixture and manually stirred. Finally, the whole mixture is degassed under vacuum (20 mbar)

2.5. Method 3: ultrasonic probe

PPy_d (between 5% and 19% by mass) is added to the matrix prepolymer diluted with acetone in order to reduce its viscosity. Then, the mixture is subjected during 6 min to an ultrasonic stirring provided by an ultrasonic probe of 13 mm diameter with a titan alloy (Ti6Al4V) tip. The probe is fed with 100 W furnished by 20 kHz ultrasonic vibracell generator (Sonics and Materials). The electric energy is transformed by the generator in high frequency (20 kHz) ultrasonic energy which is transmitted to the converter. The mechanical vibrations are amplified by the probe which provokes an alternation of compression in the liquid and produces plasts which explode violently. This phenomenon enables an important energy to be released at the extremity of the probe which provides an intense stirring of the molecules in the liquid. Then, the acetone is evaporated under reduced pressure (20 mbar) and the hardener is added to the mixture which is then manually stirred and degassed.

2.6. Method 4: manual stirring

PPy_s powder (between 1 and 5 wt%) is added to a mixture of prepolymer with hardener, hand stirred with a stick and then degassed under reduced pressure (20 mbar).

The duration of the degassing step depends on the dispersing method and the PPy content. The higher the PPy concentration or the energetic input of the dispersing method, the longer the degassing period. Once degassed all the samples are moulded by gravity in a vertical mould of rectangular shape and subjected to the thermal treatment usually applied to the system LY564/ HY2954 according to the manufacturers recommandations. The curing conditions consist of an isothermal dwell at 120°C for 20 min followed by an isothermal dwell of 4 h at 145°C. With increasing PPy concentration, the viscosity of the blends also increases so that degassing and moulding become difficult. In addition, the porosity quantity increases.

2.7. Measurement of electrical conductivity

The moulded blends of 2 mm thickness are cut into squares of about $10 \times 10\ mm^2$ and covered with a Ag paint on which the electrodes are connected. The electrical conductivity of these polymeric composites is measured, according to the four points probe method, in two different directions: along and across the samples. A stabilized direct current alimentation (Keithley model 224) is used to apply an intensity between 5×10^{-6} A and 1×10^{-3} A and the resulting tension is measured by a nanovoltmeter (Keithley 181). According to the apparatus resolution it was necessary

Table 1
Physical characteristics of the two kinds of PPy powders

PPy sort	Particles size (nm)	Density (g/cm^3)	Conductivity (S/cm)	Conductivity after cure (S/cm)
PPy$_s$	400	1.2	3–6	10^{-2}
PPy$_d$	100	1.7	3–6	10^{-2}

to perform a correction of the measured conductivity for the less conductive samples.

The four points probe method was used as well in order to measure the conductivity of the PPy powders. An intensity of 1 mA was applied by the stabilized direct current alimentation on pellets of dried PPy (200–300 mg pressed under 8 tons for 15 min) and the resulting tension is measured with a precision of 0.05%, by the nanovoltmeter exhibiting an impedance of 10^9 Ω in our measurements range.

2.8. Scanning electron microscopy (SEM)

The morphology of the two kinds of PPy powders (PPy$_s$ and PPy$_d$) is studied by SEM. The powder is placed in ethanol and shaken for a few minutes, a drop of the solution is placed on a sample holder. The ethanol evaporates quickly leaving only PPy particles. Then, a gold pattern is sputtered onto the sample holder surface and a scanning electron microscope (Cambridge stereoscan 250Mk3) is used to observe the samples.

2.9. Transmission electron microscopy

A transmission electron microscope (Philips CM20) with an accelerating tension of 200 kV is used to examine the microstructure of the PPy cluster in the epoxy matrix. Observations are performed on ultrathin sections (70 nm) of the specimens obtained by microtoming at ambient temperature with a Reichert ultracut S apparatus.

2.10. Optical microscopy

The composites samples are cut into thin sections of 2 μm thickness by an ultramicrotome (Reichert ultracut S). Then the distribution of the PPy particles within the epoxy matrix is observed in bright field with an optical microscope (Zeiss axioskop).

2.11. Laser diffraction

The PPy particle size and distribution are measured using a Mastersizer S (Malvern) which measures particle size from 50 nm to 900 μm. To reduce the agglomerates and measure the size of the individualized particles, the powder is mixed with acetone and subjected to an ultrasonic vibration (at 200 W and 20 Hz) delivered by the ultrasonic probe previously described. Then, the solution is poured into a small volume sample preparation unit MSX1 which allows a continuous agitation of the powder in aceton and the transfer of the solution through the laser beam of the granulometer.

3. Results and discussion

3.1. Powder morphology

The synthesis of PPy via different polymerization routes has allowed us to obtain powder whose characteristics (Table 1) and macroscopic aspects are different. Macroscopic observations of the synthesized PPy show that the use of a steric stabilizer during PPy$_d$ polymerization leads, after drying, to the formation of numerous PPy$_d$ agglomerates of rather large dimensions which are hard and difficult to crush. Once crushed a fine, compact and irregular black powder composed of well separated particles is obtained. However, some small agglomerates, which are to hard to be crushed, always remain. In contrast, after drying the PPy$_s$ powder agglomerates are soft and easy to crush. Once crushed a coarse, light powder exhibiting a dendritic aspect and a grape-like structure can be observed on a macroscopic level. In addition, although the amount of monomer used during both synthesis remains the same, the volume of the obtained PPy$_s$ powder is greater than that of the PPy$_d$. This observation is confirmed by the density measurements (Table 1), performed using a picnometer, which show that the density of PPy$_s$ is lower than that of PPy$_d$.

The measurements of particles size and distribution performed by laser granulometry on PPy powders in acetone solution have revealed the following facts: in dispersion polymerization, as it was already reported [24], the use of steric stabilizer, leads to particles exhibiting a straight size distribution with a small average size value (100 nm) similar to the carbon black particle size (30–80 nm). In contrast, the suspension polymerization gives a PPy particle size distribution with a greater variance and average particle size (400 nm). From Table 1, it can be seen that the PPy$_d$ particles are four times smaller than the PPy$_s$ particles.

The conductivity measurements performed on the two kinds of PPy powder after their synthesis give similar values. It can therefore be assumed that the steric stabilizer used in the dispersion polymerization, which is an electrical insulator, was eliminated from the PPy$_d$ during washing. Since, during the cure of the blends, the PPy particles introduced in the insulating matrix will also undergo the curing conditions, their electrical conductivity is likely to decrease,

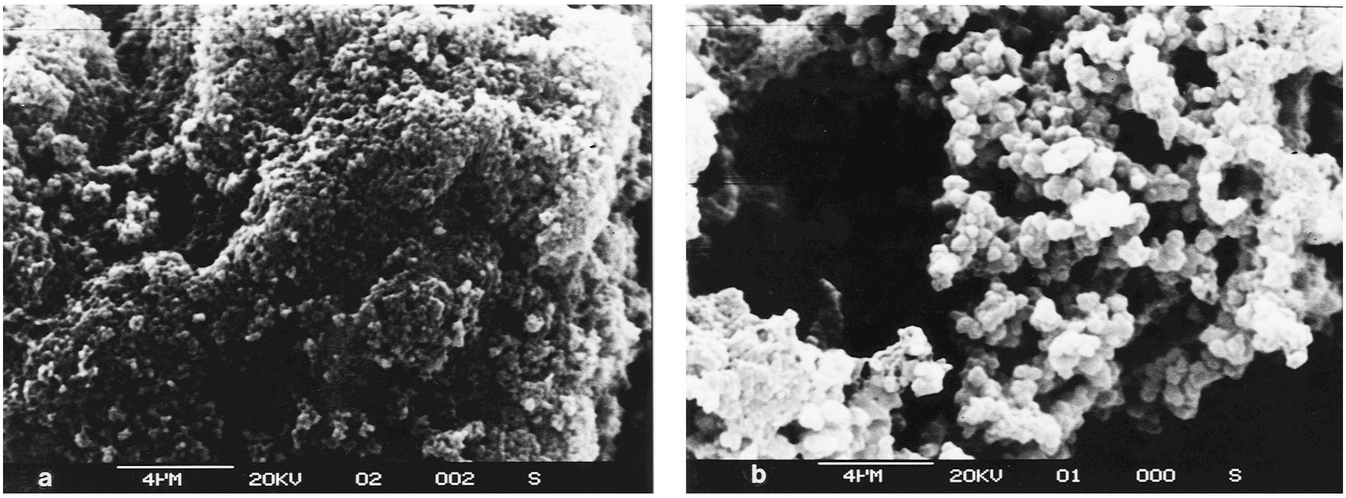

Fig. 1. Morphology of the PPy powders as observed by Scaning Electron Microscopy: (a) PPy_d; (b) PPy_s.

so the conductivity of the cured PPy powders was measured. Conductivity measurements were performed on PPy powder once subjected to the cure cycle usually applied to cure the epoxy resin. It was observed that the conductivity of PPy decreases of two order of magnitude after it was subjected to the cure cycle. This degradation of the PPy conductivity has already been noticed and its mechanism was explained by several authors [27–29].

In Fig. 1 SEM micrographs of the PPy powders are presented. Fig. 1a shows that PPy obtained by dispersion polymerization exhibits very small spherical particles of PPy_d which tend to make very compact, hard agglomerates. This behaviour is similar to that of carbon black, which equally exhibits various organization levels from the particles to the agglomerate [30]. In contrast, as it can be seen in Fig. 1b, the PPy_s obtained via suspension polymerization is composed

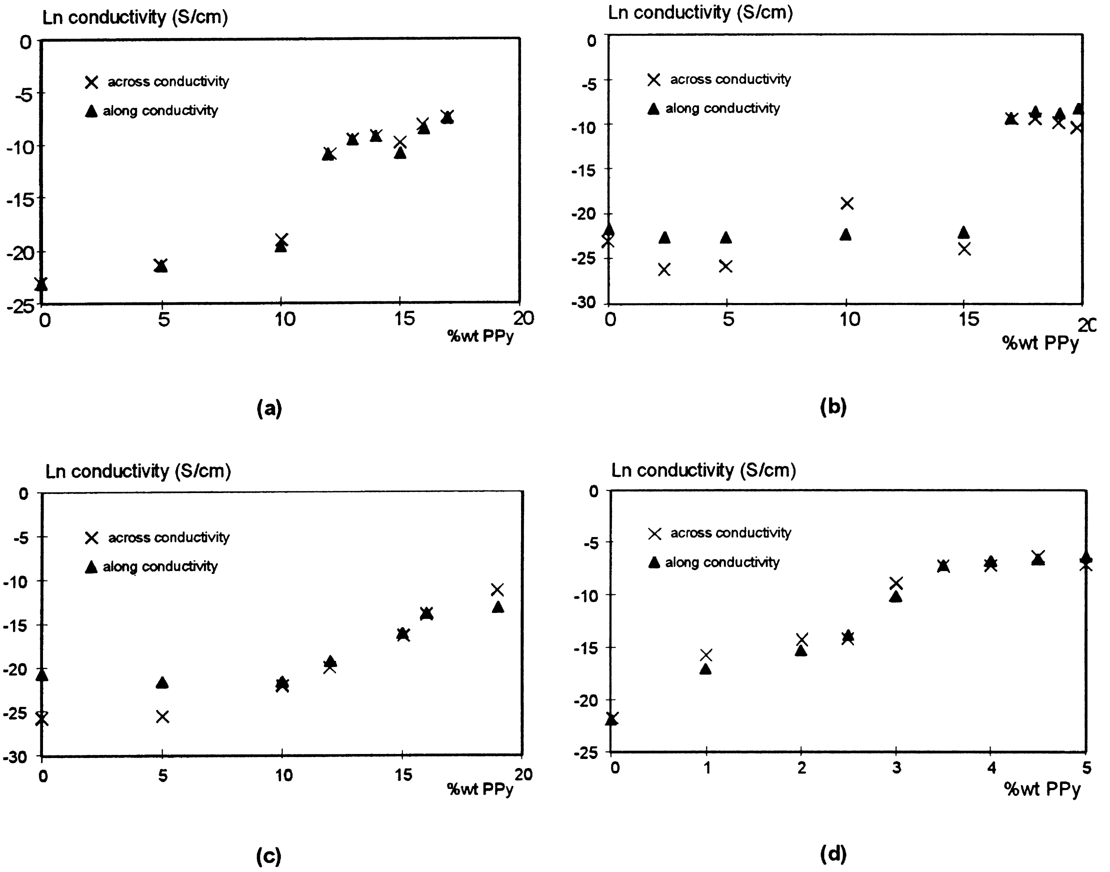

Fig. 2. Conductivity as a function of the PPy content for PPy/epoxy blends prepared with various dispersing methods: (a) PPy_d/epoxy with the turax; (b) PPy_d/epoxy with the wing mixer; (c) PPy_d/epoxy with the ultrasonic probe; (d) PPy_s/epoxy with the hand stirrer.

Table 2
Characteristics of the various set of blends at the percolation threshold

	σ_{pc} [a] (S/cm)	P_c (%vol.) [b]	P_c (%wt) [c]
PPy_d-epoxy matrix (wing mixer)	7.10^{-5}	11	16
PPy_d-epoxy matrix (turax)	2.10^{-5}	7.5	11
PPy_d-epoxy matrix (ultrasonic probe) [d]	10^{-9}	8.1	12
PPy_s-epoxy matrix (manual stirring)	4.10^{-5}	2.5	3

[a] conductivity of the blend at the percolation threshold
[b,c] percolation threshold by volume and by weight respectively
[d] The values reported here are those measured for the PPy content at which conductvity increases, they do not represent the real percolation phenomenom

of bigger spherical particles, in aerate grape like form which gives a dendritic aspect to the powder. These results confirm, at a microscopic scale, the macroscopic observations made on the crushed powder. For each powder macroscopic and microscopic structures are similar.

3.2. Percolation threshold

The first three sets of blend were realized by mixing PPy_d synthesized by dispersion polymerization (PPy_d) in the epoxy matrix using the three mixing methods previously described in the experimental part. Their conductivity and PPy content at the percolation threshold are summarized in Table 2. Fig. 2 shows the evolution of their conductivity versus mass fraction of PPy_d in the matrix.

The first two dispersion methods (wing mixer and turax) use a rotating stirrer. Although the stirring time is shorter for the turax method, the higher energetic input, caused by the elevate stirring rate, results in a percolation threshold which occurs at lower PPy concentration. This threshold, expressed in percent by mass of PPy particles, corresponds to the smallest amount of PPy which has to be added to the insulating matrix so that an infinite cluster of conductive PPy particles, ensuring the conduction, is formed throughout the sample. These observations are in good agreement with those obtained by Meraoumia [3] about the dispersion of carbon black in an epoxy matrix (DGEBF). Indeed, for these mixtures it was observed that increasing the energy input of stirring, results in a percolation threshold decrease. However, a minimum value exists which does not decrease even when combining different dispersing methods. For energetic intensive mixing (like turax), stirring time has no effect on the percolation threshold position and a homogenous dispersion of the filler in the matrix is rapidly obtained. However, the stirring time has an effect on the percolation threshold position when the dispersing method is not very energetic as it is the case for the wing mixer with a speed of 400 rpm. In this case, the percolation threshold decreases when increasing the stirring time. Since the initial mechanical properties of the epoxy matrix must be preserved and PPy is likely to modify them, the blends must show the jump of conductivity at the smallest amount of PPy. So, in order to obtain a more homogeneous distribution of the PPy_d in the epoxy matrix and to get a percolation threshold as low as possible, a long stirring time (5 min) is, therefore, applied to disperse PPy_d in the epoxy matrix when the wing mixer is used.

Although the percolation threshold of the blends prepared by the wing mixer and the turax methods are different, the shape of the conductivity curves (Fig. 2a and b) are similar. Before reaching the percolation threshold, the mixtures have a conductivity as low as the pure matrix, remaining constant with increasing PPy concentration. Then, at the percolation threshold the conductivity jumps of five magnitude orders and keeps this value for higher PPy contents. To get information about the homogeneity of PPy in the epoxy matrix, the conductivity was measured along and across every samples. For the set of blends prepared by the turax method, the same conductivity value is obtained when measuring in the two directions, so that a homogeneous distribution of the PPy_d in the matrix can be assumed. For the blends prepared by a wing mixer, the curve of conductivity values measured along the sample, exhibit the classical shape with the percolation threshold value previously reported (Table 2). The measurements obtained across the sample are very irregular and totally different from those measured in the other direction. The assumption of a heterogeneous distribution of PPy_d particles in the blend can, therefore, be made. A possible explanation for this is that the casting of the mixture into the mould introduce an orientation of the PPy_d particles. This orientation leads to the presence of resin layers near the walls of the mold caused by border effects which account for the irregularity of conductivity measurements performed across the samples. With the turax the vigorous stirring ensures an intimate distribution of the PPy particles in the matrix, so that no PPy free resin layer is formed.

A third set of experiments was performed using an ultrasonic probe to disperse PPy_d in the epoxy matrix. To show that the vibrations of the probe do not damage the PPy_d conductivity, PPy_d powder was mixed with acetone and submitted to ultrasonic vibrations (200 W, 20 Hz). Conductivity measurements performed on the dried PPy_d before and after sonication have shown that the conductivity of the pure PPy_d remains the same. Therefore, the blends can be prepared, without reservation, using the ultrasonic probe according to the process previously explained in the experimental part. As it has already been shown during laser

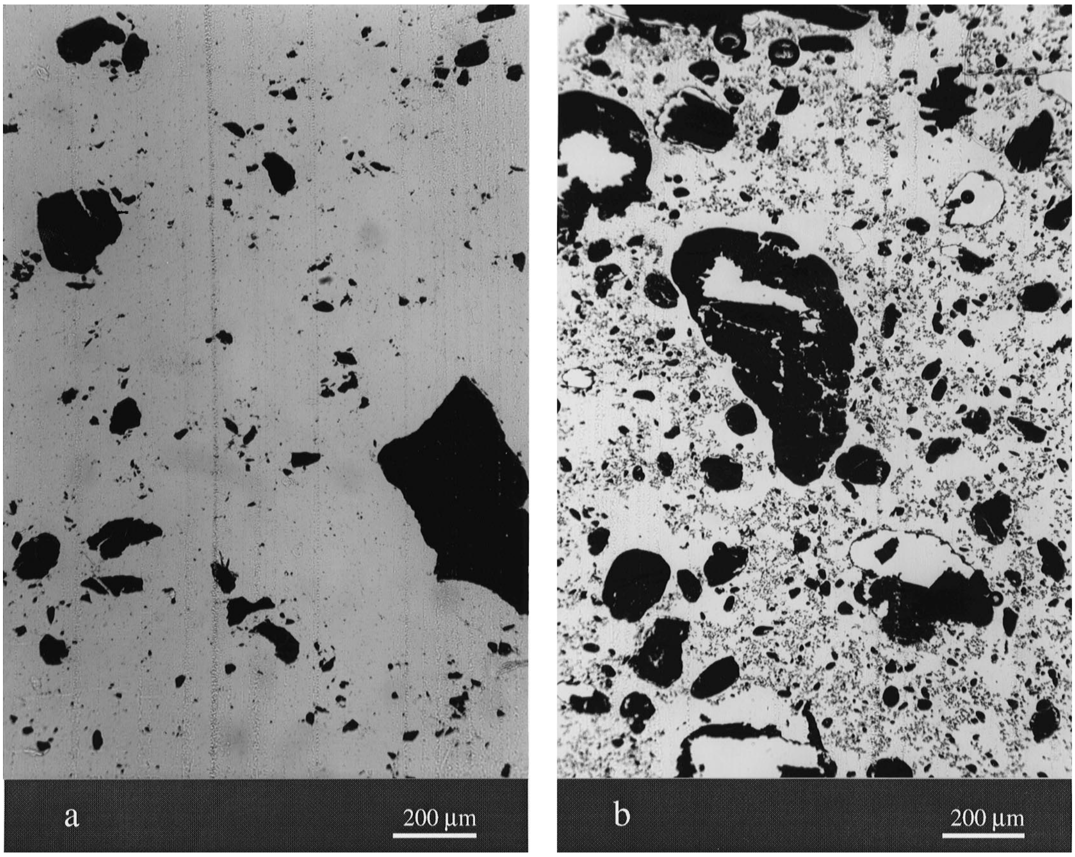

Fig. 3. Optical micrographs of PPy_d distribution in the epoxy matrix for the blends prepared with the wing mixer: (a) 5 wt% PPy_d, (b) 17 wt% PPy_d.

granulometry measurements, the ultrasonic vibrations break the PPy_d agglomerates and provoke a vigorous stirring which disperses the PPy particles into the matrix prepolymer. However, during mixing an important amount of PPy_d particles migrate out of the sonicated PPy/epoxy mixture along the ultrasonic probe. This migration phenomenon increases with increasing PPy_d concentration, so that higher amount of PPy_d are no longer subjected to the ultrasonic vibrations. In addition, high PPy concentration results in an increase of the solution viscosity and lowers the efficiency of the breaking. At high viscosity the adsorption of the vibration increases and hinders the propagation of the ultrasonic waves, so that all agglomerates cannot be broken. At a PPy concentration higher than 16%, PPy particles come in such close contact that through absorptive forces they form one mass and they can no longer be separated by the ultrasonic vibrations. As a consequence, and as it is shown in Fig. 2c, from 12 wt% PPy_d the conductivity increases slowly and continuously of three orders of magnitude until 16 wt% PPy_d and does not show any upper stabilisation. It remains very low even at high PPy content (10^{-6} S/cm at 16 wt% PPy_d) and does not exhibit any important jump, so that no percolation threshold can be observed. However, excepted at low concentration, conductivity measurements performed along and across the blends give similar values. This indicates a rather homogeneous distribution of PPy particles in the blend.

The last set of blends consists of an epoxy matrix mixed with increasing amounts of PPy_s (synthesized via suspension polymerization). Since PPy_s has a density close to that of RTM120 and does not exhibit any hard agglomerates, no energetic mixing methods are necessary to obtain a good dispersion of the PPy_s in the epoxy matrix. Therefore, mixing of the PPy particles and epoxy resin is realized with a glass stirrer. This method makes it possible to avoid the formation of air bubbles in the blends which can lead to an important porosity in the cured sample, particularly at high PPy_s concentration. The conductivity measurement (Fig. 2d) shows that, in contrast to blends prepared with PPy_d, where no significant initial increase in conductivity is observed, the addition of a small amount (1%) of PPy_s in the epoxy matrix induces an increase in the conductivity. These results have already been observed by other authors [17] on compression moulded samples of polypropylene (PP) particles coated with PPy. Although the PPy_d blends were prepared with very energetic dispersing methods, like for example the turax, their percolation threshold is higher than for that of the PPy_s blends. At the threshold, the conductivity shows an important jump of three orders of magnitude, and then remains constant at higher PPy content. The conductivity measurements performed along and across the blends give similar values, which once again indicate a homogeneous distribution of PPy in the blend.

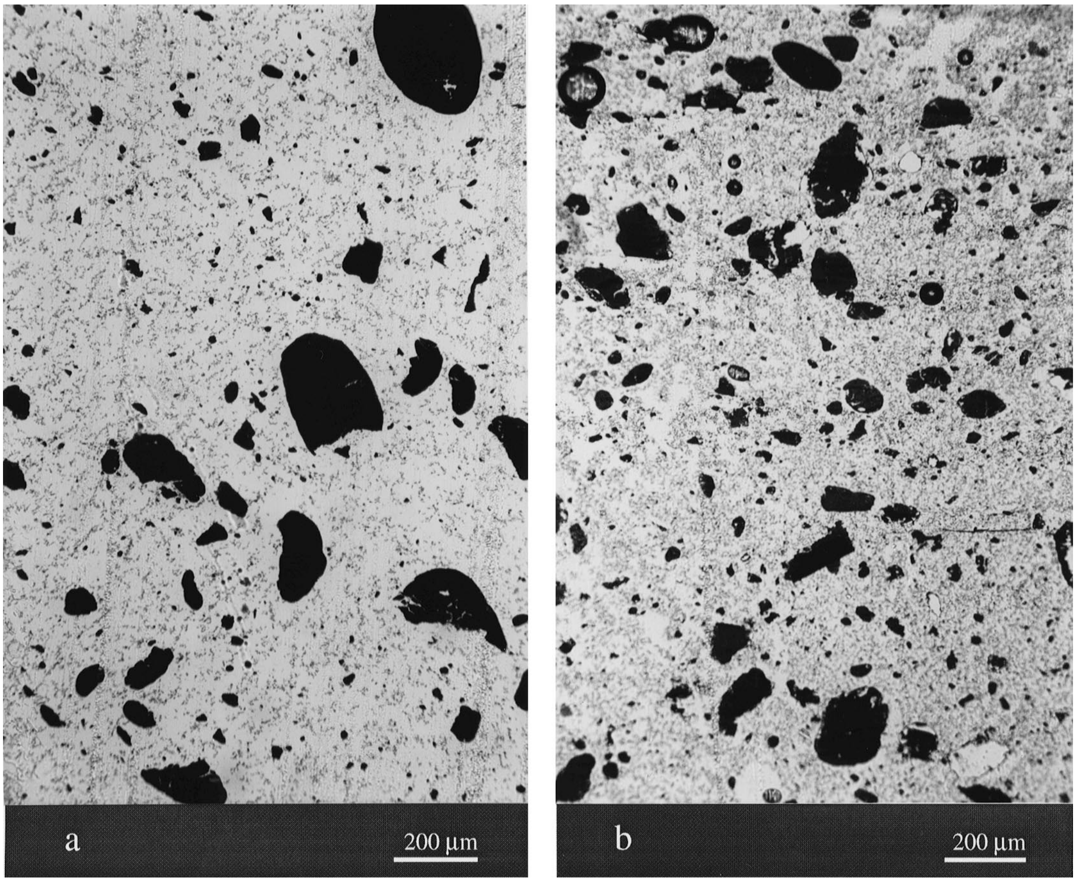

Fig. 4. Optical micrographs of PPy_d distribution in the epoxy matrix for the blends prepared with the turax: (a) 5 wt% PPy_d; (b) 17 wt% PPy_d.

According to these results, for the epoxy matrix filled with PPy_d, the turax method seems to be the most efficient dispersing method, leading to a more homogeneous dispersion and, thus, to a lower percolation threshold. However, PPy_s which exhibits larger particle size can easily be dispersed without energetic dispersing methods and provide easy to process blends with the lowest percolation threshold.

3.3. PPy distribution in the epoxy matrix

Photographs of optical microscopy were performed on blends elaborated with the wing mixer (Fig. 3), the turax (Fig. 4) and the ultrasonic probe (Fig. 5) for PPy_d content lower ($a = 5$ wt%) and higher ($b = 17$ wt%) than the percolation threshold. These experiments will make it possible to determine the distribution of the PPy in the epoxy matrix.

For all the optical micrographs, two different superimposed regions representing two kinds of PPy distribution can be distinguished. On one hand, a dispersed region consisting of fine particles or small aggregates (ten to thirty particles arranged together) can be observed in the background. Below the percolation threshold, these conductive fillers are assembled in small isolated clusters. In contrast above the percolation threshold, they form a continuous network throughout the blend. At both concentrations, the PPy distribution in the dispersed region of the blends appears to be denser for the turax method than for the others. Besides, the agglomerated region consists of agglomerates (hundreds of particles) of various sizes. They are compact and exhibit a very well defined outline. For the samples made with the wing mixer, the agglomerates size and quantity increase with PPy concentration (Fig. 3a and b), whereas, for the turax method the agglomerates size remains steady only their quantity increases (Fig. 4a and b). In the case of high PPy content (Fig. 3b, Fig. 4b), the number and size of PPy agglomerates in the blends appear to be smaller for the turax method than for the wing mixer. However, for all dispersing methods, even at a PPy concentration above the percolation threshold, the agglomerates have no contact with each other.

For the blends prepared with the wing mixer (Fig. 3), the PPy particles are mainly present in the agglomerated region. As the PPy concentration increases the number of agglomerates increases, representing an important surface area on the micrographs at high PPy content (Fig. 3b). However, even above the percolation threshold the agglomerates have no contact with each other and therefore, cannot enable the electron transfer. Simultaneously, with increasing PPy_d content in the blends, the population of PPy particles in the dispersed region increases slowly, forming clusters of various size. The agglomerates grow and become sensible to the shearing forces produced by the mixer, so they begin

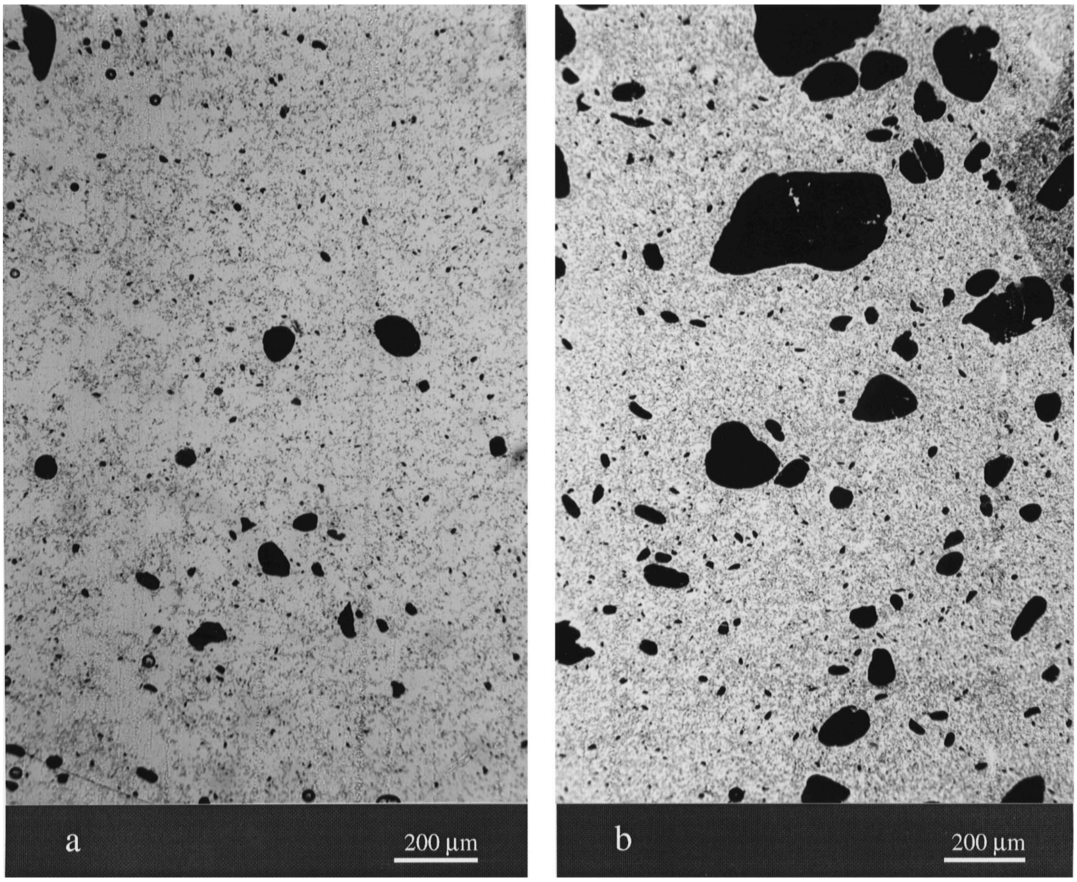

Fig. 5. Optical micrographs of the PPy_d distribution in the epoxy matrix for the blends prepared with the ultrasonic probe: (a) 5 wt% PPy_d, (b) 17 wt% PPy_d.

to break, increasing gradually the number of fine particles. Above the percolation threshold (Fig. 3b), the clusters of individualized particles touch each other, forming a continuous network of electrically conductive particles.

In contrast, already at low PPy_d concentration, the energy intensive turax method reduces the size and the number of agglomerates by breaking them, so that the quantity of individualized particles and small clusters are rapidly increased. Thus, as the area of the dispersed region grows, the agglomerated region becomes smaller, representing a small area even at elevated concentration (Fig. 4b). This rapid increase in the number of conductive fillers in the dispersed region allows the formation of an infinite cluster at a lower PPy concentration than for the blends made with the wing mixer. It can therefore, be concluded that the rapid increase in individualized particles and small aggregates, lowers the PPy concentration at which the network of conductive particles appears and therefore the percolation occurs earlier.

As it was already observed on CB/epoxy blends [3] the continuous network of dispersed particles enables electron transfers and, thus, is responsible for the direct-current conduction of the blends. As noticed, independent from the conductive filler's overall concentration in the blend, the jump of conductivity occurs always for the same concentration of conductive entities in the dispersed region. The obtained threshold depends on the appearance of this filler concentration in the dispersed region which is a function of the dispersing method. To obtain a jump of the conductivity at low PPy concentration the dispersing method has to break the agglomerates efficiently and form a fine network of dispersed particles.

At low PPy concentration (Fig. 5a), the blends prepared with the ultrasonic probe shows the best distribution of the PPy particles in the epoxy matrix. The agglomerates are small and rare, and the individualized particles are numerous and well distributed. With increasing PPy_d content the efficiency of this method decreases, the agglomerates grow and become larger than in the blends prepared with the turax. The concentration of the particles in the dispersed region increases as well and appears to be very dense (Fig. 5b). Nevertheless, the conductivity at high PPy_d concentration (17 %wt PPy) remains low and no percolation phenomenon can be observed. The reasons of this effect are not totally clear. Acetone decreases the initial volume fraction of PPy_d in the mixture leading to a lower viscosity. This solvent may also interfere with the polymer bridge formation between the PPy particles. However, a similar behaviour was already noticed for PPy/epoxy + diamine systems [14] elaborated in the presence of acetone.

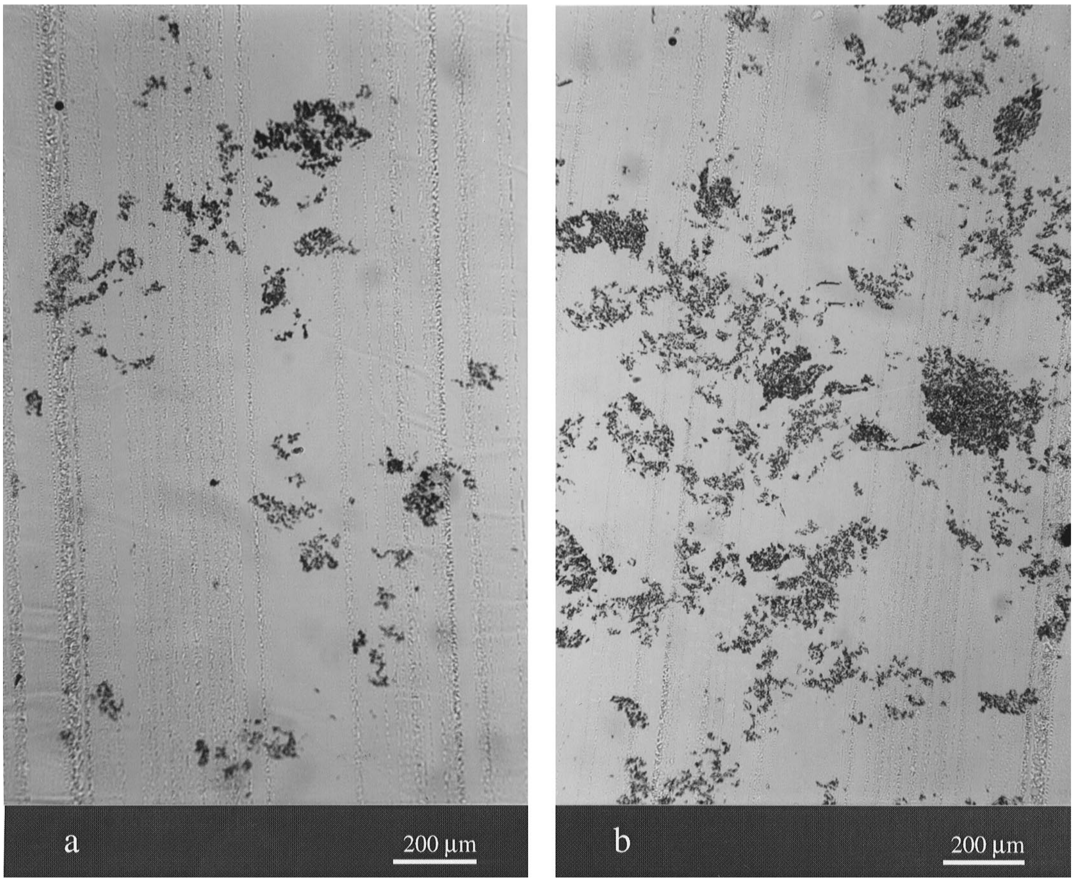

Fig. 6. Optical micrographs of PPy_s distribution in the epoxy matrix for the blends prepared with a hand stirrer: (a) 1 wt% PPy_d, (b) 3 wt% PPy_d.

Optical micrographs were performed on the blends elaborated with PPy_s (Fig. 6) at concentration below ($a = 1\%$) and slightly above ($b = 3\%$) the percolation threshold. The structure of PPy_s in the blends observed by optical microscopy is very different from that of PPy_d. For these samples as well, two different regions can be observed but only one kind of PPy distribution appears. The first region is an empty area of epoxy matrix alone, the other contains PPy particles which are arranged in irregular, aerate clusters with no defined outline. This region is similar to the dispersed region present in the previous blends. For concentrations lower than the percolation threshold, the clusters are isolated in the matrix (Fig. 6a). With increasing PPy_s content (Fig. 6b), the size of the clusters increases, gradually touching each other and finally forming at a given concentration a dense network of conducting particles making the blend electrically conductive. Even at elevated concentration, this kind of PPy with higher particles size does not show any tendency to agglomeration. This set of blends exhibits the lowest percolation threshold.

So, it can be seen that the morphology of the PPy mixed with the epoxy matrix is crucial for the final distribution of the PPy in the blends and consequently for the formation of the conductive network and the electrical characteristics of the blends. In contrast to the first three sets of blends made with PPy_d, in which the formation of large PPy_d particles agglomerates represents a loss of conductive entity, in the fourth set all the PPy_s particles participate to the formation of a conductive network. Therefore, the use of PPy_s particles as filler seems to be the most promising way to elaborate the conductive epoxy matrix.

3.4. Microstructure of the blends

The microstructure of the PPY_s and PPY_d distribution were observed by transmission electron microscopy performed on a epoxy matrix/5 wt% PPy_d blend made with the turax (Fig. 7) and on a hand stirred epoxy matrix/ 5 wt% PPy_s blend (Fig. 8).

The agglomerated region of blend made with the turax can be observed on Fig. 7a which shows the microstructure of the compact, black agglomerates seen on the optical micrographs. This view confirms the spherical shape and the homogeneous size (100 nm) of the PPy_d particles obtained by a dispersion polymerization route. Their distribution in the agglomerate appears to be dense and each particle is surrounded by the resin. So, it can be seen that the matrix has consequently diffused through the agglomerate leading to well defined and separated particles. Indeed, as it was described for the carbon black [31], this diffusion

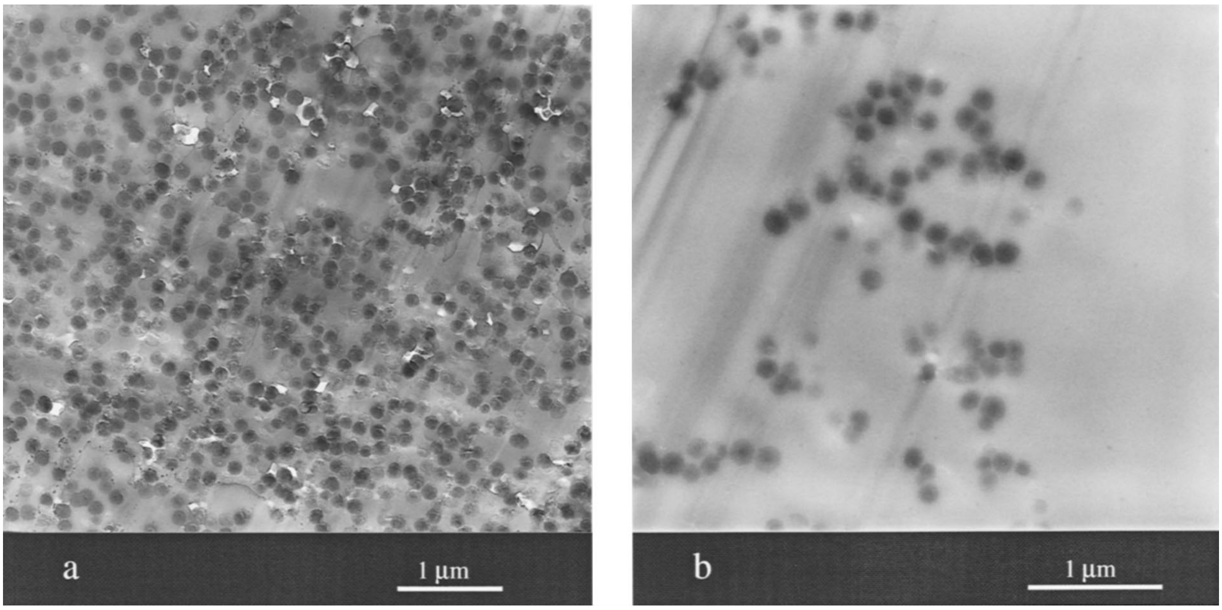

Fig. 7. Transmission electron micrographs of the epoxy/PPy$_d$ blends prepared with the turax: (a) microstructure of an agglomerate, (b) cluster of the dispersed region.

of the matrix between the PPy$_d$ particles takes place during the first step of the mixing process: First, agglomerates are formed by penetration of the matrix in the voids between the PPy$_d$ particles under the pressure which builds up during the mix. Once the voids were filled, PPy is incorporated but not dispersed. Then, as soon as they are formed, these agglomerates are exposed to the shearing forces and are eventually dispersed, leading to smaller aggregates or individualized particles which form the dispersed region. This dispersed region observed on the background of the optical micrographs is shown in Fig. 7b. It consists of small clusters of about thirty individual particles, isolated and randomly distributed in the matrix which exhibit a grape like structure.

The microstructure of the PPy$_s$ clusters observed on the optical micrographs of the hand made blends is shown in Fig. 8a. The PPy$_s$ particles are arranged in a grape like structure as well. At higher magnification (Fig. 8b), it can be seen that these PPy$_s$ particles are also spherical but they are joining and their outline is fuzzy.

So, it can be noticed that although the two kinds of PPy exhibit different macroscopic aspect, the microstructure of the PPy$_d$ clusters in the dispersed region (Fig. 7b) and those of the PPy$_s$ (Fig. 8b) are the same. At this scale however one difference can be distinguished, the PPy$_d$ particles are well separated whereas the PPy$_s$ ones are joining. So it can be assumed that the nature of the electrical conduction is not the same in the blends prepared with PPy$_d$ and those prepared with PPy$_s$.

4. Conclusion

In this study, various attempts were made to elaborate a PPy/epoxy blend which will provide the percolation threshold at the lowest PPy concentration and so will ensure the conservation of the mechanical properties of the matrix.

While the classical percolation theory predict in the case of a three-dimensional system a percolation threshold of 16% vol of filler concentration, none of the blends elaborated in this study meet this theoretical value. In fact, this prediction was obtained assuming the presence of spherical, isotropic, monodispersed and randomly dispersed filler particles in the matrix. However, the PPy particles, although of spherical shape, are arranged in agglomerates or clusters of various size with an irregular grape like structure. Further, the influence of the dispersing method on the percolation threshold position, which is well illustrated in this work, is not taken into account in the percolation theory. Indeed, it was shown that energy intensive dispersing methods, like turax, favour the formation of conductive networks and, therefore, lower the PPy percolation concentration.

The influence of filler morphology on the percolation threshold was studied as well. Although it was reported [18] that small particles lead to a lower percolation threshold this is not confirmed by the present study, since the conductive PPy exhibiting the higher particle size leads to the blends which show the lowest percolation threshold. Indeed, the low particle size increases the tendency to agglomeration. Therefore, in the blends prepared with the PPy exhibiting the smallest particles size, i.e. PPy synthesized by dispersion polymerization, a great fraction of the small PPy$_d$ particles form agglomerates. These large agglomerates become the conductive entities and consequently, a high PPy concentration is necessary to form an infinite cluster which ensures the electrical conduction throughout the blend. For PPy$_s$ particles synthesized by suspension polymerization, which are larger than the PPy$_d$

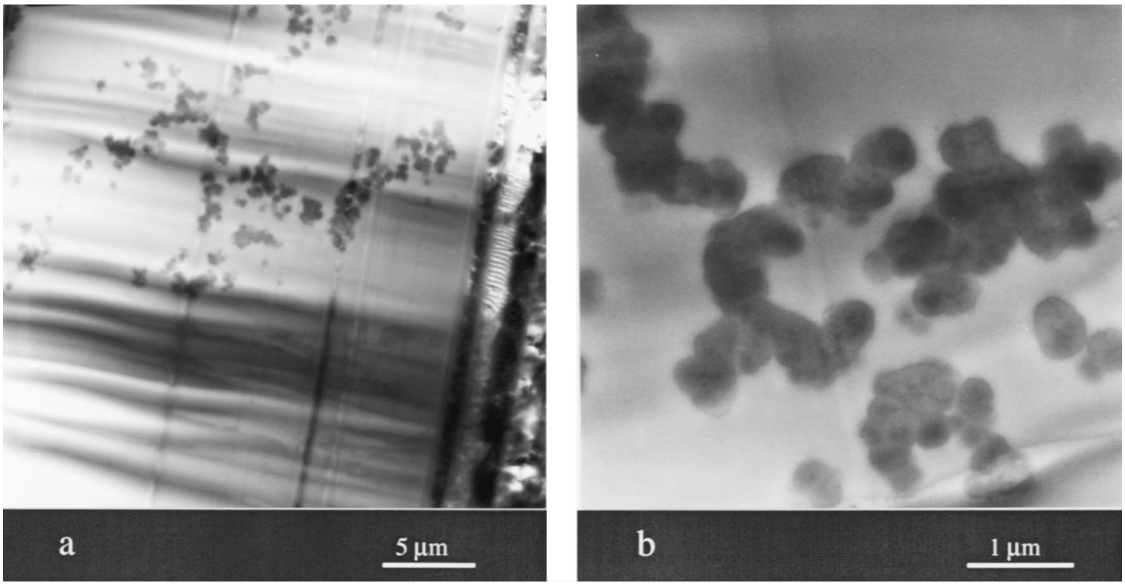

Fig. 8. Transmission electron micrographs of the epoxy/PPy_s blends prepared with the hand stirrer: (a) isolated clusters, (b) microstructure of a cluster.

particles, the tendency to form agglomerates is lower which leads to more homogeneous distributions in the matrix. This makes it possible to reach the percolation threshold at a lower PPy_s concentration.

In addition, since in the blends the PPy_s particles are joining and the PPy_d particles are separated, the assumption of a difference in nature of the electrical conduction in the blends made with the two kinds of PPy was made. In this case, the role of the steric stabiliser PVA on the surface of the PPy particles has to be studied, so as to clarify its influence on the structural arrangement of the particles in the matrix, i.e. separated or joining particles, arranged in agglomerate or not.

Finally, according to the results of this work, the PPy prepared via supension polymerization is the most convenient filler to make the epoxy matrix electrically conductive. As the PPy_s/epoxy blend reaches the percolation threshold at a lower PPy concentration, the influence of the filler on the mechanical properties of the blends is minimized. In contrast, the large agglomerates present in the PPy_d/epoxy matrix can act as failure initiating flaws and can give rise to poor mechanical properties. Indeed, agglomerates larger than the inherent flaw size for the epoxy matrix can be responsible for the decrease in material stiffness, failure energy and fatigue resistance. However, PPy synthesized by suspension polymerization provokes an important increase in the epoxy resin viscosity, so further viscosity measurements have to be performed on the blends to verify that they meet the requirement of low viscosity (lower than 0.5 Pa s) necessary for their process.

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