

Properties and Nanoscale Structure of Polypropylene-Layered Double Hydroxide Composites Prepared by Compatibilizer-Free Way

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ABSTRACT: Polypropylene (PP) is the second most widespread commodity polyolefin. Even a small quantity of inorganic component is sufficient to achieve significant improvement of stiffness, strength, thermal stability, biodegradability, etc. The major drawback of inorgano-organic composite materials is insufficient compatibility of the PP matrix with inorganic filler. A suitable choice of the layered double hydroxide-modifying anion opens a possibility to obtain PP-inorganic nanocomposites without a need to use compatibilizers like maleic anhydride grafted PP. The nanocomposites were prepared by melt blending in a twin-screw mini-extruder and characterized by dynamic mechanical thermal analysis, and electron microscopy. Nonpolar PP matrix mix uniformly with clay organophilized with functionalized surfactant acids, giving rise to composites with improved thermo-mechanical properties. Influences of the anionic modifier and the filler content (2 or 5% w/w) on mechanical properties and nanoscale structure of the composites are discussed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2429–2438, 2013

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INTRODUCTION

Nanocomposites containing polyolefins and inorganic solids are in the focus of vigorous interest, owing to significant improvement of peculiar polymer properties, and because Polyolefins occupy the largest share of the plastic market. Polypropylene (PP) is the second most widespread commodity polyolefin. Inorganic additives enhance physical and chemical properties such as stiffness, strength, ductility, impact strength, heat resistance, fire retardancy, barrier properties, thermal stability, biodegradability, etc.¹ Remarkably, even a small quantity of inorganic component is sufficient to achieve significant improvement of valuable properties or to provide new value-added ones, without adding excessive weight and sacrificing inherent processability and mechanical properties of the polymer.² The major drawback of inorgano-organic composite materials is insufficient compatibility of organic PP matrix with inorganic filler due to different nature of both components and to lack of functionality in the former. Solution of this problem is of paramount importance for material chemistry.

In order to achieve compatibility with inorganic additives like natural clay minerals or synthetic clays (layered double

hydroxides, LDH), it is necessary to diminish the enthalpy of the interface by modifying either the polymer (e.g., grafting) or the inorganic component (e.g., organophilization). The former are often used as “macro-surfactants” that can interact with the solid particle surface and with the polymer matrix.³ For example, PP grafted with maleic anhydride (PP-g-MA) has become a widely accepted standard compatibilizing component in PP nanocomposites,⁴ since it is miscible both with PP matrix and includes a certain amount of polar functional groups. The latter are responsible for a strong hydrogen bonding between the anhydride groups and the polar clay surface.¹ This approach has allowed their commercialization to go forward, despite the fact that PP-clay nanocomposites containing PP-g-MA are usually not well exfoliated.^{5,6} Clearly more extensive applications of PP-based nanocomposites would be possible if a more effective or less expensive compatibilizer would be available.⁶

As far as inorganic layered components are concerned, extensive deal of research was dedicated to natural clay minerals and their organophilic derivatives.^{1,4,7,8} The main reasons of such interest were a low cost, relatively low layer charge density and hence, easy exfoliation of phyllosilicate-based materials.⁹ However, their

composition and functional properties may vary in a quite broad range owing to compositional nonhomogeneity and structural nonuniformity of naturally occurring clay minerals, which depend much upon their place of origin, conditioning and grinding technologies. On the contrary, the layered double hydroxides of general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_x/n \cdot zH_2O]$ (where M^{2+} and M^{3+} are di- and trivalent metal cations; $x = 0.2/0.33$; and A^{n-} stands for anions) are synthetic anionic clays that could easily be obtained as particles of uniform composition throughout the material.^{10–12} They find a variety of applications as catalysts, ion-exchangers, drugs, agricultural, cosmetic, and nutritional ingredients.¹³ Nowadays, Mg–Al LDH may be considered as “green” filler to improve mechanical properties, enhance fire retardancy, and reduce photodegradation of PP.^{14–17} Preparation and characterization of different polyolefin-LDH composites reported in the literature^{16–18} involve the inorganic phases modified by long-chain aliphatic fatty acid anions like stearate or lauryl sulphate in combination with PP-g-MA compatibilizer.

This article shows that a suitable choice of the modifying anion opens a possibility to obtain PP-LDH nanocomposites without compatibilizers like PP-g-MA. The nanocomposites were prepared by melt blending in a twin-screw mini-extruder and characterized by dynamic mechanical thermal analysis (DMTA), X-ray diffraction (XRD), and electron microscopy. The influence of anionic modifier, the divalent layer building cation (Mg^{2+} or Zn^{2+}), and the filler content (2 or 5% w/w) on mechanical properties and microstructure of the composites is discussed.

EXPERIMENTAL

Materials

Commercial samples of PP (HP-550K, Braskem (Brazil), MFI = 3.5 g/10 min), PP grafted with maleic anhydride (PP-g-MA, Chemtura, Brazil, Polybond® 3200, M_w 127,000, MA content 1% w/w), clay minerals Argel 40N (Bentonit Union Nordeste S.A., Brazil) and Cloisite 15A (Southern Clay Products, USA, modified with dimethyl-diHT ammonium chloride, where HT contains ~65% C_{18} ; ~30% C_{16} ; ~5% C_{14} aliphatic residues), and dioxycholic acid (New Zealand Pharmaceuticals) were used as supplied. Other reagents were purchased from Aldrich, Brazil, and used as supplied.

Synthesis of Modified Layered Double Hydroxides

The LDHs were obtained in a carbonate form by urea precipitation method from a solution containing M^{2+} (Mg^{2+} or Zn^{2+}) and Al^{3+} precursors in a desired molar ratio of $[M^{2+}]/([M^{2+}] + [Al^{3+}]) = 0.33$.^{10,19} Formation of the materials was followed by XRD. In our conditions, the precipitates were aged for 120 h to improve the crystallinity degree and then washed thoroughly with deionized water by repeated suspending-centrifugation cycles. The products $[M^{2+}_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165} \cdot xH_2O$ were identified by XRD patterns and FT-IR spectroscopy.

In order to obtain a modified form, the LDH in carbonate form had been calcined at 720 K overnight and the resulting mixed oxides were rehydrated with an aqueous solution containing a 10% excess from the stoichiometric amount of sodium salt of the modifying organic acid (Figure 1). Rehydration was

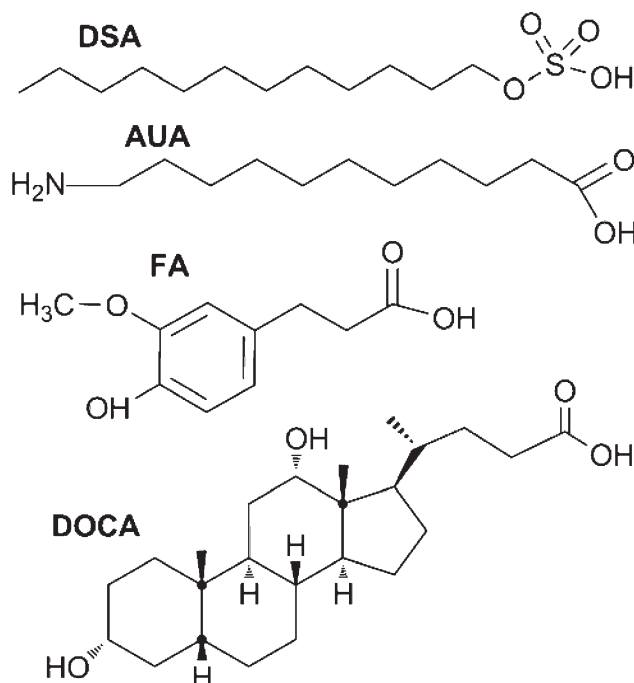


Figure 1. LDH modifiers: dodecylsulfonic acid (DSA) and functionalized surfactants 11-aminoundecanoic acid (AUA), ferulic acid (FA), deoxycholic acid (DOCA).

performed under controlled CO_2 -free atmosphere in a flow cell of the ultrasonic device UP400S (Hielscher Ultrasonics GmbH, Germany) using a fresh Milli-Q water. The precipitates were separated by centrifugation, washed several times with fresh Milli-Q water, and dried at 80°C overnight. The modifier content in the final LDH material was estimated to be in the range of $0.65 \pm 0.15\%$ of the stoichiometric amount, according to the HPLC and TGA data.

Preparation of PP-Modified LDH Nanocomposites

All materials were dried in vacuo at 80°C before use. The composites were obtained by melt compounding as moulded films using a counter-rotating twin-screw mini-extruder (HAAKE MiniLab, Thermo Scientific, Germany) at 180°C for 15 min. The screw was rotating at constant speed of 60 rpm to ensure uniform heating and maintaining the temperature of the melt. The amount of modified LDH added to the PP matrix was fixed at 2 and 5 wt %. The samples were grinded in cutting mill for further use.

Characterization

X-Ray Diffractometry. X-ray diffractograms were recorded on X'Pert PRO MPD instrument (PANalytical) operating at 45 kV, 40 mA using a built-in goniometer and Cu K α radiation. Diffractograms were collected from $2\theta = 4$ to 70° using steps of 0.02°.

Dynamic Mechanical Thermal Analysis. Analyses were performed on DMA Q800 instrument (TA Instruments, USA) in a single cantilever mode. Rectangular samples $18 \times 14 \times 2$ mm³ of composites were obtained by pressing at 200°C for 10 min with subsequent conditioning at 80°C for 48 h. DMTA measurements were performed at the following conditions: frequency

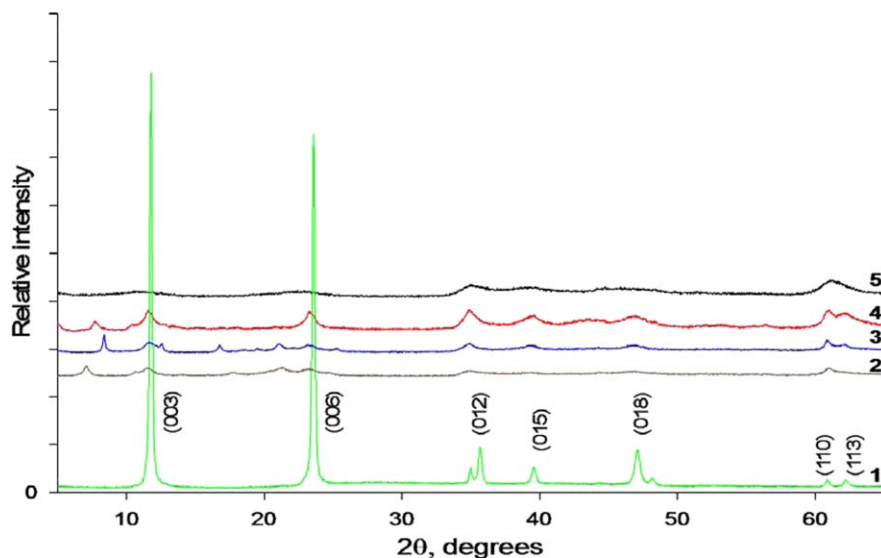


Figure 2. XRD patterns of Mg/Al-LDH (1); and Mg/Al-LDH modified with organic anions: DDS^- (2), AUA^- (3), DOCA^- (4), and FA^- (5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1 Hz, deformation 6.1%, temperature range -40 to 140°C . The values reported are the average of five repeated experiments.

Electron Microscopy. The FESEM images were acquired with a Hitachi S-4800 field emission scanning electron microscope. In order to investigate the fracture zone, rectangular samples identical to those prepared for DMTA were immersed for 30 min into liquid nitrogen and crushed there. Prior to imaging, all samples were coated with 3 nm of Pt/Pd using a Cressington 208HR Sputter Coater, in order to enhance their conductivity.

RESULTS AND DISCUSSION

In order to achieve better dispersion and compatibility of the LDH phase in the nanocomposite, the former was obtained in an exfoliated form using a combination of rehydration and sonication techniques. A series of different organic acids possessing surfactant properties were used for surface modification of the double hydroxide particles (Figure 1). In such a way, one could compare the compatibilizing performance of a long-chain aliphatic sulfonic acid (DSA), functionalized long-chain aliphatic carboxylic acid (AUA), 4-hydroxy-3-methoxycinnamic or ferulic acid (FA), and deoxycholic acid (DOCA). The last two species may also enhance the biodegradability of both the layered double hydroxides and the composite material. FA is also well known for its significant antioxidant activity.²⁰

Modified LDH Preparation

Upon rehydration, the samples of modified clays re-gain the initial hydroxide-like structure typical for Mg/Al-LDH derivatives,^{10,12,19} as the Figure 2 show. In the case of Mg/Al-LDH-DOCA (Figure 2), the modification did not lead to enhancement of the interlayer distance, but a certain exfoliation degree may be derived from the diminution of sharpness and intensity of the basal lines at low values of 2θ , corresponding to successive orders of the basal spacing ℓ .¹⁰ In the case of long-chain AUA^- anion-modifier, the interlayer distance enhances similarly

to known DSA^- one.^{16,21} However, the former treatment provides even more complete exfoliation as a result. Modification of the clay with FA lead to a slight enhancement in the inter-layer distance (Figure 2) and practically complete delamination of the material. At the same time, more intense reflections related to a hexagonal axis (the layer building blocks) may be observed, since they are independent on the layer stacking.

The above layered materials were used for obtaining of PP-synthetic clay nanocomposites by melt processing.

Mechanical Properties

Mechanical properties of new LDH-containing nanocomposites were compared with those of processed commercial PP-550 and two commercial clay minerals: Na-form Argel 40N and organophilized Cloisite 15A (Table I). Both are natural montmorillonites, the latter being modified with long-chain quaternary ammonium salts. Most Cloisite® organoclays are well known as fillers for composite materials. However, ammonium salts are thermally unstable and can degrade at temperatures as low as 170°C . It is clear that such surfactants are not suitable for use with a major part of engineering plastics to produce polymer-clay nanocomposites by melt processing technology.²² Moreover, Cloisites® possess irregular structure and considerable polydispersity. Although more thermally stable surfactants are known, for example, phosphonium salts, they are too expensive for commercialization.

Both commercial clays have to be additionally compatibilized with PP-550 using PP-g-MA. However, due to the chain scission that occurs during grafting, the PP-g-MA has lower mechanical properties, when compared with neat PP. Thus, it has a negative influence on mechanical properties of the final composite.²³ High loading of the macro-surfactant will have detrimental effects on mechanical properties of the composition, while low loading levels will not be sufficient for the desirable degree of PP-clay compatibilization.²⁴

Table I. Materials Composition and DMTA Results for Commercial Polypropylene and PP-Inorganic Nanocomposites

Sample no.	Material/composite	$E_{(-40^{\circ}\text{C})}$ (MPa)	$E_{(25^{\circ}\text{C})}$ (MPa)	T_g by E ($^{\circ}\text{C}$)	T_g by $\text{Tan}\delta$ ($^{\circ}\text{C}$)	$\text{Tan}\delta_{\text{max}}$
1	PP-550 processed	1943 \pm 100	819 \pm 48	4.0	6.7	0.07267
2	PP-550 + 5% Argel 40N/PP-MA	1853 \pm 93	792 \pm 42	3.7	6.8	0.06977
3	PP-550 + 5% Cloisite 15A/PP-MA	2522 \pm 130	1165 \pm 60	2.3	4.8	0.06532
4	PP-550 + 2% Mg/Al LDH—DOCA	1664 \pm 80	968 \pm 56	6.9	10.9	0.05864
5	PP-550 + 5% Mg/Al LDH—DOCA	2463 \pm 120	1330 \pm 69	6.6	10.3	0.05497
6	PP-550 + 2% Zn/Al LDH—DOCA	1431 \pm 75	841 \pm 44	6.6	10.6	0.05727
7	PP-550 + 5% Zn/Al LDH—DOCA	2204 \pm 105	1155 \pm 58	4.8	9.1	0.06191
8	PP-550 + 2% Mg/Al LDH—DSA	1870 \pm 102	998 \pm 53	7.2	10.6	0.05872
9	PP-550 + 5% Mg/Al LDH—DSA	1902 \pm 95	998 \pm 55	5.7	10.3	0.06115
10	PP-550 + 2% Mg/Al LDH—FA	1835 \pm 93	960 \pm 60	6.0	10.6	0.05801
11	PP-550 + 5% Mg/Al LDH—FA	2533 \pm 120	1362 \pm 70	6.6	11.2	0.06497
12	PP-550 + 2% Mg/Al LDH—AUA	2090 \pm 109	1089 \pm 54	6.9	10.0	0.05714
13	PP-550 + 5% Mg/Al LDH—AUA	2399 \pm 137	1238 \pm 65	6.9	10.6	0.05949

The Table I shows the values of storage moduli at -40°C and 25°C , the damping factor $\text{tan}\delta_{\text{max}}$, as well as the glass transition temperature determined both at the maximum of the loss modulus and at the maximum of $\text{tan}\delta$ curve.

The addition of 5% w/w of the organophilic clay Cloisite 15A compatibilized with 5% of PP-g-MA led to an increase of E' and E'' both below the polymer T_g and at 25°C by a factor of 30 and 42%, respectively, in comparison with that of PP-550. Introduction of the same amount of Argel clay in a Na-form led to a decrease of both moduli even in the presence of PP-g-MA. The glass transition temperature did not vary with Argel-Na, but it has slightly decreased with Cloisite. The increase of the storage moduli and therefore, the material stiffness in a wide range of temperatures shows the importance of mineral clay organophilization. Better dispersion of those particles in the polymer matrix result in higher mechanical properties.

In the case of the LDH as reinforcing filler, a suitable choice of the anionic modifier resulted in no necessity to use any compatibilizing agent, such as PP-g-MA. A series of experiments were carried out with different types of surfactants at the same processing conditions with the same commercial PP, employing 2 and 5% w/w contents of the filler.

A remarkable increase of the storage modulus was evidenced over the full temperature range by addition of modified clays to the PP matrix even without any additional compatibilizing agents, thus indicating that incorporation of the modified filler enhanced the stiffness and reinforced the material. Such relative stiffness improvement with temperature shows a better thermal stability of the composite provided by the presence of the LDH nanoparticles and related to a stronger reinforcement effect of the clay particles for temperatures higher than T_g , a point above which a polymer becomes softer. The effect was stronger when 5% w/w of the filler were added to the polymer. Moreover, the modification with FA gave rise to the highest increase of the storage modulus at 5% w/w compared to all other modifiers [Table I and Figure 3(a,b)].

Most likely, the FA^- anion acted as interfacial compatibilizer, increasing the dispersion and enhancing the interfacial area. As a result, interaction between the filler and the matrix increased, thus increasing the reinforcing effect. Interestingly, the long-chain aliphatic DSA^- anion typically used in a majority of published works alongside with stearate as the LDH modifier, showed rather modest mechanical properties improvement.

Evidently, the presence of nonfunctionalized aliphatic chains absorbed on the surface of the clay particles is necessary, but not sufficient for efficient compatibilization with the PP matrix. Our results show that a certain degree of the surfactant molecule functionalization is crucial for better compatibilizing performance.

Substitution of Mg for Zn in the hydrotalcite layers led to lower stiffness of the nanocomposites with both amounts of the filler (Table I and Figure 3).

The following trend was observed for the storage modulus of PP/Mg-Al-LDH nanocomposites containing 5% w/w of the inorganic filler, according to the surfactant employed for modification: $\text{PP} < \text{PP/Zn-LDH-DOCA} < \text{PP/LDH-DSA} < \text{PP/LDH-AUA} < \text{PP/LDH-DOCA} < \text{PP/LDH-FA}$.

The results always show an increase in both moduli at -40°C and especially at 25°C with all modifiers, as well as with the increase of the filler content from 2 to 5% w/w, with respect to pure PP. The highest storage moduli E'_{-40} and E'_{25} were achieved with FA and DOCA modified clays. The values are well above those of the original PP-550, increasing by 27 and 62% for DOCA, and 30 and 66% for FA, respectively. The storage modulus at 25°C of the PP/LDH-FA nanocomposite was 12% superior to the PP/Cloisite-15A one prepared with the compatibilizing agent PP-g-MA.

Moreover, the T_g (also known as β relaxation) of the nanocomposites with modified layered double hydroxides was higher compared to the polymer without filler (T_g determined by E'' reached 7°C while that of PP-550 is 4°C), indicating lower

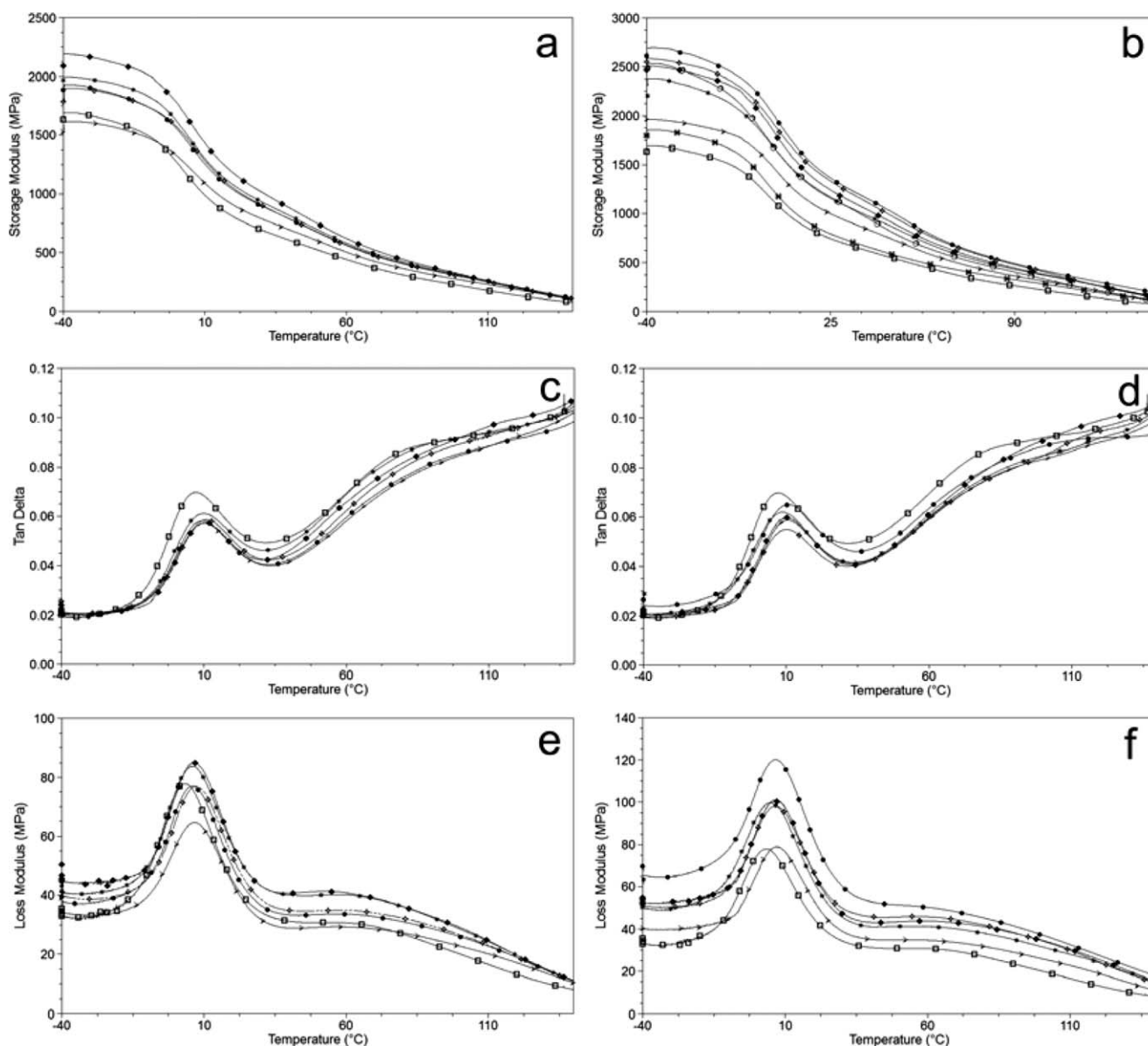


Figure 3. DMTA data as a function of temperature: storage modulus for composites reinforced with 2% LDH (a) and 5% LDH (b); damping factor ($\tan\delta$) for composites reinforced with 2% LDH (c) and 5% LDH (d); loss modulus for composites reinforced with 2% LDH (e) and 5% LDH (f). The symbols correspond to the following sample numbers in the Table I: \square - 1, \otimes - 2, \circ - 3, \diamond - 5, \triangleright - 7, \star - 9, \bullet - 11, \blacklozenge - 13

mobility of the amorphous phase and lower free volume at the interface of the inorganic phase and PP chains. This means a better wettability of the clay surface by the polymer and an increase in T_g as a result.

On the other hand, regarding the values obtained for the damping factor $\tan\delta_{\max}$, all composites showed a slight decrease in this parameter, which is an indication of better adhesion between polymer chains and the filler, due to the presence of modifier anions on the surface of inorganic nanolamellae that results in a macromolecular phase with a more restricted mobility. Those values may also be regarded as an indication of better impact resistance of the composite material.

The glass transition temperature (T_g) of PP was determined as the temperature corresponding to the damping peak on the

$\tan\delta$ versus T curves [Figure 3(c,d)]. The higher is $\tan\delta_{\max}$ the greater are mechanical losses, related to higher energy input required for motion of the macromolecular chains, as the transition is being approached. It may be noted, it is the filler addition that was responsible for an increase of elastic behavior of the composites (reduced $\tan\delta_{\max}$) at both filler contents. Another observation concerns the overall width of the $\tan\delta$ peaks. Broadening of the peaks became especially remarkable in the rubbery region that indicates greater dynamic mechanical losses there.

A shift to higher temperatures and broadening of the peak indicate a segmental relaxation restriction, observed for all the evaluated PP/LDH nanocomposites. In general, the increase in T_g was more effective in the composites containing 5% w/w of the

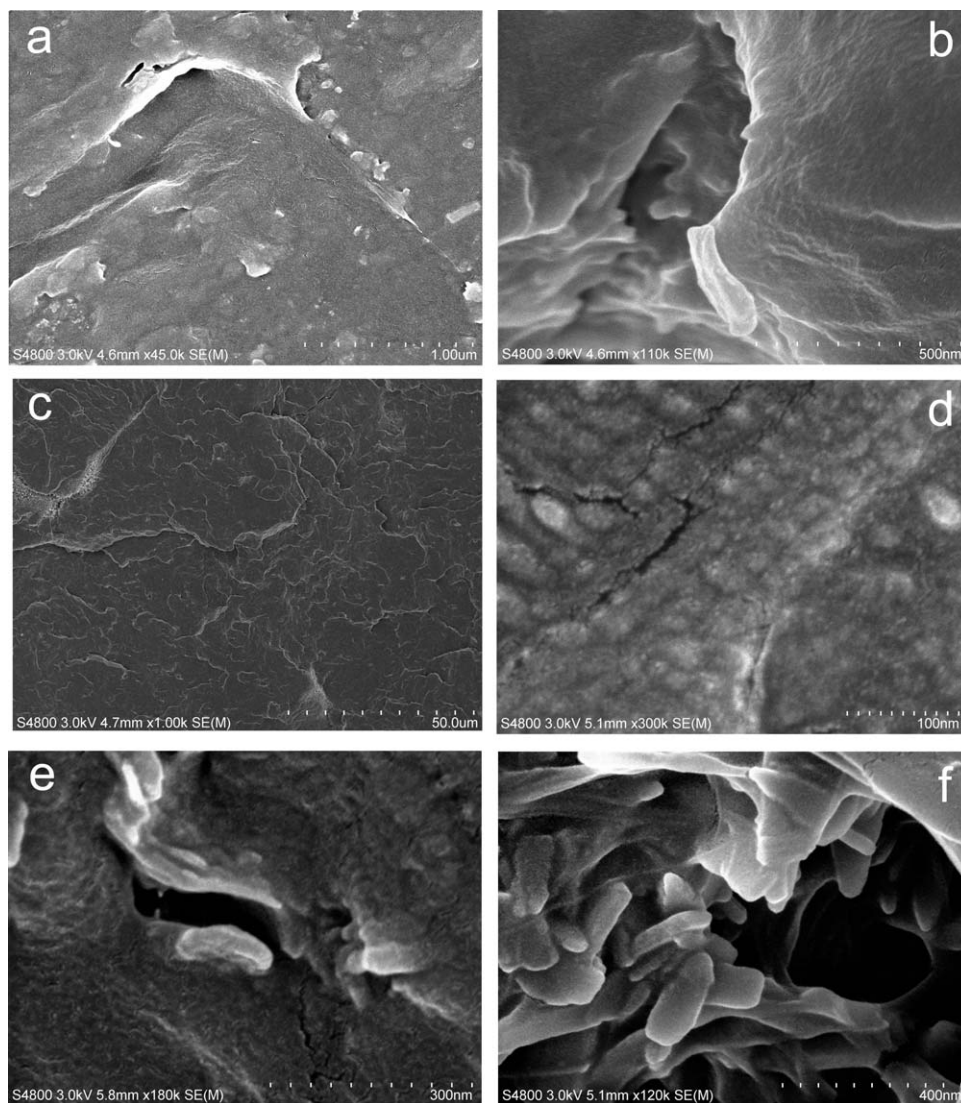


Figure 4. SEM micrographs of PP/LDH-DSA nanocomposites: the sample containing 2% w/w of the filler, surface (a,b) and cross-section (c); the sample containing 5% w/w of the filler, surface (d,f) and cross-section (e).

filler. This fact indicates that polymer-filler interactions are strong, and therefore, they restrict the PP chain segment mobility. In particular, the modification of the LDH particles with AUA, DOCA, and FA anions led to the most pronounced increase in T_g of PP, and the latter nanocomposite also showed the highest value of $\tan\delta_{\max}$, indicating higher impact resistance of the material.

Another secondary relaxation (known as α') is a relaxation related to crystal morphology.¹⁶ It can be observed between 45 and 70°C when analysing the loss modulus curves presented in Figure 3(e,f). As it can be seen, the position and intensity of this relaxation changes between the nanocomposites in question, probably due to structural features of each PP-inorganic nanocomposite. Amorphous and crystalline phase microstructures are different in pure PP and the nanocomposites, the latter presenting the amorphous phase with decreased molecular mobility (higher T_g and lower $\tan\delta$). The temperature of the α'

relaxation in the nanocomposites shifted to higher values in comparison with pure PP, which means that the crystalline phase has lower molecular mobility and therefore the material has improved thermal stability.

Microstructure of PP-LDH Nanocomposites

FESEM microscopic investigation of the samples demonstrates convincingly the formation of PP/LDH nanocomposites without addition of any compatibilizer. All samples of the materials under investigation were studied both on the surface and in a perpendicular fracture zone.

Addition of 2% w/w of the clay treated with traditional sodium dodecylsulphate surfactant to the polymer without PP-g-MA compatibilizer results in a mixture that was not completely homogenized. It contained some inclusions of the inorganic phase [Figure 4(a)]. Such material is breakable [Figure 4(b)] or even contains honey-combed and spongy domains [Figure 4(c)].

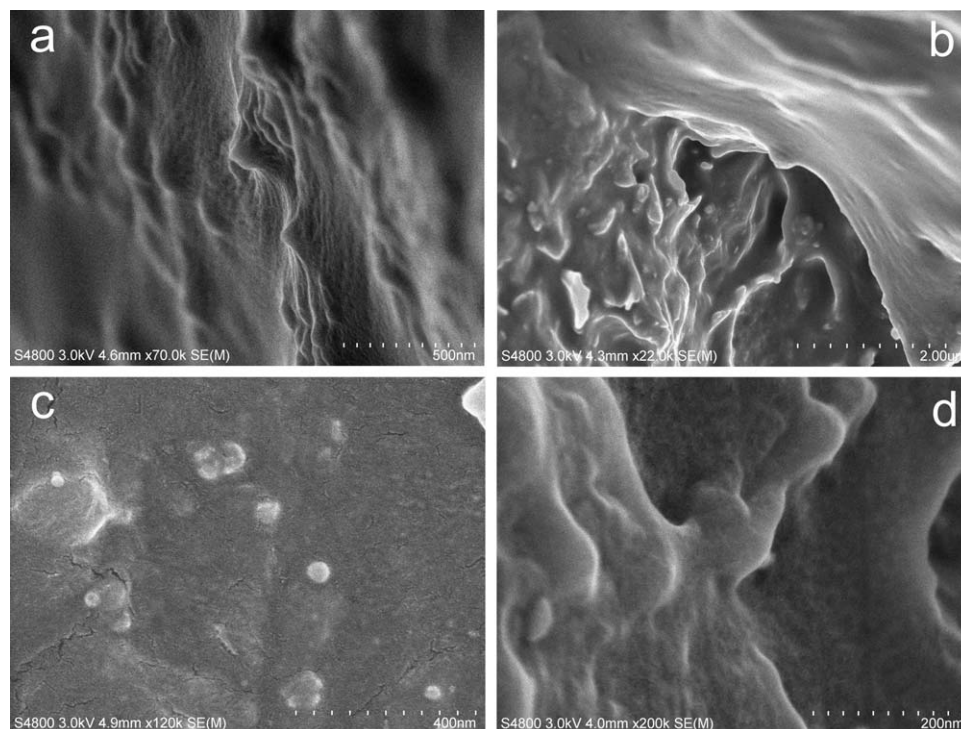


Figure 5. SEM micrographs of PP/LDH-AUA nanocomposites: the sample containing 2% w/w of the filler, surface (a) and cross-section (b); the sample containing 5% w/w of the filler, surface (c) and cross-section (d).

The heterogeneity decreases, when quantity of the additive rises to 5% w/w. This is visible for instance, on the Figure 4(d) (the sample surface) and Figure 4(e) (cross-section). Inclusions of lamellar inorganic material may be observed within cavities on the surface [Figure 4(f)]. DMTA data showed (Figure 3, Table I) that nanocomposites obtained with functionalized modifiers (AUA, FA, DOCA), that is, those possessing a functional group in addition to sulfonic or carboxylic, which are bound to the particle; revealed improved mechanical properties with respect to LDH-DSA (possessing the long alkyl chain only). A certain microstructural improvement may be also observed by FESEM. For example, the material obtained with addition of AUA-modified clay has more homogeneous morphology presented on the Figure 5. Sample of the composites reveal certain features visible on cross-section images [Figure 5(b,d)] that may be attributed to exfoliated platelets of the inorganic component. They are smoothly covered by the polymer.

Modification with surfactants of natural origin (DOCA and FA) increases the affinity of inorganic component to the macromolecular chain. All the micrographs reveal uniform surface and homogeneous inner part of the samples. The interfacial adhesion of those modified clays to PP is sufficient, thus, there is no need to add any compatibilizer.

Images of the PP nanocomposite with Mg/Al-LDH-DOCA exhibit high homogeneity of the materials [Figure 6(a–g)]. The absence of inclusions means that composite materials are formed, for example, smooth phase without cracks is observed both on the surface and cross-section of the sample containing 2% w/w of DOCA-modified clay [Figure 6(a,b)]. Light

filamentous profiles on the firm surface may possibly be attributed to aggregates of PP macromolecules [Figure 6(b,c)]. FESEM examination of the material containing 5% w/w of the same nanofiller demonstrates more feature-rich structure of the composite obtained [Figure 6(d)]. A fissure visible on the cross-section evidently occurs on the crystallite edges. Nanolamellae of the filler are hardly distinguishable, due to perfect compatibility with the polymer matrix [Figure 6(e)]. Inner part of the cavity in the fissure's region is also quite smooth [Figure 6(f,g)]. A feature appearing at the left side of the Figure 6(f) may be attributed to an LDH nanolamella, smoothly incorporated into the PP matrix.

It is interesting to note, that addition of Zn-Al LDH-DOCA filler, that is, Mg^{2+} to Zn^{2+} substitution in the brucite layer, leads to a material of different morphology. For example, surface of the sample with 2% of the additive is not very even, the material is more brittle [Figure 6(h)]. The correspondent material with 5% of Zn-Al LDH-DOCA contains more rough zones and its surface is slightly hillocky [Figure 6(i)]. However, the adhesion between inorganic phase and the polymer is very good, since a nanolamella occurring in the neck between two separating pieces of the fissure remains smoothly incorporated into the matrix [Figure 6(k)]. Thus, FESEM data are in a good agreement with the DMTA, which showed a deterioration of mechanical properties for Zn-containing filler.

Composite samples containing the nanofiller modified with FA revealed the most promising mechanical properties according to DMTA. This fact is supported by FESEM. Surface of the composite obtained with 2% of the additive is smooth and

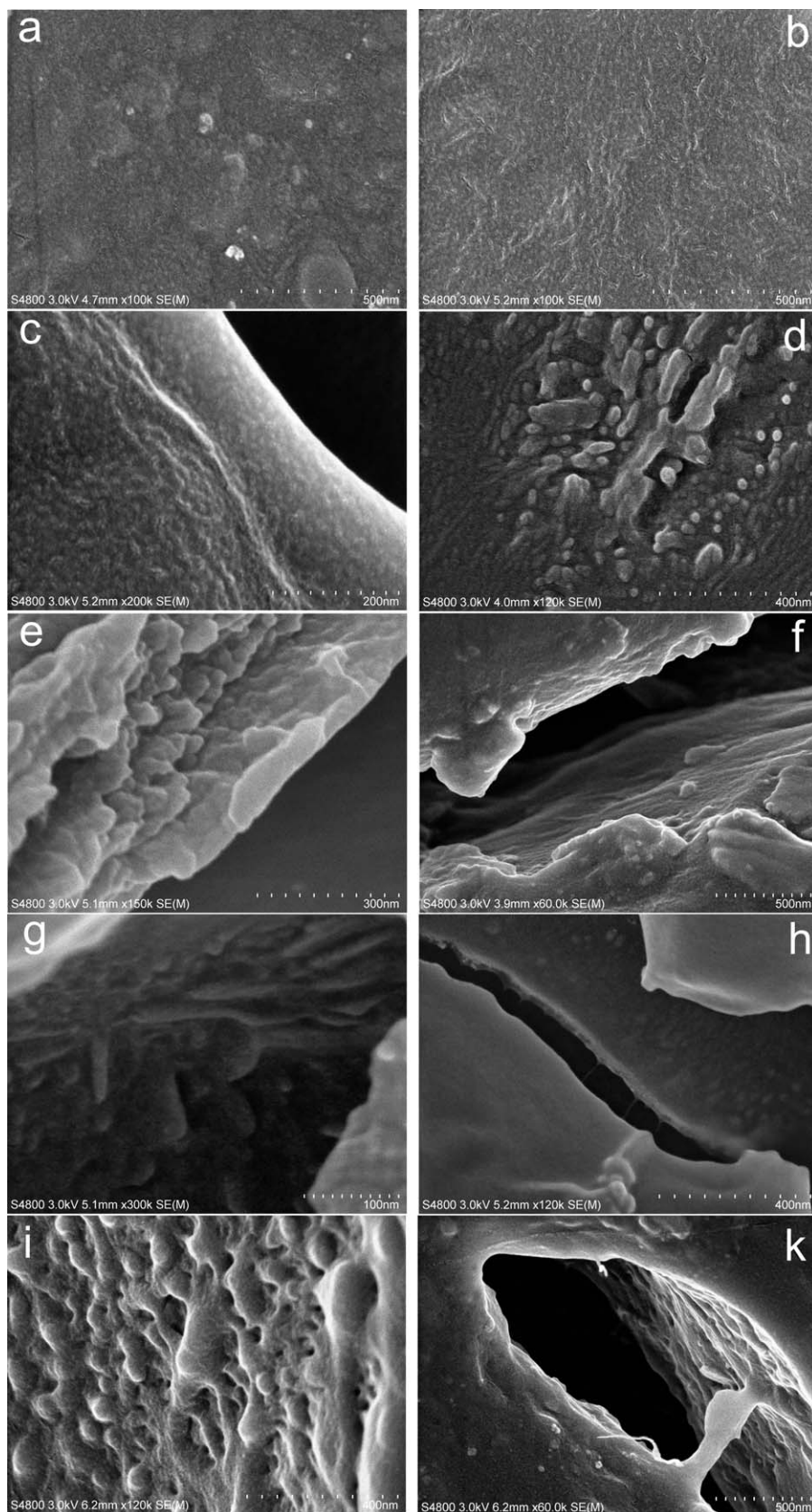


Figure 6. SEM micrographs of PP/Mg-Al-LDH-DOCA nanocomposites (a–g): surfacial view (a–d), cross-section view (e–g); and PP/Zn-Al-LDH-DOCA nanocomposites (h–k): surfacial view (h,i), cross-section view (k).

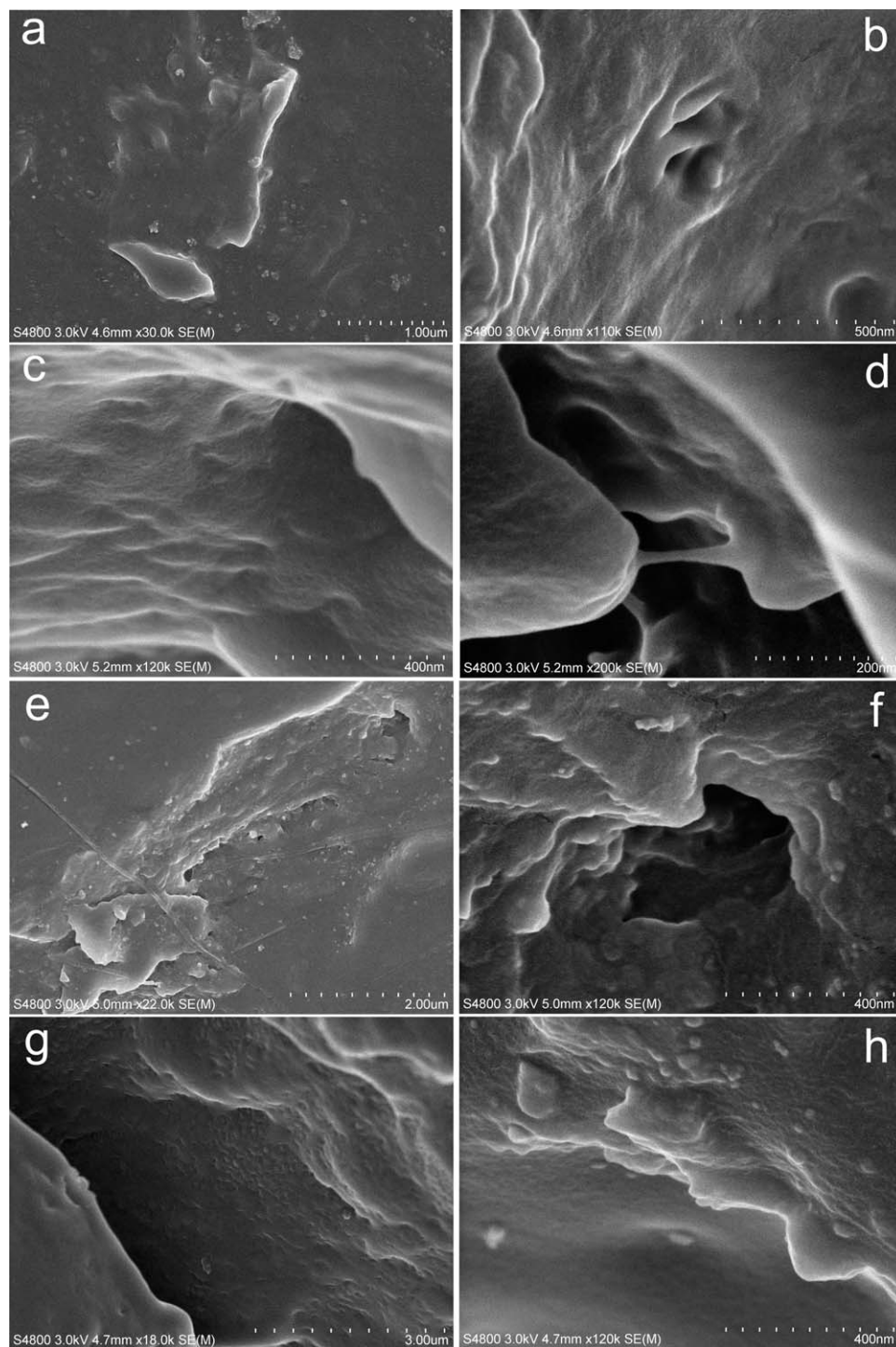


Figure 7. SEM micrographs of PP/LDH-FA nanocomposites: the sample containing 2% w/w of the filler, surface (a,b) and cross-section (c,d); the sample containing 5% w/w of the filler, surface (e,f) and cross-section (g,h).

unruffled, it may occasionally contain some smooth nano-sized cavities [Figure 7(a,b)]. Cross-section of the sample is smooth and uniform as well [Figure 7(c,d)]. Appearance of the material with 5% of the LDH-FA on the FESEM images is also very smooth, so that some features appear only in the moulding defect area [Figure 7(e,f)]. The cross-section of the composite

is homogeneous and without cracks even at the nano-level [Figure 7(g,h)]. Some features prominent from the matrix on the Figure 7(h) may be attributed to the filler nanolamellae, incorporated in polymer matrix. No cracks or phase separation were observed indicating perfect adhesion between the components.

CONCLUSION

This study shows the possibility to obtain PP/LDH nanocomposites without use of compatibilizers. Differently modified exfoliated inorganic nanoparticles perfectly mix with nonpolar PP matrix and alter the microstructure and thermo-mechanical properties of PP/LDH nanocomposites. Organophilization of the clay particles with different functionalized surfactants leads to different degrees of their dispersion in the PP matrix, thus affecting T_g , stiffness, and relaxation capacity of the composite.

A stiffer interface and better balance of thermo-mechanical properties were observed for DOCA and FA modified LDHs, as compared to the pure polymer and to the most traditional nanocomposite of PP with organophilic montmorillonite (Cloisite 15A) using PP grafted with maleic anhydride as compatibilizer. This conclusion was also supported by FESEM microscopic study at the nanoscale that revealed inorganic nanolamellae smoothly incorporated into the polymer matrix without any additional compatibilizing agent.

Comparison of our results with those previously published^{14–18} indicates the presence of nonfunctionalized aliphatic chains absorbed on the clay particle surface is necessary, but evidently not sufficient for efficient compatibilization with the PP matrix. A certain degree of the surfactant molecule functionalization is crucial for better compatibilizing performance. The use of natural or nature identical biodegradable surfactants (e.g., DOCA and FA) will lead to formation of more easily biodegradable nanocomposites. Experiments on biodegradability in soil are actually ongoing.

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