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Preparation and characterisation of blends based on polyamide 6 and hyperbranched aramids as palladium nanoparticle supports

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Abstract

Solution and melt blends have been prepared by mixing polyamide 6 (PA6) with hyperbranched (HB) aromatic polyamides (aramids) synthesized from A_2 (*p*-phenylenediamine) + B_3 (trimesic acid) reactants. The HB aramids (pPDT), were obtained using various polymerization conditions, hence were characterized by different content and ratio of –COOH and –NH_2 end group functionalities, as well as different architectures.

For comparison, the characteristics of the above blends have been matched to those based on PA6 and the HB aramid synthesised from an AB_2 monomer (namely 5-(4-aminobenzoylamino)isophthalic acid, named ABZAIA), which was the topic of a previous paper of ours [O. Monticelli, D. Oliva, S. Russo, C. Clausnitzer, P. Pötschke, B. Voit, Macromol Mater Eng 288 (2003) 318–25. [1]]. Viscosity data and glass transition temperatures of solution and melt blends underlined the good miscibility between the blend components. Blend properties, namely glass transition temperature and rheological behaviour, have been found to depend on concentration and type of the HB aramid. Indeed, the presence of pPDT aramids in the blends caused a weaker variation of the rheological behaviour, with respect to neat PA6, as compared to poly(ABZAIA).

Both the above solution and melt blends have been used as supports of palladium nanoparticles. The metal-retaining capability of neat PA6 was greatly enhanced by blending it with pPDT polymers. In these blends, the Pd loading has been found directly proportional to the amino group content of the HB aramid, thus justifying better performances of pPDTs over poly(ABZAIA). The large increase of metal loading in the above blends has not been carried out at expenses of Pd nanoparticle dimensions, as revealed by the unchanged size distribution of metal dispersion by TEM.

Keywords: Blends; Hyperbranched aramids; Palladium nanoparticles

1. Introduction

A recent study of ours has reported on a hyperbranched (HB) aramid of poly(AB_2)-type, named poly(ABZAIA), characterised by a molecular structure similar to that of poly(*p*-benzamide) in terms of sequences of CO and NH along the branches, an amino focal point and several carboxy end groups [1]. The above HB aramid was solution- and melt-blended with polyamide 6. The characterisation data of the solution blends indicated a full miscibility between the hyperbranched and the linear polyamide. Moreover, blends prepared by melt mixing turned out to be somehow reactive as shown by the rheological measurements, which revealed that the HB aramid formed either a covalently bonded network or, at least, a strong physical network within the PA6 phase.

Recently, several types of hyperbranched polymers have found interesting applications as blend components [1–8]. One of the most promising exploitation of blends based on HB polymers is the use of the hyperbranched component as carrier of different types of molecules. Schmaljohann et al. [6] used modified HB polyesters as dye carriers in polyolefin blends. The resulting materials showed a homogeneous distribution of the dye inside the polymer blend. On the contrary, large and poorly distributed dye crystals were observed when neat polyolefin was used as the matrix.

Besides being carriers of organic molecules, HB

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polymers can be used as supports of metal catalysts, in order to increase the metal loading of the polymer matrix, still preserving a fairly good catalyst dispersion. Recently, some of us reported on the first example of the use of HB aramids (both of poly(A_2+B_3)- and poly(AB_2)-type) as support materials for palladium nanoparticles in heterogeneous catalysis applications [9].

The capability of HB aramids to form miscible blends with PA6, joined to their property to support metal nanoparticles, induced us to investigate the characteristics of blends prepared from the above polymers and to study palladium deposition on the obtained blends.

On these grounds, we report in the present work on the preparation of solution and melt blends made of polyamide 6 and hyperbranched aramids from (A_2+B_3) reactants. The blend properties have been investigated by several characterisation methods and techniques (DSC, IR, SEM, solution viscosity and rheological measurements). As mentioned above, the prepared blends were used as supports for palladium nanoparticles. Metal loading of the blend has been evaluated by SEM–EDS while TEM measurements allowed to characterise the metallic dispersion.

2. Experimental section

2.1. Materials

The HB aramids were obtained according to the procedure given in Refs. [10,11]. Polymer characterisation was given in the above papers. Three poly(A2+B3) aramids were used in the present work, being prepared by varying the reactant ratio as well as the polymerisation time (Table 1).

Polyamide 6, supplied by Radici company, had a [NH_2]/[COOH] ratio equal to 34/32. The above values are expressed in N equiv./kg.

2.2. Blend preparation

Solution blends were obtained by overnight dissolution of the two polyamides in a common solvent (H_2SO_4, 96 wt%) at room temperature. Dilute solutions (concentration 0.5 wt%) were prepared in order to obtain finely dispersed powders by precipitation with an excess of non-solvent (water). The powders were filtered, washed several times with water and dried overnight in a vacuum oven at 60 °C.

Table 1
Experimental conditions for the poly(A2+B3) aramid synthesis

Sample code	Polymerization time (t_p) (min)	T (°C)	[NH_2/COOH] in the feed
pPDT1	60	80	2/3
pPDT2	90	80	2/3
pPDT3	90	80	1/1

Melt blends were prepared by using a twin-screw microcompounder (DACA-Instruments, USA) with a mixing compartment volume of approximately 5 ml. Both polymers were simultaneously added as powders and mixed at a screw speed of 100 rpm for 5 min at 240 °C. The material was passed out into air in a strand shape. During the experiments, both torque and load were measured.

2.3. Preparation of blend-supported Pd clusters

Blend powders were stirred in an aqueous solution of acetic acid containing $PdCl_2$ (Aldrich, 0.01 wt%) at room temperature for 48 h. The polymer/$PdCl_2$ ratio was 10/1 (w/w). The powders were filtered, washed several times with deionized water and dried overnight at 60 °C. Palladium reduction was carried out using an aqueous solution of $NaBH_4$ (0.1 M) at 50 °C for 2 h. After reduction, the powders were washed extensively to remove the excess of reducing agent and dried at 60 °C under vacuum for at least 24 h. The same procedure for both powder impregnation and reduction was followed for melt blends and neat PA6.

2.4. Blend characterisation techniques

Solution viscosity of each blend was measured in H_2SO_4 (96 wt% in water) at 20 °C in a suspended level Ubbelohde viscometer.

Differential scanning calorimetry (DSC) runs were performed on a Mettler calorimetric apparatus, mod. TC10A, at a heating rate of 10 °C/min, using a sample mass of approximately 10 mg.

Morphology was evaluated using a LEO scanning electron microscope (SEM) Model Stereoscan 440. The powders, suspended in methanol, were deposited on a metal disk, dried and finally sputtered with gold, by means of a SCD 030 sputtering device, for SEM observations.

Melt rheological investigations were performed at 250 °C using a Rheometrics ARES with plate–plate geometry in the oscillation mode under nitrogen atmosphere. The plate diameter was 25 mm and the gap ranged from 0.9 to 1.5 mm. A frequency range between 0.1 and 100 rad/s and a strain within the linear viscoelastic range were used. Speciments from the extruded strands were investigated.

2.5. Characterisation techniques of blend-supported Pd clusters

The amount of palladium retained by the various samples was measured by SEM–EDS analysis using a Leo Steroscan-440 scanning electron microscopy, equipped with an EDS system (Oxford Link-Gem). The samples were prepared as previously described but coated with carbon before analysis. The technique does not allow to evaluate the absolute atomic amount but the relative concentration only.

TEM measurements, which allowed to calculate the metallic dispersion (MD), were performed with a high-resolution transmission electron microscope (JEOL 2010). The powders were suspended in iso-propanol and a drop of the resultant mixture was deposited on a carbon grid.

MD was evaluated by high magnification TEM micrographs. In order to obtain a representative value of the palladium nanocluster dimensions, the diameter of at least 200 particles, belonging to different sample regions, was measured.

The metallic dispersion was calculated as the ratio between the superficial ($N(s)_m$) and the total ($N(t)_m$) number of metallic atoms, while metal particle diameter was reported as both number diameter (dn) and volume/area diameter (dva $=6\sum(V_i)/\sum(A_i)$; V_i; A_i: volume and area of a single cluster). The calculation of dva was performed considering the particles spherical, using the following expression:

$$\mathrm{dva} = 6\left[\frac{\sum(V_i)}{\sum(A_i)}\right] = 6\frac{v_M N(t)_m}{a_M N(s)_m} = \frac{6\left(\frac{v_M}{a_M}\right)}{\mathrm{MD}}$$

where v_M and a_M are respectively 1.47×10^{-29} m^3 and 7.87×10^{-20} m^2.

3. Results and discussion

3.1. Solution and melt blends based on PA6 and HB aramids from A_2+B_3 reactants

The three types of hyperbranched poly(A_2+B_3) aramids mentioned above (Table 1), have been mixed with PA6 in solution in order to obtain the corresponding blends.

As the HB aramid structure may influence blend formation and properties, it is relevant to recall here some characteristics of its features.

^{1}H NMR studies [11,12] have demonstrated that both polymerisation time (t_p) and reactant ratio (i.e. the [NH_2]/[COOH] ratio) influence the relative content of dendritic, linear and terminal units, hence the total amount of functional groups.

By comparing the properties of the three pPDT samples, it resulted that the HB aramid formed at the longest polymerisation time showed the lowest content of free amino groups. The above parameter, i.e. t_p, influenced also the aramid structure, as HB aramids synthesized at low t_ps were characterised by a more open structure, namely by a higher content of accessible end groups, in comparison to polymers prepared using longer polymerisation times. Moreover, the sample pPDT3, prepared by using an amino to carboxy group molar ratio equal to 1, showed enhanced amide formation with the total number of remaining acidic functions reduced.

In the present work, some results related to blends based on poly(ABZAIA) are also reported for comparison. As is well known, the above HB aramid is completely different from pPDT samples as it holds a single amino focal unit and all other end groups are carboxylic acid functionalities [10].

On the basis of these relevant differences, it is possible to explain the various blend properties. Table 2 summarises intrinsic viscosity data and thermal behaviour of the solution blends prepared from the three pPDT samples mentioned above, in comparison to the corresponding values of both a blend based on poly(ABZAIA) and the neat polymer.

Analogously to what has been previously reported for blends based on PA6 and poly(ABZAIA) [1] and in contrast to the simple additivity rule, intrinsic viscosity values of the blends increase as the content of pPDT aramid increases.

The aramid sample exerting less influence on the solution viscosity of the corresponding blend is pPDT3. By adding an increasing amount of the above polymer to PA6, the viscosity of the solution blend increases only slightly. In order to explain this behaviour, it is necessary to take into account, as previously reported, that the above aramid is characterised by a rather low concentration of COOH groups. As we have found in our previous work [1], the interactions between the linear and the hyperbranched polyamide (most probably via hydrogen bonding), should involve the COOH groups of the HB aramid and the amide NH groups of PA6. As a consequence, the low concentration of carboxy groups of pPDT3 would lead to a reduction of the interactions between the two blend components. On this basis, it is clear that poly(ABZAIA), characterised by COOH end groups only, is capable to have a higher degree of interactions with PA6 and a higher contribution to the viscosity increase.

Making a comparison between the aramids prepared at two different t_ps starting from the same [NH_2]/[COOH] ratio, it has been found that the sample pPDT1 ($t_p=60$ min) is able to modify the blend viscosity a little more than the HB aramid pPDT2 ($t_p=90$ min). In this case, it is the polymer structure, which seems to affect blend properties more than the concentration of functional end groups. In fact, the higher accessibility of the functional groups of the aramid prepared at a shorter polymerisation time should favour the interactions with polyamide 6.

Besides viscosity, the presence of hyperbranched aramids also influences the thermal behaviour of the blends. Namely, glass transition temperature (T_g) increases by increasing the pPDT concentration in the blends. The good correlation of our data with those calculated from Fox equation [13] and the occurrence of a single T_g support the hypothesis of an excellent miscibility of the blend components. Once more, the T_g increase depends on the specific HB aramid used considering the blends based on pPDT polymers, the extent of this increase follows the same trend found for intrinsic viscosity. Namely, pPDT3 is capable to modify blend T_g less than the other pPDT aramids. Despite the reduced interactions between the above

Table 2
Characterization data of the solution blends PA6/pPDT and PA6/p(ABZAIA)

Sample code	HB monomer type	$[NH_2]$/[COOH] in the feed	t_p (min)	HB (wt%)	$[\eta]_{20\,°C\ H_2SO_4}$ (dl/g)	$[\eta]_{\text{calculated}}$[a] (dl/g)	T_g[b] (°C)	$T_{gF\text{–}F}$[c] (°C)	ΔH_{mI}[d] (J/g)	ΔH_{mII}[e] (J/g)	$T_m$onsetI[f] (°C)	$T_m$onsetII[b] (°C)
PA6(s)	–	–		0	2.17	–	56	–	58.8	54.5	206.2	204.1
PA(pPD-T1)5(s)	A_2+B_3	2/3	60	5	2.27	2.07	63	58	48.9	54.2	207.7	197.9
PA(pPD-T1)10(s)	A_2+B_3	2/3	60	10	2.47	1.97	68	60	43.0	48.1	207.8	197.5
pPDT1(s)	A_2+B_3	2/3	60	100	0.17	–	160	–	–	–	–	–
PA(pPD-T2)5(s)	A_2+B_3	2/3	90	5	2.15	2.10	61	57	52.7	50.7	212.0	199.2
PA(pPD-T2)10(s)	A_2+B_3	2/3	90	10	2.30	2.02	64	59	48.9	44.4	205.3	195.4
PA(pPD-T2)20(s)	A_2+B_3	2/3	90	20	2.47	1.87	71	64	38.3	23.1	199.0	156.2
pPDT2(s)	A_2+B_3	2/3	90	100	0.67	–	150	–	–	–	–	–
PA(pPD-T3)5(s)	A_2+B_3	1/1	90	5	2.15	2.08	–	57	–	–	–	–
PA(pPD-T3)10(s)	A_2+B_3	1/1	90	10	2.17	1.99	62	59	43.2	48.6	206.5	193.2
PA(pPD-T3)20(s)	A_2+B_3	1/1	90	20	2.20	1.82	68	64	30.6	31.8	203.4	172.0
pPDT3	A_2+B_3	1/1	90	100	0.41	–	150	–	–	–	–	–
PA(pAB-ZAIA)10(s)[a]	AB_2	–	–	5	2.67	2.08	61	57	53.8	47.3	205.0	195.5
p(ABZAIA)	AB_2	–	–	100	0.40	–	150	–	–	–	–	–

[a] $[\eta]$ theoretically calculated bases on the additivity rule.
[b] Calculated from the second heating run of DSC measurements.
[c] Glass transition temperature theoretically calculated using Fox equation.
[d] Melting enthalpy calculated from the first heating run of DSC measurements.
[e] Melting enthalpy calculated from the second heating run of DSC measurements.
[f] Calculated from the first heating run of DSC measurements.

hyperbranched aramid and PA6, both viscosity and t_g data confirm that also in this case the blend components are fully miscible.

Data in Table 2 also show that both the crystallinity content, i.e. the melting enthalpy, and the melting temperature decrease by increasing the concentration of pPDT aramids in the blend.

Analogously to what has been previously reported for blend containing poly(ABZAIA) [1], powders obtained by precipitation of dilute (pPDT+PA6) solutions are constituted of well-dispersed and very homogeneous spherical particle, characterised by very similar dimensions (average size ca. 400 nm).

Two pPDT samples, namely pPDT2 and pPDT3, have been extruded together with PA6 in the microcompounder described in the Section 2. Thermal properties of the melt blends based on the above polymers are given in Table 3, together with the corresponding data of both the neat PA6 and the blend based on poly(ABZAIA).

As already reported for the solution blends, the excellent miscibility of blend components can be inferred by the increase of t_g by increasing the HB aramid content. Comparing solution and melt blends containing the same pPDT polymer amount, it results that the former ones are characterised by a slightly higher t_g (compare samples PA(pPDT2)5(s) and PA(pPDT2)5(m)).

In order to verify the formation of a network linked to possible chemical reactions at high T between the blend components, similarly to what has been found in other blends containing HB polymers [7], solubility tests in H_2SO_4 at room temperature have been carried out. Melt blends based on poly(ABZAIA) turned out only to swell in the above solvent and the degree of swelling was a function of the HB aramid content in the blend. On the contrary, all blends containing pPDT aramids, except the sample PA(pPDT2)5(m), were found fully soluble in H_2SO_4. Once again, these results support the idea that the interactions between the two polymers occur by carboxy terminal groups. Indeed, also the blends based on pPDT aramids have been found to be miscible with PA6, but the relatively low concentration of carboxy end groups prevented network formation. Clearly, when the content of the above functional groups is increased, as in the case of the aforementioned PA(pPDT2)5(m) blend, chemical reactions, responsible for the network formation, are more likely to occur.

It is important to underline that, in the case of pPDT aramids, in order to obtain soluble material, polymerisations were stopped prior to the attainment of the gel point [11,12]. Thus, the final hyperbranched polymers still contain active groups, which could react with PA6 to form the above network and even with themselves to develop a gel, during compounding at high temperatures.

Melt blends containing the highest concentration of HB aramids, namely 5 wt%, have been studied in terms of their rheological behaviour, in comparison to that of neat PA6

Table 3
Characterization data of the melt blends PA6/pPDT and PA6/p(ABZAIA)

Sample code	HB monomer type	$[NH_2]/[COOH]$	t_p (min)	HB (wt%)	$T_g{}^a$ (°C)	$T_{gF-F}{}^b$ (°C)	$\Delta H_{mI}{}^c$ (J/g)	$\Delta H_{mI}{}^d$ (J/g)	$T_m$onsetI^e (°C)	$T_m$onsetII^a (°C)
PA6(m)	–	–		0	56	–	58.4	59.21	206.2	204.1
PA(pPDT2)2(m)	A_2+B_3	2/3	90	2	57	56	48.7	–	210.8	204.4
PA(pPDT2)5(m)	A_2+B_3	2/3	90	5	58	57	50.2	–	210.1	200.3
PA(pPDT3)2(m)	A_2+B_3	1/1	90	2	56	56	47.0	–	211.8	202.4
PA(pPDT3)5(m)	A_2+B_3	1/1	90	5	59	57	54.3	–	210.8	200.2
PA(pABZAIA)5(m)	AB_2	–	–	5	61	57	49.8	46.5	205.4	203.2

[a] Calculated from the second heating run of DSC measurements.

[b] Glass transition temperature theoretically calculated using Fox equation.

[c] Melting enthalpy calculated from the first heating run of DSC measurements.

[d] Melting enthalpy calculated from the second heating run of DSC measurements.

[e] Calculated from the first heating run of DSC measurements.

and of a blend containing poly(ABZAIA). The trend of the melt viscosity as a function of frequency is completely different in neat PA6 and in the above blends (Fig. 1).

While PA6 exhibits a Newtonian behaviour, the viscosity of our blends strongly decreases with frequency. The same phenomenon has been found for other hyperbranched polymers with carboxylic or phenolic end groups [8,14].

Although all our blends do not exhibit a Newtonian behaviour, those based on pPDT show a lower complex viscosity, especially at low frequencies.

The difference in their rheological behaviour is even more evident considering the loss modulus, G'', and the storage modulus, G' (Fig. 2).

In contrast to neat PA6, which exhibits a prevailing viscous behaviour ($G''>G'$), blends based on poly(ABZAIA) have a predominant elastic behaviour ($G''<G'$). However, in blends containing pPDT aramids, G'' is still above G', similarly as for linear PA6 but to a lesser extent, indicating already the influence of the more elastic and strongly interacting hyperbranched polymer. Moreover, it is interesting to point out that in blends of PA6 with pPDT2 the storage modulus is higher than in the blend based on pPDT3, which we assume to be a result of the stronger interactions of pPDT2 compared to pPDT3.

3.2. Palladium nanoparticles supported on solution and melt blends based on PA6 and pPDT aramids

(PA6+pPDT) solution and melt blends have been used as supports for palladium nanoparticles. Tables 4 and 5 summarise the main features of the two types of blends, respectively, in terms of both Pd loading and dispersion (Pd cluster volume/area diameter, dva, and metallic dispersion, MD) as calculated by TEM.

Making a comparison between the solution blends and the neat PA6 in terms of the amount of retained metal (Table 4), it comes out that Pd content is much higher in the above blends than in PA6. In order to explain this result it is important to make some additional comments.

Table 4
Characterization data of the Pd containing-solution blends PA6/pPDT and PA6/p(ABZAIA)

Sample code	Pd content (%)	dva (nm)	dn (nm)	MD (%)
PA6Pd(s)	5.3	6.3	4.6	18.0
pPDT1Pd(s)	12.8	6.0	3.5	18.7
PA(pPDT1)10Pd(s)	7.3	5.7	3.5	19.6
PA(pPDT2)10Pd(s)	7.7	–	–	–
PA(pPDT3)10Pd(s)	11.8	5.4	4.3	20.1
PA(pABZAIA)10(s)	5.4	–	–	–

Since the pioneering works on the potential use of polymers as carriers for metal catalyst, polyamide 6 turned out to have rather interesting properties [15]. XRD and IR characterisation of the above polymer impregnated with a metallic precursor, namely $PdCl_2$, showed the formation of a chelate bond of Pd(II) with the amide groups of the polyamide. Moreover, the system PA6/Pd exhibited high selectivity in the hydrogenation of the olefinic bond without any reduction of other groups. On the other hand, it is clear that the anchoring of the metal precursor to amide groups might be hindered by competitive interactions among the macromolecules, involving NH and CO groups.

As far as our HB aramids are concerned, interactions of the metal precursor with aromatic amide groups are prevented because of the stabilisation effect induced by the aromatic ring on the amide nitrogen. On the other hand, we already reported that only the NH_2 end groups in their molecule are able to bind palladium [9]. As pPDT aramids are characterised by a relatively large content of NH_2 end groups, which are more easily accessible than the amide NH groups of PA6, the above aramids turned out to retain higher

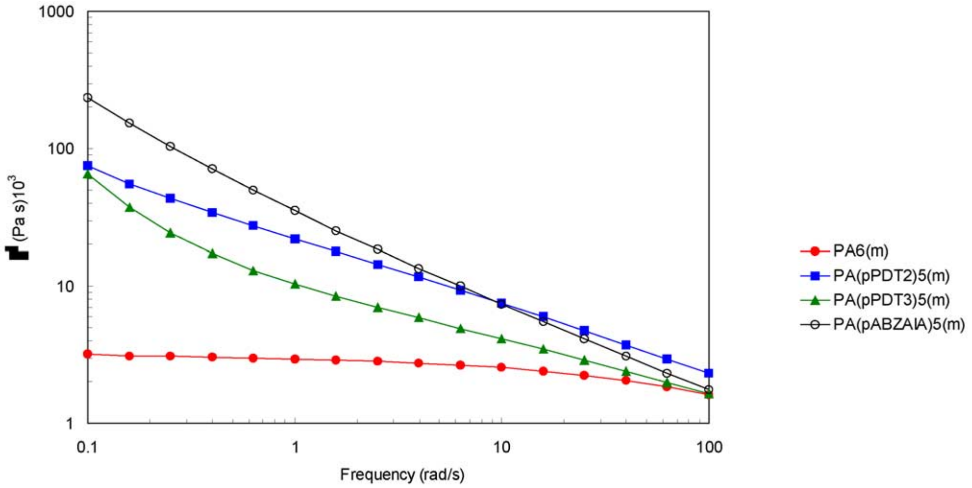

Fig. 1. Complex viscosity $|\eta^*|$ of PA6(m) and its melt mixed blends (based on pPDT2, pPDT3 and poly(ABZAIA) HB aramids) vs. frequency ($T=250$ °C).

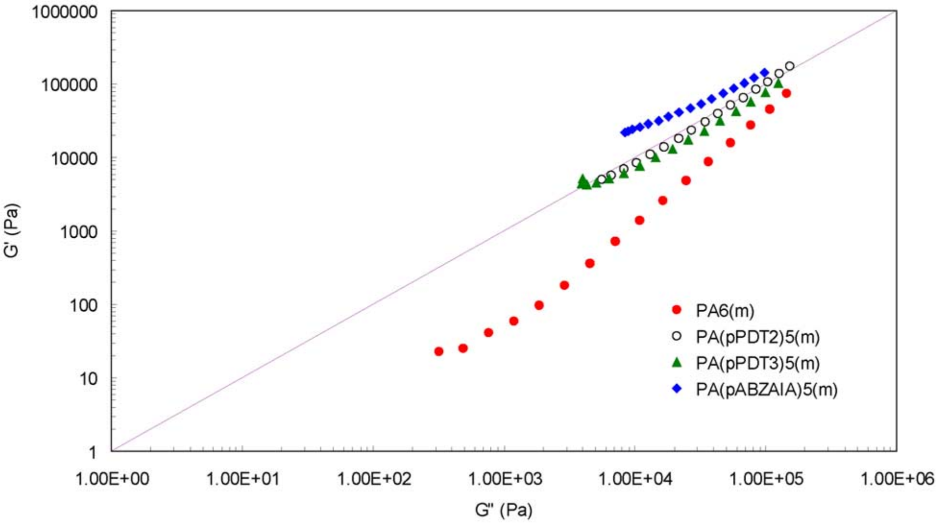

Fig. 2. Storage modulus G' of PAi1(m) and its melt mixed blends, based on samples pPDT2, pPDT3 and poly(ABZAIA), vs. loss modulus G' ($T=250$ °C, frequency sweep 0.1–100 rad/s). Diagonal represents $G'=G''$.

metal amount than PA6. This effect is clearly evident from the data in Table 4, where the sample pPDT1(s) is capable to retain 12.8% of metal, while Pd content retained by neat PA6 is only 5.3%.

On this basis, the presence of our hyperbranched aramids, homogeneously dispersed in PA6 matrix, would increase the amount of catalyst retained by the latter.

Clearly, the capability of retaining palladium by the various blends we prepared is different, depending on the type of HB aramid used. Our results clearly show that blends based on pPDT aramids are capable to retain a higher amount of Pd than those prepared with poly(ABZAIA), due to the higher concentration of the terminal amino groups responsible for the interaction with the metal.

Furthermore, it is interesting to point out that the metal content in the blends strictly follows the amino group concentration in the HB aramid. As already mentioned, the sample pPDT3, polymerised with an equal molar ratio of primary amino to carboxyl groups, is characterized by the highest content of NH_2 end groups. With respect to neat PA6, the presence of 10 wt% only of the above HB aramid in the blend allows to get twice the amount of retained Pd. The high metal retention capability of blends based on pPDT samples is also explained taking in account that the functional groups responsible for the interactions with PA6, namely COOH groups, are not involved in the interactions with the metal precursor, thus leaving the NH_2 functionalities completely accessible to Pd(II).

Table 5
Characterization data of the Pd containing-melt blends PA6/pPDT and PA6/p(ABZAIA)

Sample code	HB (wt%)	Pd content (%)
PA6Pd(m)	0	1.8
PA(pPDT2)2Pd(m)	2	2.0
PA(pPDT2)5Pd(m)	5	2.5
PA(pPDT3)2Pd(m)	2	2.4
PA(pPDT3)5Pd(m)	5	3.4
PA(pABZAIA)5(m)	5	1.9

Obviously, for the exploitation of a catalytic system, besides the metal concentration on the carrier, it is important to consider also the metal dimensions, which are related to the available metal atoms on the catalyst surface. As an example, Figs. 3 and 4 show TEM micrographs of PA6Pd(s) and of the blend PA(pPDT1)10Pd(s), respectively.

The results in terms of Pd dimensions and dispersion are also summarised in Table 4. Although the two carriers, namely neat PA6 and the blend containing pPDT aramid, hold quite different Pd amounts, metal particles resulted to have similar diameters. It is important to underline that the absence of palladium aggregation in the blend again supports the good miscibility of the hyperbranched aramids with PA6.

The above results point out the possibility to increase the metal retaining capability of a linear polymer, by forming a blend with an appropriate HB counterpart, without reducing the catalyst dispersion. Obviously, the concurrence of both a high concentration and a high dispersion of metal catalyst makes our blend/Pd system a promising catalytic system.

As already mentioned, the metal deposition on the corresponding melt blends has also been studied (Table 5). Namely, the properties of two blends based on pPDT2 and pPDT3, together with the effect of HB aramid concentration, have been investigated.

The results seem to confirm the behaviour of the solution blends. Once more, blends containing pPDT3 retain the highest metal concentration. The amount of retained palladium not only is increased in the blend containing HB aramids, as compared to neat PA6, but its increase follows the increased concentration of the above aramids in the blend.

Thermal and solubility behaviour of the various blends,

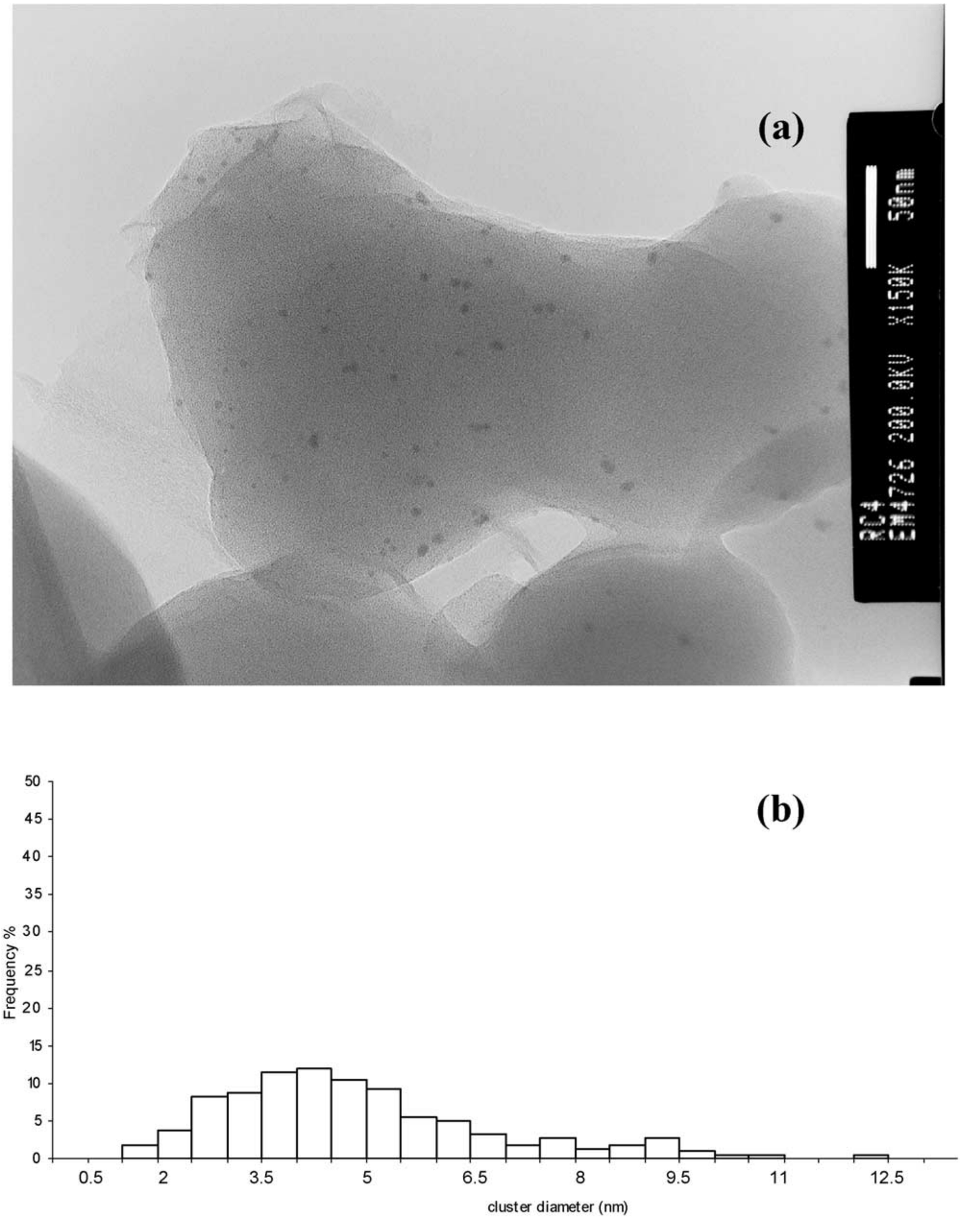

Fig. 3. (a) TEM micrograph of PA6(s)/Pd, (b) histogram of the relative population as a function of Pd particle diameter.

both from solution and melt, seem not to be altered by the presence of palladium nanoclusters.

The catalytic behaviour of the above systems, namely of our blends based on PA6 and pPDT aramids loaded with palladium nanoclusters, will be the topic of a forthcoming paper [16] focused on the specific role, linked to presence of hyperbranched aramids, on the selectivity of various catalytic reactions.

4. Conclusion

Solution and melt blends based on PA6 and HB aramids, synthesised from A_2(*p*-phenylenediamine) + B_3(trimesic acid) reactants, have been prepared. The two blend components have been found to be fully miscible in solution as well as in the melt blends. Since polymer interactions should involve the carboxy end groups of HB aramid and the amide NH groups of PA6, the HB aramid, characterised by the highest concentration of COOH groups, is capable to influence more the corresponding blend properties (solution viscosity, glass transition temperature and rheological behaviour). Namely, poly(ABZAIA) synthesised from an AB_2 monomer, and characterised by COOH end groups only, has the highest degree of interactions with PA6 and provides the highest contribution to modifications of the above blend properties.

Both solution and melt blends have been used as support material for palladium nanoparticles. The presence of HB aramids in the blends largely increases the metal-retaining

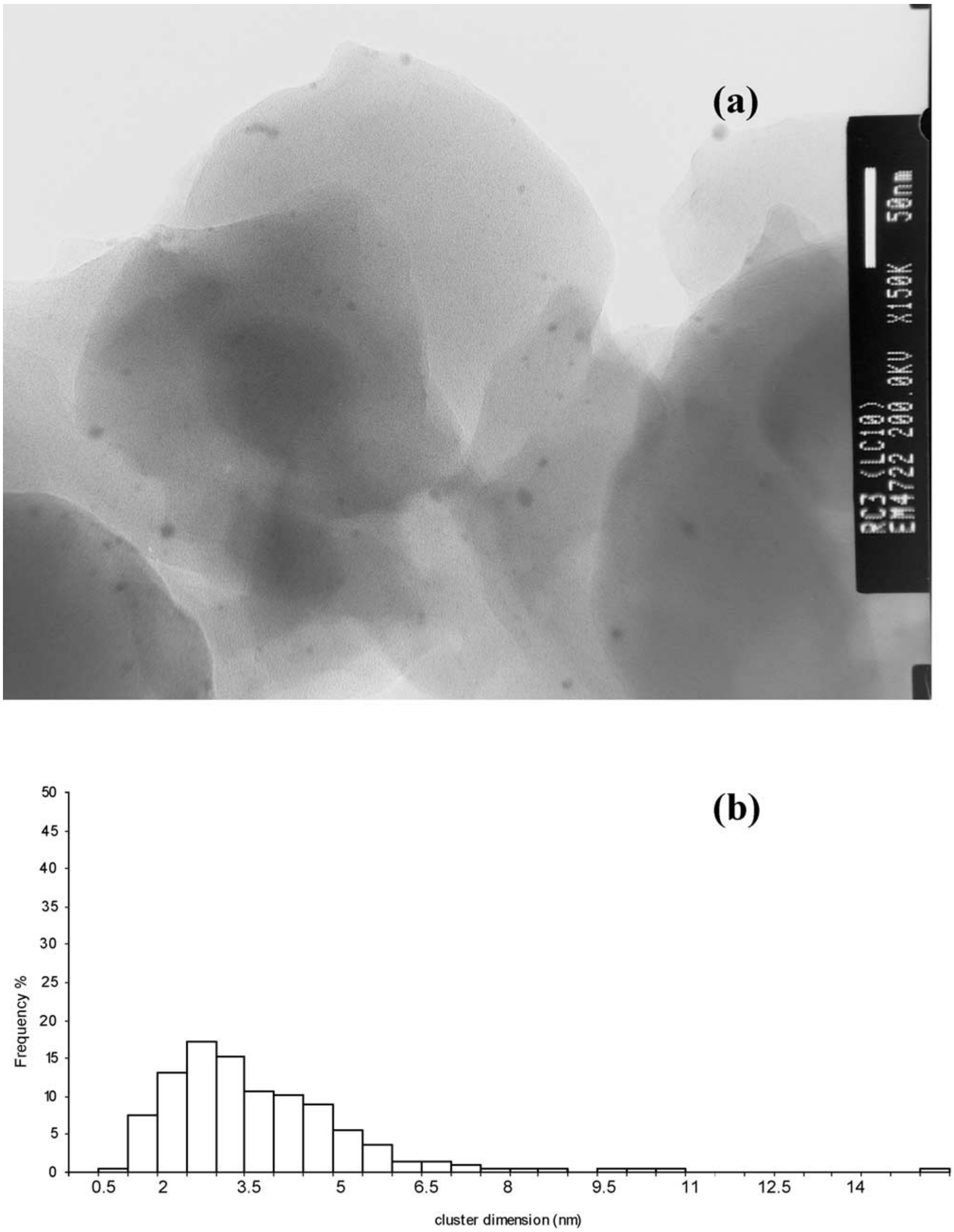

Fig. 4. (a) TEM micrograph of the blend PA(pPDT1)10(s)/Pd, (b) histogram of the relative population as a function Pd particle diameter.

capability of neat PA6. Pd content has been found to increase, when increasing the amino group concentration in the HB polymer.

Although the blends containing pPDT aramids hold a higher Pd amount than neat PA6, TEM has not detected any palladium large cluster. The concurrence of both a high concentration and a high dispersion of metal catalyst renders our HB aramid blend/Pd system a promising catalyst carrier.

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