Polyketone Nanocomposites by Palladium-Catalyzed Ethylene-Carbon Monoxide-(Propene) Co(Ter)polymerization Inside an Unmodified Layered Silicate

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Abstract: Composites from Na-montmorillonite with a content in inorganic material ranging from 3 to 98 wt % were prepared in situ either by copolymerization of ethylene and CO or by terpolymerization of ethylene, propene and CO using a palladium(II) catalyst modified with 1,3-bis(diphenylphosphino)propane. This catalytic system is active in polar media and allowed to produce nanocomposites starting from unmodified Na-montmorillonite in water-methanol solutions. The morphological analysis, performed on samples with less than 40 wt % silicate by XRD and TEM, showed the formation of either intercalated or exfoliated (nanocomposite) structures, depending on the initial amount of the layered silicate in the reactor as well as the presence of propene as comonomer. Improved thermal stability of the hybrid materials, as compared to the corresponding organic polymers, was shown by TGA. A preliminary study of the blending of some polyketone nanocomposites with polyamide (nylon-6) was carried out by melt mixing at high temperature in a Brabender mixer.

Introduction

Polymer-layered silicate nanocomposites constitute a new class of hybrid materials composed of an organic polymer matrix that is imbedded with inorganic particles

having at least one dimension in the nanometer size range [1]. These materials can exhibit enhanced physical properties such as stiffness, toughness, barrier properties and resistance to fire and ignition [2]. A common source of the inorganic material is 2:1 layered phyllosilicates such as montmorillonite. Improved properties are not usually obtained by simply mixing a polymer with an intact multilayered silicate. The polymer must separate the individual silicate sheets either by simple intercalation where the silicate retains its layered structure or by complete exfoliation or delamination of the layer structure, leaving dispersed nanometric silicate sheets. A successful method for the production of hybrid materials based on polyolefins involves in-situ polymerization whereby a transition metal catalyst is inserted within the silicate layers so that the polymer grows within the layers. As a result, the silicate structure breaks up leading to isolated silicate particles within the polymer matrix (Fig. 1 a).

The validity of the in-situ polymerization approach has been demonstrated using metallocenes (Fig. 1c), Ziegler-Natta type and nickel/palladium based catalysts (Fig. 1d) [3-8]. However, naturally-occurring silicate materials, on which these materials are based, are completely incompatible with these catalyst systems and extensive pre-treatment is required before use. Usually, the silicates are organically modified via exchange of the sodium cations with long-chain alkylammonium cations to increase their organophilic character. Intercalation of large organic molecules serves also to widen the gap between the layers, so as to favour the insertion of bulky transition metal catalysts. Since this treatment is generally insufficient to render the material catalyst friendly, a large excess of co-catalyst, MAO for instance, is commonly required to neutralize traces of water or of acidic groups on the silicate surface.

Fig 1: Preparation scheme of polyethylene organomodified-montmorillonite nanocomposites (a) and polyketone Na-montmorillonite nanocomposites (b).

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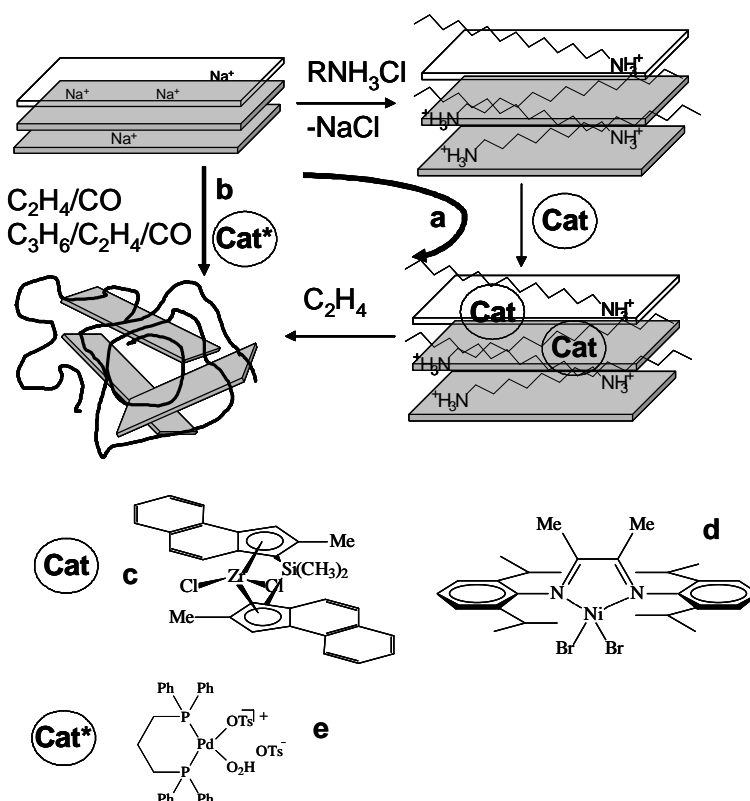
This paper reports the synthesis of polyketone composites by in-situ copolimerization of CO/ethylene or terpolymerization of CO/ethylene/propene [9-13] in the presence of Na-montmorillonite (Fig. 1 b). As copolymerization catalyst was chosen the precursor [(dppp)Pd(OTs)(H₂O)]OTs (dppp = 1,3-bis(diphenylphosphino)propane; OTs = p-toluensulfonate Fig. 1e)) which is known to generate an effective catalyst for the homogeneous copolymerization of CO and alkenes [14-16].

Results and discussion

Nanocomposites based on CO/ethylene copolymerization

The palladium(II) catalyst/acid co-catalyst (HOTs, 20 equiv.) combination was mixed with a suspension of the silicate in water/methanol (1:1, v:v) for 24 hours. Under these conditions, the catalysts were apparently stable as no palladium metal was detected in the reaction mixture. The acid treatment of Na-montmorillonite (performed with the same amount of HOTs) did not change the structure of the silicate, especially as regards the interlayer distance (XRD analysis). Treatment with a 1:1 ethylene/CO mixture (30 bar), followed by heating to 80 °C with stirring, produced polyketone(pk)/silicate composite materials as pale-grey homogeneous powders.

The materials synthesized are listed in Table 1 that also reports experimental conditions and productivity data.

Tab. 1. Ethylene/CO copolymerization in the presence of Na-montmorillonite.[a]

| Sample	Cat in µmol	Silicate in feed % wt.	Time in min	Yield in g	Interlayer distance in Å	Activity[b]	Silicate in pk in %wt.
Na-mont					12.62	-	100
1	20.1	0	45	8.05	-	5.09	0
2	28.5	0.38	90	11.10	>40	2.44	3
3	29.4	1.11	150	9.82	>40	1.26	10
4	23.9	2.88	180	4.44	>40	0.28	51
5	29.1	5.69	360	7.09	14.72	0.16	64
6	27.5	9.48	120	4.60	14.13	0.02	98

[a] 30 bar 1:1 CO/C₂H₄; 1200 rpm; 80 °C; MeOH/H₂O (1:1 vv).

[b] in [kg(pk)·g(Pd)$^{-1}$·h^{-1}]

The silicate content in the composite materials could be varied between 3 and 98 %wt by changing the initial amount of Na-montmorillonite as well as varying the copolymerization time.

The formation of CO/ethylene copolymers in the presence of Na-montmorillonite was confirmed by the appearance of an infrared C=O stretching band at 1690 cm^{-1}, which is characteristic of perfectly alternating polyketones [9-15] (Fig. 2).

**Fig. 2**. FT-IR spectra of polyketone composites and montmorillonite
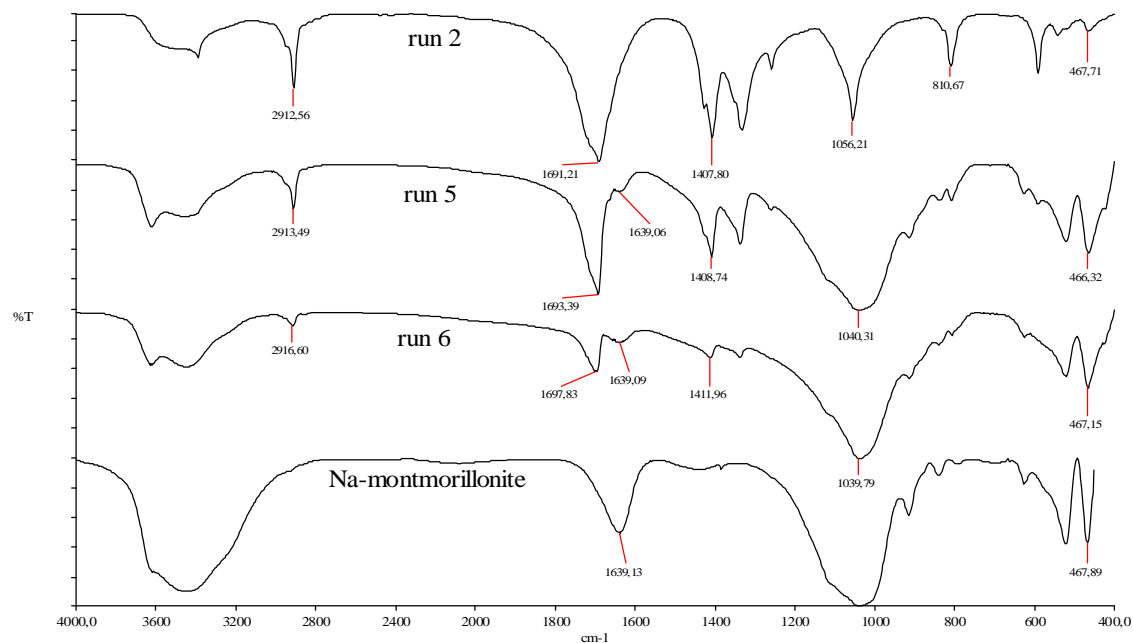
In the products with low silicate content, the Si-O band at 1031 cm^{-1} was obscured by a polyketone band at 1056 cm^{-1}, while it was visible in the spectra of the materials containing more than 40 % silicate. The typical polyketone bands were substantially unaffected by increasing the silica content.

The most common techniques used for the morphology characterization of nanocomposites are X-Ray Diffraction (XRD) and Transition Electron Microscopy (TEM). Both methodologies have limitations and generally have to be used together for a complete investigation of nanocomposites structure. The XRD analysis is more helpful in the case of intercalated structure; the 001 diffraction peak reveals the changes about the spacing between the silicate layers. TEM is a useful complement of the XRD technique, especially when 001 peak is missing in the diffraction pattern like in the case of completely exfoliated morphology, but TEM results have to be considered a local characterization focusing on a very small area. By considering these assumptions the morphology characteristics of the polyketone composites were evaluated by means of XRD analysis to determine the interlayer distance of the silicate (Table 1) and by TEM on different portions of materials to check the degree of dispersion of the silicate. For the final silicate content lower than 10% wt (composite 2 and 4), the XRD pattern showed the disappearance of the 001 diffraction peak. This experimental evidence takes place for interlayer distance larger than 40 Å and has been considered by many authors [17, 18] as an indication of the presence of essentially exfoliated morphology.

Higher levels of montmorillonite resulted in semi-exfoliated samples with the remaining silicate intercalated by at least single polymer strands (the interlayer distance increased by ca. 2-3 Å). The X-ray diffraction data were confirmed by TEM analyses which showed a good intercalation and a partial exfoliation of the layered silicates. This result suggested an effective polymerization within the inorganic materials, especially for the samples characterized by a low inorganic content (Fig. 3 a-d). Indeed, almost negligible changes in the clay were observed by its mixing with

preformed polyketone. Therefore, we do think that the in-situ polymerization takes place when the catalyst penetrated into the silicate layers as illustrated in Fig. 1. Just the cationic nature of the catalyst precursor would favour the catalyst intercalation within the layers of unmodified Na-montmorillonite.

**Fig. 3**. TEM micrographs of samples 2 (a), 3 (b) and 4 (c-d)
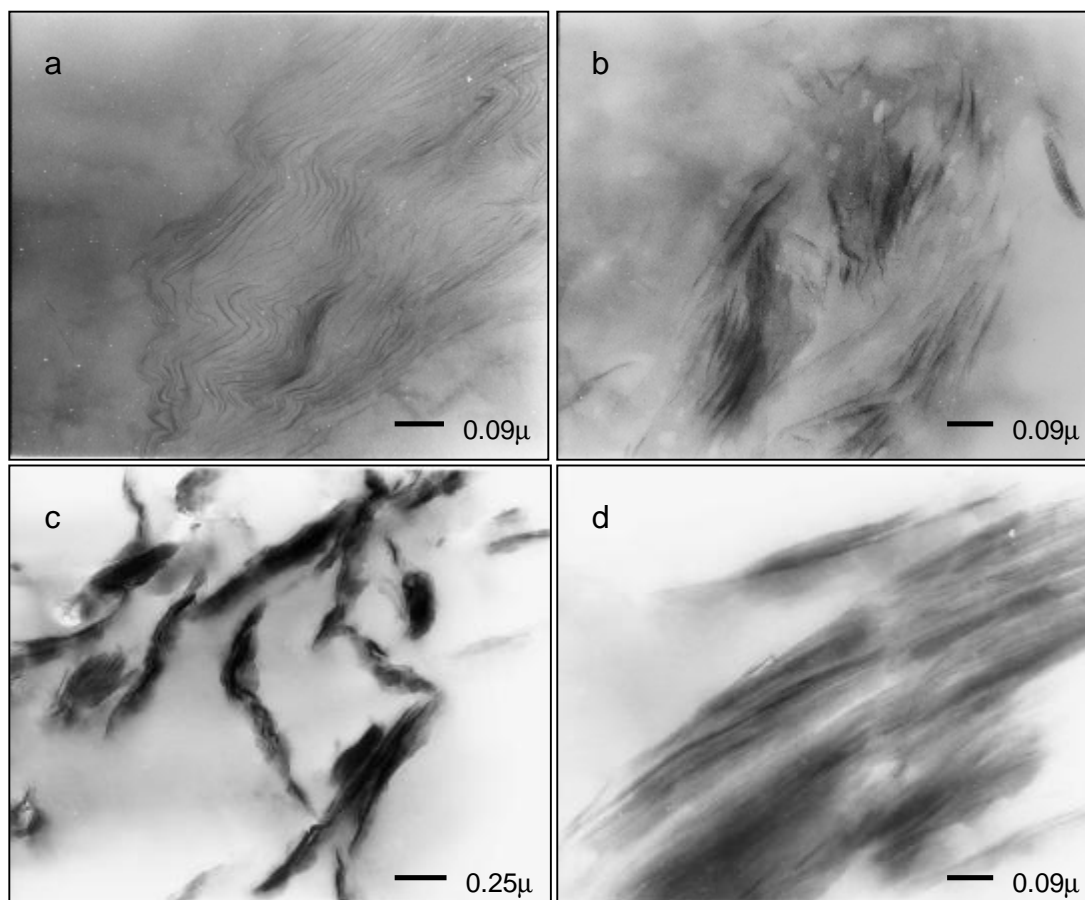
A partial poisoning of the catalyst and the hindered mass transfer of the monomers, especially for ethylene, within the polar environment of the silicate layers well accounts for the low productivities. Moreover, the access of monomers to the catalyst might be further reduced once the growing polymer has covered the silicate material containing the active species.

The polyketone was separated by extraction with 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) from the materials containing 0, 10 and 50 % silicate content (samples 1, 3 and 4). ^{1}H and ^{13}C{1H} NMR analysis in HFIP-d_2 showed the presence of both keto and ester end-groups (Fig. 4), [9-15] with the latter increasing with the amount of silicate material in the starting mixture. The average molecular weight, calculated by ^{1}H NMR integration of the signals of the CH_3 and CH_2 end-groups vs. the CH_2 groups of the polymer backbone, [14,15,19] was rather low (4-9 Kg mol^{-1}) and was not significantly influenced by the initial amount of silicate. Under comparable experimental conditions, but in the absence of montmorillonite, the catalyst is known to produce polyketones with average molecular weight between 10 to 20 Kg mol^{-1} [14,15,16]. The low molecular weight of the polyketone produced inside the montmorillonite layers is likely due to a slower propagation rate caused by the difficult

diffusion of the monomers inside the silicate, while the termination rate should not be significantly affected.

Fig. 4. Structure of polyketones
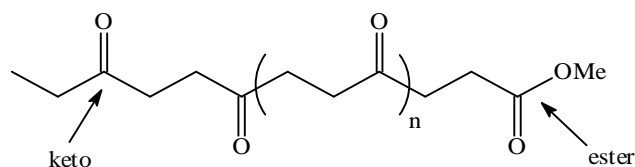
The thermal decomposition of polyketones is a complicated process, which involves various independent transitions; for example, the on-set temperature of the thermal decomposition may depend on several factors such as the average macromolecular chain length and the nature of the terminal groups which, in turn, may vary even in polymers produced under similar conditions. Consequently, it is difficult to asses the effect of the silicate nanoparticles in the polymer matrix on the thermal stability of the polyketone; in fact, any difference might be caused or masked by the specific macromolecular structure [20].

Tab. 2. Representative TGA temperatures of some polyketone nanocomposites.

Sample	% silicate present	On-set (°C)	Inflection points (°C)
1	0	252	291, 409
2	3	298	334, 400
3	10	278	309, 397
4	51	257	292, 401
5	64	259	294, 400

Nevertheless higher on-set temperatures were observed for the samples with a low silicate content (Table 2) and with exfoliated morphology, while increasing the amount of silicate above 50% (samples 4 and 5) the on-set temperature decreased to the value of free polyketone, which confirms that the thermal stability of nanocomposites is strongly affected by the morphology as well as the dispersion of the inorganic substrate in the matrix.

The melting temperature of the polyketone in the first heating scan was around 250 °C, while the freezing temperature was more variable around 190 °C (Table 3). In the second heating scan, the melting temperature decreased by ca. 10-30 °C. Likewise, the melting enthalpy decreased by about half, which is consistent with extensive structural changes of the materials attributable to cross-linking due to condensation reactions occurring at high temperatures in the melting range [21]. On the other hand, it is well known that CO/ethylene copolymers are unstable in the region of the melting temperature, which is largely responsible for their low workability [9-13,19].

Tab. 3. DSC data of some polyketone nanocomposites.

Sample	Silicate in %wt	1st heat. T_m (°C) [ΔH (J/mol)]	1st cool. T_c (°C) [ΔH (J/mol)]	2nd heat. T_m (°C) [ΔH (J/mol)]
2	3	249 [79.3]	195 [32.7]	220 [30.0]
4	51	254 [117.4]	220 [118.1]	245 [118.0]
5	64	249 [34.9]	194 [14.2]	223 [17.2]

Nanocomposites based on CO/ethylene/propene terpolymerization

The use of propene as a third monomer in the CO/ethylene polymerizations can allow to enlarge the range of workability of the polymer, leaving the degradation temperature substantially unchanged and lowering the melting temperature [19]. For this reason terpolymerization of ethylene, propylene and CO was performed in the presence of montmorillonite (Table 4).

Tab. 4. Propene/ethylene/CO terpolymerization in presence of Na-montmorillonite.[a]

Sample	Cat. µmol	Silicate in feed %wt.	Time in min.	Yield in g	Interlayer distance in Å	Activity[b]	Silicate in pk %wt.
Na-mont					12.62		
7	27.1	0	55	17.06	-	5.92	0
8	27.7	0.4	180	5.12	18.6	0.54	8
9	27.5	0.6	150	4.04	18.6	0.49	11
10	30.8	2.0	200	4.93	16.1	0.27	40
11	29.4	2.2	205	3.96	n.d[c]	0.18	50

[a] 30 bar 1:1 CO/C_2H_4, 10 g propene, 1200 rpm, 80 °C, 100 mL MeOH/H_2O (9:1 vv).

[b] in [kg(pk).g $(Pd)^{-1}h^{-1}$]

[c] not determined

Again the presence of the silicate markedly reduced the catalytic activity. The contemporaneous presence of both polyketone and silicate phases in the composites was demonstrated by IR spectroscopy (C=O stretching at ca.1690 cm^{-1}; Si-O bending at ca.1040 cm^{-1}). The XRD data showed an increase of interlayer distance with respect to pure Na-montmorillonite (Table 4), but a lower interlayer distance as compared to the ethylene/CO copolymers (Table 1 samples 3, 4; Table 4 samples 9, 10).

In the presence of propene, the nanocomposites were exclusively featured by intercalated structure. This suggests a minor compatibility of the terpolymers with the inorganic substrate, which may ultimately result in less effective interactions for the exfoliation of the silicate during the growing of the polyketone macromolecular chains.

The polyketone component of selected products was extracted with HFIP and analyzed by ^{1}H NMR spectroscopy to determine the average molecular weight, the

propene incorporation and the nature of the end groups (Table 5). The presence of montmorillonite during the polymerization increased both the chain length and the number of ketone end-groups (chain-transfer by protonolysis) [9-13]. The increased molecular weight of polyketone chains can be attributed to a minor number of catalytic sites available for the monomers which is also supported by the lower catalytic productivity (Table 4). This result can be related to the fact that the catalyst inside the layers interacts to a minor extent with monomers with smaller incorporation of propene into the polyketone with increasing the initial amount of montmorillonite, according to the lower affinity of the hydrophobic propene-containing units towards the silicate.

Tab. 5. ^{1}H NMR analysis of terpolymers and nanocomposites obtained by ethylene/propene/CO terpolymerization.

Sample	Silicate in polymer in % wt	M_w (ketone:ester)	Propene incorporated in % mol
7	0	4200 (1:1)	11.3
8	8	10700 (6:1)	7.2
9	11	20600 (6:1)	6.7

The terpolymer nanocomposites exhibit a significant improved thermal stability as compared to pure polyketones (run 7). Indeed, for all the samples containing the inorganic substrate, TGA measurements showed higher on-set degradation temperatures as well as higher inflection peak temperatures associated to the first main degradation step (Table 6). As for the copolymer nanocomposites, the thermal stability of the terpolymer hybrids was higher for the samples containing a low amount of dispersed silicate. The samples characterized by a larger increase of the interlayer distance (samples 8, 9) showed a significant increase in the degradation temperature, in a range of 130 – 60 °C depending on the hybrid composition. By increasing the amount of silicate the thermal stability decreased in connection with a broader morphology and minor exfoliation.

Tab. 6. Representative TGA temperatures of some polyketone terpolymer nanocomposites.

Sample	% silicate present	On-set (°C)	Inflection points (°C)
7	0	201	254, 409
8	8	342	396
9	11	275	313, 398
10	41	255	288, 367
11	51	244	279, 390

The DSC analysis of the terpolymer hybrids revealed the occurrence of a complex melting behaviour (Table 7) featured by a very broad melting endothermic transition

and by two main maxima due to the prevalence of either α or β crystalline forms [22]. All the samples showed a melting temperature appreciably lower than that of the corresponding copolymer, which was somewhat expected [23].

Tab. 7. DSC data of some polyketone terpolymer nanocomposites.

Sample	Silicate in %wt	Propene in %wt	1st heat. T_m (°C) [ΔH (J/mol)]
7	0	11.3	189.2, 205.0 [77.8]
8	8	7.2	177.7, 188.3 [51.9]
9	11	6.7	175.7, 184.8 [37.1]

Blending of polyketone-montomorillonite nanocomposite with nylon-6

With the aim to employ the new polyketone composites some hybrid samples were blended with nylon-6 to produce polyamide based nanocomposite. The better processability in the melt of terpolymers with respect to copolymers which suffer of degradation processes at the temperatures near to the melting point allowed us to use samples 10 and 11 as mastebatches containing very high amount of Na-montmorillonite partially intercalated by polyketone chains.

Besides, previous studies had shown, that alternating polyketones are compatible with polyamides [24] by blending in solution or in the melt nylon-6 and polyketone in a very large range of components ratio. The terpolymer nanocomposites layered silicate rich were initially chosen to be melt processed with nylon-6 at 225 °C very near the melting temperature of the polyamide (that is at 223°C as determined by DSC measurement) and below the temperature at which the degradation process starts (> 240 °C).

In order to obtain materials containing about 3-6 % by weight of silicate, the polyamide was mixed with samples 10 and 11.

Tab. 8. Blending of nylon 6 with polyketone terpolymers.

Sample	Polyketone terpolymer sample	Final content of PA6 in % wt	Final content of silicate in % wt	Final content of polyketone in % wt	Interlayer distance in Å
PA1	7	94.3	5.7[a]	0	18.6
PA2	11	94.0	3	3	21.7
PA3	10[b]	85.7	5.7	8.6	20.9

[a] by adding separately Na-montmorillonite (interlayer distance=12.6 Å).

[b] interlayer distance=16.1 Å

The morphology of the samples was preliminary investigated by XRD that revealed an increase in the interlayer distance for the composites, as a consequence of the intercalation of the polyamide chains within the silicate layers. Indeed, the

polyketone, being partially miscible with the polyamide, might favour the interactions between nylon-6 and the montmorillonite.

Experimental part

All reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk-type techniques. [(dppp)Pd(OTs)(H$_2$O)]OTs was prepared as described previously [14,15,16]. Na-montmorillonite, obtained from Laviosa Chimica Miniera S.P.A., has the following characteristics: weight decrease on ignition = 10.8 wt %, particles size = 6-8μm, cation exchange capacity (CEC) = 128 meq/100g and interlayer distance = 12.40 Å. Nylon-6 (PA6) was purchased commercially (Ultramid, BASF) and used without purification. The morphology of the nanocomposite products was investigated by a Transmission Electron Microscope (TEM) ZEISS EM 900 apparatus, applying an acceleration voltage of 80 kV. Ultrathin sections, about 50 nm thick, were prepared with a Leica EM FCS ultracryomicrotome, equipped with a diamond knife cooled at -60 °C keeping the sample at -85 °C. X-ray diffraction (XRD) was carried out at room temperature by using a diffractometer D 500/501 Siemens Kristalloflex 810 (Cu Kα1 radiation with λ = 0.15406 nm) at room temperature The diffractograms were collected in 2θ ranges from 1.8 to 30, where the basal reflection of the interlayer d spacing appears, at a scanning rate of 0.016 degree/sec. The composite materials were analyzed as powders. FT-IR and ATR spectra were recorded on a Perkin-Elmer System 3600 Fourier-transform infrared spectrophotometer. DSC analyses were carried out under a nitrogen atmosphere using a Perkin-Elmer DSC-7 differential scanning calorimeter thermal analyzer with a CCA-7 cooling equipment. The instrument was accurately calibrated using melting temperatures and enthalpies of indium and zinc as references. The samples were heated from 30 to 200-250 °C (depending on the composition) to eliminate their heat history then cooled to 30°C and heated again to 200-250 °C at a cooling/heating rate of 20 °C/min. The thermodegradation of the materials obtained was determined on approx. 10 mg samples in a TGA balance (TG-50 Mettler) with alumina sample pan in a nitrogen flow and with a 10 °C/min heating ramp from 25 to 700 °C. ^{1}H and ^{13}C{1H} NMR spectra were obtained with a Bruker ACP 200 spectrometer (200.13 MHz) in deuterated 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP-d$_2$). Chemical shifts are reported in ppm (δ) with reference to TMS as an internal standard.

Catalytic reactions

The copolymerization reactions were performed at constant pressure in a 250 mL stainless steel autoclave, constructed at ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller [14,15]. The autoclave was connected to a high-pressure gas reservoir from which a 1:1 ethylene/CO mixture (30 bar) was automatically supplied to the reactor in order to maintain a constant pressure all over the catalytic reactions. The consumption of the gaseous reagents with time was monitored following the pressure drop in the gas reservoir by means of a pressure transducer. The catalyst/HOTs combination was mixed with the montmorillonite suspension in water/methanol (1:1 v:v) for 4 hours under nitrogen atmosphere. The reactor was then charged with the suspension and pressurized with 15 bar ethylene and 15 bar CO. For the production of the CO/ethylene/propene terpolymers, the reactor was first charged with 10 g of propene prior to pressurizing with CO/ethylene to 30 bar. The temperature was rapidly

increased to 80 °C with stirring at 1200 rpm. The pressure was kept constant by the continuous addition of a 1:1 CO/ethylene mixture. The reaction was stopped by rapid cooling to room temperature. The solid product was collected by filtration, washed with acetone, methanol and dried under vacuum to constant weight. The silicate content in the resultant materials was varied by controlling both the amount of silicate in the feed and the polymerization time.

Blending of the polyketone nanocomposites with nylon-6

Mixtures between selected polyketone nanocomposites (obtained by terpolymerization in the presence of a large amount of silicate, samples 10 and 11) were produced by using a Brabender mixer (Plastigraph OGH 47055) at 225°C and 50 rpm for 10 min. The products were collected from the chamber of the mixer and analysed by XRD measurements (Table 8)

Conclusions

Polymeric nanocomposites containing dispersed nanosized silicates were obtained for the first time by palladium(II)-catalyzed alternating copolymerization in a polar medium (CH_3OH/H_2O) of CO and ethylene or terpolymerization of CO, ethylene and propene in the presence of a natural phyllosilicate such as Na-montmorillonite without the need of a previous treatment to increase the interlayer distance.

Nanocomposites based on ethylene/CO copolymerization with a silicate content lower than 10 % contained essentially exfoliated silicate particles dispersed within the polymer matrix, while the materials containing a higher level of silicate (> 40 %) showed only partially exfoliated silicate with the remaining layered montmorillonite containing intercalated polymer macromolecules. Nanocomposites obtained by in-situ terpolymerization of CO/ethylene/propene were characterized by an intercalated morphology even for low montmorillonite content. DSC and TGA analysis showed better thermal resistance of terpolymers nanocomposites with respect to the copolymer composites in spite of the lower dispersion degree of the silicate in the polymer matrix.

On the basis of this feature, nanocomposites obtained by in-situ terpolymerization were successfully employed as master-batches in the melt mixing with commercial polyamide to preliminary produce polyketone/polyamide nanocomposites.

Further research in this direction is being carried out in our laboratories.

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