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Communications to the Editor

Oxidation−Migration Cycle in Polypropylene-Based Nanocomposites

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Polypropylene (PP) appears to be the most widely investigated polymer for use in the preparation and application of nanocomposites. PP as a highly hydrophobic and nonpolar polymer can be used for the preparation of nanococmposites only after a compatibilzing process in which polar groups are introduced.[1] Among the modifications described in the current literature, the most prevalent consists of grafting maleic anhydride (MA) onto PP. However, this treatment is connected with a number of complications including such side reactions as β-scission, chain transfer, coupling, and, above all, severe decrease of the molecular weight.[2−5] One of the aims of this study is to explore the possibility of dispersing organo-layered silicates (OLS) in pristine PP in the presence of air, without pretreatment. Preliminary experiments showed that clay can be dispersed by melt processing in the presence of air as well as by annealing in the presence of air.

The interaction of pristine PP and of PP/OLS with oxygen has been studied by several investigators.[6−12] These studies were concerned mainly with the degradation of the polymer by thermal oxidation. The extent of oxidation was monitored by determining the carbonyl groups spectroscopically by ATR-FTIR. The above studies were not concerned with investigating the effect of oxidation on the structure of PP-based nanocomposites.[13,14] A preliminary study on the effect of air oxidation of poly(ethylene-*co*-vinyl acetate) (EVA) was reported in the literature, and whereas changes in the nanocomposite structure were noticed, they do not pertain to PP nanocomposites due to the differences in chemical structure between the two matrix polymers.[15]

A preliminary study of the effect of oxygen on the structure of PP/OLS was recently carried out in these laboratories.[16] It was shown that whereas the structure of PolyOne PP does not change upon annealing with N_2, profound changes occur in the PP/OLS structure upon annealing under a stream of air. These changes were monitored by XRD and by migration of clay to the surface as determined by ATR-FTIR.[16,17] Additional results on the effect of oxygen during annealing of maleic anhydride (MA) grafted PP were also recently obtained.[18] In this study a limited concentration of air, up to 25% of the purging gas, was used, and effects of two structure modifiers were studied simultaneously, one of the grafted MA and the other of the oxygen. In the present study the effects of increasing concentrations of air up to 100% of the purging gas were studied on pristine PP without any other compatibilizers.

The experiments described in the present communication were carried out at 180 and 190 °C. These temperatures are below the onset temperature of the decomposition of the surfactant in the clay. This was confirmed by dynamic and isothermal TGA measurements, carried out in these laboratories, and not reported here, which showed a very small weight loss in the temperature range when the TGA was carried out at an atmosphere of N_2 as well as N_2 containing 12.5% air. In the experiments reported below the PP was mixed in the Brabender with 5 wt % clay. The preparation of the samples, the annealing experiments, the regulation of the composition of the purging gas, the determination of the extent of migration and the concentration of carbonyl groups, and the XRD measurements were carried out as described previously.[18]

A series of experiments that involved annealing under pure N_2 and under several concentrations of air in the N_2 purging gas were carried out at 190 °C for 60 min. Five nitrogen−air mixtures with increasing concentrations of O_2 were used for purging the samples: 6.25, 12.5, 25, 50, and 100%. The results of these five experiments are presented in Table 1 and Figure 1a,b. Each of the data points in the figure pertains to one experiment in which a specified amount of air was used. The results shown in Figure 1 enable an approximate estimation of the change in the extent of migration (R_2) with respect to the amount of oxygen applied. These experiments were not designed for the precise determination of the amount of oxygen consumed by the sample. However, since the rate of flow of the nitrogen−air mixture was identical in all experiments, and since the temperature in all these experiments was the same, as were the sizes of the samples, it was assumed as a first approximation that the amount of oxygen diffused and consumed by the sample was roughly proportional to the amount of oxygen flowing over the surface of the sample in 1 h. It is evident from Table 1 and Figure 1b that the R_2 values increase upon increase in concentration of O_2 in the purging gas. The highest increase occurs in the case when the purging gas contains only air. Migration reaches a maximum value of $R_2 = 4.35$ for sample 7 (i.e., 100% air). As mentioned above, the PP used in this study was not compatibilized. It did not contain MA or any other polar group, and the dispersion of the clay, the intercalation, and the exfoliation occurred only due to the effect of the oxygen during annealing and the progressive formation of polar groups on the polymeric matrix as a result of oxidation by oxygen. At the outset, therefore, the clay was not dispersed, and the interlayer distance (d) as determined by XRD was that of original nonintercalated clay (see Table 1).

No migration of the clay to the surface was observed for samples annealed at all temperatures under a stream of N_2 only (sample 2, Table 1). This situation changed when the annealing was done under a stream of nitrogen containing air. The oxygen in the stream of purging gas penetrated and diffused into the polymeric melt, and oxidation of the polymeric chains took

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Table 1. Samples Annealed at 190 °C under Different Concentrations of Air for 60 min[a]

sample no.	% air	migration by ATR				R_2/wt O_2	R_4/wt O_2	XRD "*d*" value (nm)
		R_1	R_2	R_3	R_4			
1	control	$0.48 \pm 0.13 = R_0$	1	$0.21 \pm 0.05 = R_c$	1			2.61
2	N_2 only	0.49 ± 0.04	1.02 ± 0.08	0.19 ± 0.09	0.90 ± 0.42			2.93
3	6.25	0.57 ± 0.07	1.19 ± 0.14	0.23 ± 0.02	1.10 ± 0.10	1.43	1.33	2.97
4	12.5	1.15 ± 0.27	2.40 ± 0.56	0.26 ± 0.06	1.24 ± 0.29	1.44	0.75	3.11
5	25	1.35 ± 0.10	2.81 ± 0.21	0.31 ± 0.08	1.48 ± 0.38	0.85	0.45	3.12
6	50	1.73 ± 0.14	3.60 ± 0.29	0.33 ± 0.02	1.57 ± 0.10	0.55	0.25	3.51
7	100	2.09 ± 0.11	4.35 ± 0.23	0.60 ± 0.02	2.86 ± 0.10	0.33	0.22	3.76
8 (pristine PP)	100			0.36 ± 0.09	1.71 ± 0.42			

[a] R_0 = the concentration of clay on the surface of the sample before annealing at 25 °C as determined by the normalized intensities of the clay peak −Si−O− at 1047 cm^{-1} measured at room temperature; R_1 = the concentration of clay after annealing; R_2 = the extent of migration = R_1/R_0; R_c = the concentration of the carbonyl groups on the surface of the sample before annealing at 25 °C as determined by the normalized intensity of the CO at region of 1640−1714 cm^{-1}; R_3 = the concentration of the carbonyl groups as after annealing; R_4 = the carbonyl index R_3/R_c.

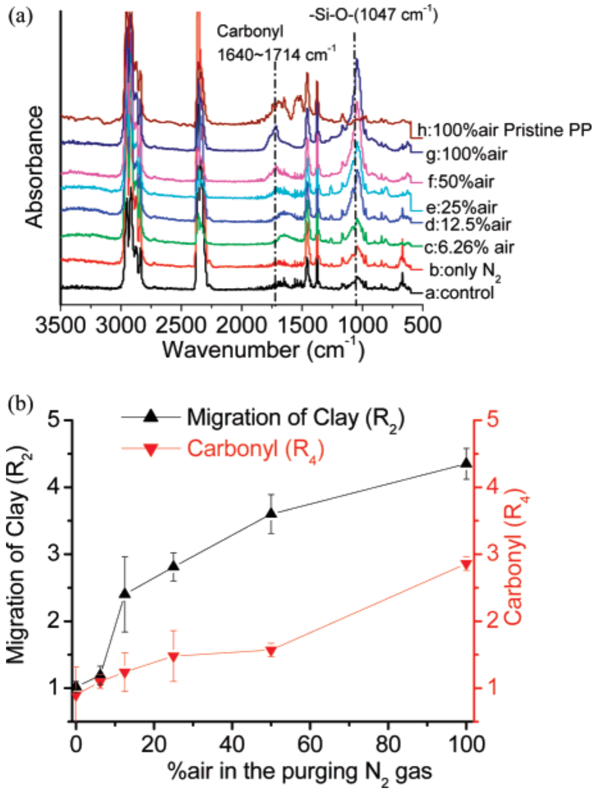


Figure 1. Extent of migration and carbonyl content of samples annealed at 190 °C under different concentrations of air for 60 min: (a) ATR spectra, (b) R_2 and R_4 vs % air.

place. According to recent publications, the oxidation reaction which occurred via the formation of peroxide radicals on the C−H of PP chains produced several oxidation products, i.e., ketones, hydroxyls, aldehydes, and carboxyls (see Scheme 1).[14,19] At the same time, the polymer chain is cleaved. The aldehyde and carboxyl groups decompose during annealing at elevated temperatures with the evolution of CO and CO_2.[19] This oxidation is evidenced by the carbonyl groups determined spectroscopically (see Table 1). Evidence of carbonyl groups on the surface, and double bonds below the surface, as determined by Ramen laser spectroscopy, has been recently reported.[20] When comparing the fourth and sixth columns of Table 1 and plotting R_2 against R_4, it is seen that a straight line is obtained with a slope of 2. The increases in R_2 and R_4 are clearly a function of the higher concentration of O_2 in the annealing gas. It may be considered that the carbonyl groups are not the only polar group formed and that additional polar groups, such as hydroxyls, also contribute to polarity of the polymeric matrix and to migration.[19] It is also possible that a part of the carbonyl groups formed decompose during annealing. It is of interest to note that the carbonyl content found upon annealing of pristine PP (sample 8) is considerably lower than that obtained in sample 7 containing 5% clay, annealed under a stream of 100% air. This can be explained by taking into consideration the effect of the antioxidants contained in the PP. It has been reported in the literature[21] that the antioxidants contained in commercial PP are being partly absorbed by the clay and are, therefore, unavailable for the protection of the PP from oxidation. The carbonyl content found in a clay containing sample will, therefore, be higher than in pristine PP, which contains the full amount of the antioxidant additive.

The oxidized PP chains containing polar groups intercalate into the clay gallery. The increase in extent of intercalation, as evidenced by the increase in the interlayer distance *d* (see Table 1), promotes the exfoliation process. Exfoliated layers which are delaminated from intercalated stacks are dispersed in the matrix and free to migrate to the surface.[16] The fact that the sample simultaneously contains both the intercalated and exfoliated moieties can be clearly seen in Figure 2. This figure represents two HRTEM images taken at two different spots from the same sample 7, prepared by annealing. The intercalated moiety, as indicated by *d*, and the exfoliated moiety, which has a silent XRD scan, but is shown by the migration, exist simultaneously. Parts a and b of Figure 2 show respectively intercalated and exfoliated domains taken from sample 7. The exfoliated part seems to be well-dispersed in the PP matrix.

The intercalated clay layers which are organized in relatively bulky stacks cannot migrate to the surface. They do exist in this sample, simultaneously with and alongside the exfoliated platelets. Evidence for the migration of the exfoliated platelets was presented earlier for PA 6 nanocomposites by both ATR-FTIR and ARXPS.[22,23] It is evident from the seventh and eighth columns of Table 1 that the rate of migration (R_2/wt O_2) decreases very significantly with the increase in concentration of oxygen in the gas mixture, whereas the cumulative extent of migration increases continuously, as seen in Figure 1b. It is suggested that the cause responsible for the decrease in this rate is due to the accumulation of clay on the surface of the sample as a result of the migration process. The diffusion of O_2 in the melt is slowed down by the fact that O_2 molecules cannot penetrate the clay platelets on the surface. In order to diffuse into the sample, they have to circumnavigate the clay particles, thus increasing the path of diffusion. Less O_2 penetrates the sample per unit time, thus decreasing the rate of oxidation.[6,7] An R_2 value of 3 corresponds to a 15% concentration of clay on the surface. Thus, the properties of the surface are very different from the original 5 wt % clay containing nanocomposites. A similar trend is observed in the change in concentration of carbonyl groups per unit of O_2. This change also decreases with the concentration of O_2. It is to be expected that

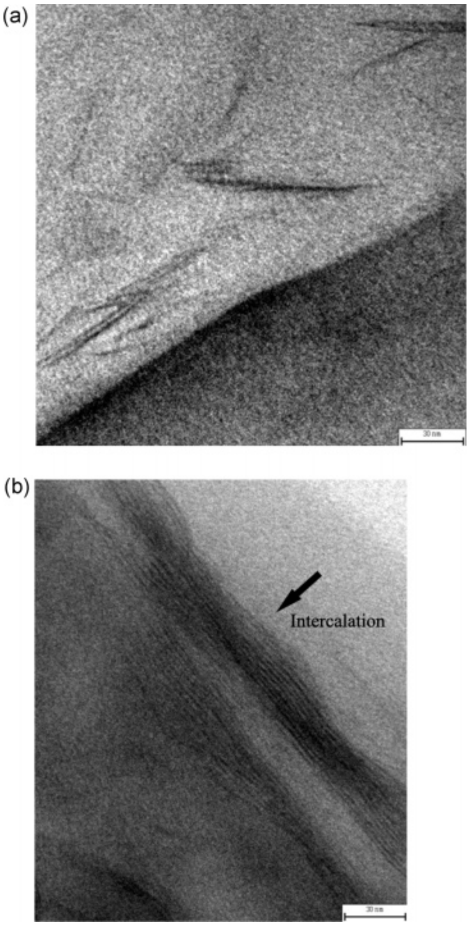


Figure 2. HREM image of sample 7: (a) exfoliation and (b) intercalation.

the permeability of gases and liquids will be much lower with increases in extent of migration. A new surface is created by the migration of the exfoliated platelets. This new clay-rich surface has new barrier properties. It slows down and hinders the penetration of oxygen and thus the oxidation and slow combustion of the sample. It is basically similar to the barrier created at much higher temperatures during the combustion of nanocomposite samples.[24] This would indicate an increase in the aging and storage stability of nanocomposites with increase in extent of migration. The extent of protection afforded to samples with the new clay-rich surfaces as well as the consequent increase in shelf life of such samples is presently being investigated in these laboratories, both for aging in air and for photooxidation.

A separate series of experiments were carried out in order to determine the rate and energy of activation of the migration process. The rate was determined from a series of annealing experiments in an atmosphere of 100% air, carried out at 180 and 190 °C for three time intervals. This concentration of air brings about a mild oxidation so that any oxidation of the sample occurring during the annealing will be relatively slow and easy to measure. Both temperatures used for the rate measurements are well above the melting point, and the mobility of the polymeric chains was assumed to be not very different. The times of the annealing experiments were 5, 15, and 30 min in order to keep the extent of migration relatively low so that the diffusion of oxygen was not greatly hindered due to increase in concentration of clay on the surface.

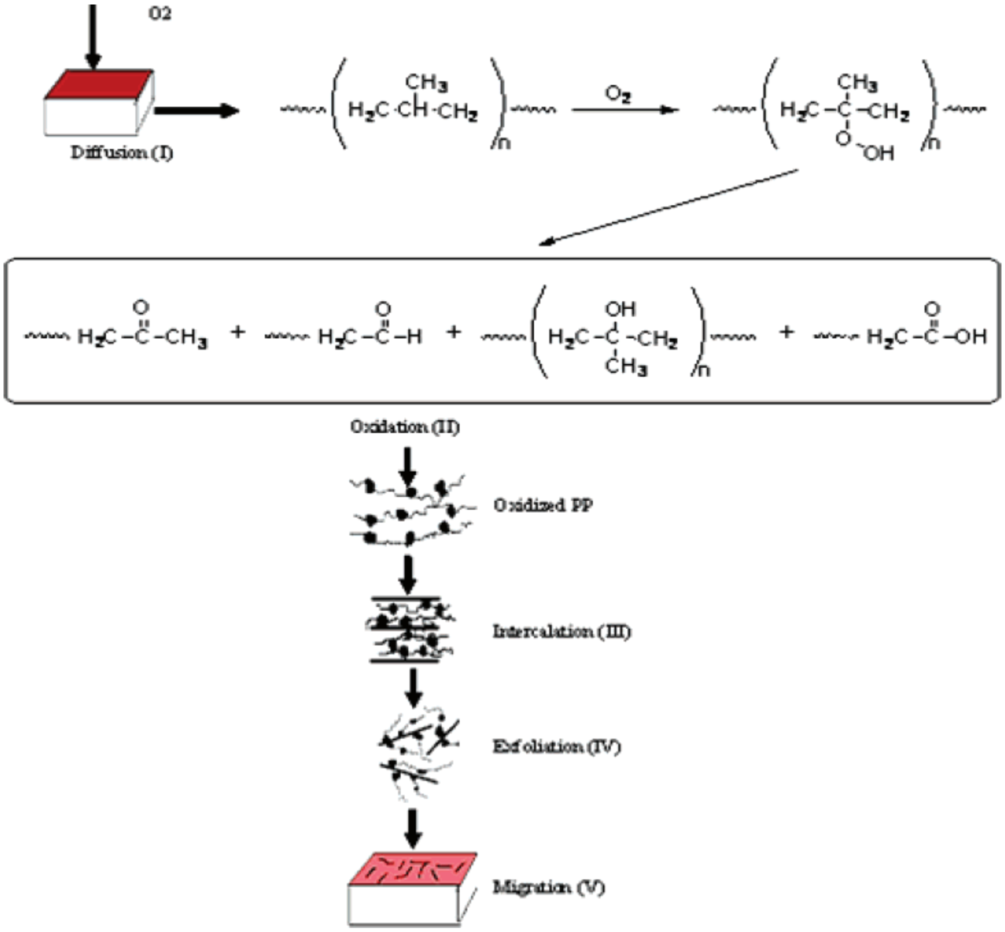
It can be seen in Figure 3 that the migration proceeded for the first 30 min in a straight line. The rate of reaction can therefore be determined as the slope of the lines in the figures. The energy of activation as calculated by the Arrhenius equation is 37.82 kJ/mol. This value corresponds to a reaction with diffusion as the rate-determining step. These data do not provide information about the rate of the actual migration of the clay units to the surface. This migration step is the last of five steps of an oxidation−migration cycle comprising the processes occurring in the melt during annealing in the presence of oxygen (see Scheme 1). Step one is the diffusion of O_2 into the melt during annealing. It is possible that this step is the rate-determining step. However, further work and more evidence is needed to decide whether the rate-determining step is not one of the other steps in this cycle. Step 2 is the oxidation of PP by the diffused oxygen and the formation of polar groups. This oxidation appears to be composed of a number of free radical reactions initiated by the formation of a peroxide radical on the tertiary carbon of the PP, as discussed above.[19] These radical reactions are more rapid than the oxygen diffusion process.

The third step is the intercalation of the polar moieties of the newly formed polar matrix molecules into the clay gallery. Very little is known about the rate of intercalation. This rate depends on many parameters, such as length of the surfactant molecules, chain length and polarity of the matrix molecules, density in the gallery, negativity of the clay layers, interaction between the molecules of the surfactant and of the matrix, and geometric structure of the matrix molecules. The intercalated units are usually organized in relatively large stacks which are difficult to disperse in the polymer. They are relatively bulky and their migration to the surface is unlikely.[16]

The fourth step is exfoliation. When the number of matrix molecules intercalated increases to a critical value, exfoliation occurs.[16] The clay particle splits and the two layers separate. Single clay layers containing surfactant and matrix molecules are delaminated from the intercalated stacks and dispersed in the melt. Each of these layers contains, in addition to the clay layer, the adhering surfactant molecules and the polar molecules of the polymeric matrix. The composition of the exfoliated units depends on the nature of the surfactant, on temperature, and on the polarity of the matrix molecules. In the range of temperatures 180−200 °C the exfoliated units may be considered to be relatively stable since the onset of the decomposition of the ammonium-based surfactants begins at temperatures above 200 °C. Similar to intercalation, very little is known about the kinetics of exfoliation. It is to be expected that the rate will depend greatly on the viscosity of the polymeric matrix, the mobility of the polymeric chains, the size of the platelets, the orientation of the platelets, and the nature of the polymer. This may vary from polymer to polymer.

Step five is migration of the exfoliated units to the surface. The dispersed individual exfoliated units aggregated with matrix molecules migrate to the surface. The interfacial surface tension for the interface between the exfoliated platelets and the PP matrix was calculated as 2.52 dyn/cm as compared to the surface tension at 250 °C of 16.76 dyn/cm for the PP matrix.[24] The aggregate will migrate to the surface so as to decrease the free energy of the surface of the sample.[24−26] The rate of migration may depend on a number of factors. An important factor is the orientation of the platelet relative to the surface. The dimensions of the exfoliated platelets are believed to be much larger than the 1−2 nm thickness, and the aspect ratio is high. These dimensions may hinder the motion of the platelets to the surface. The rate will also depend on the viscosity of the polymeric matrix and the mobility of the chains. The migration can be hindered by molecular clusters, entanglements in the polymeric

Scheme 1. Oxidation−Migration Cycle Occurring in the Melt during Annealing in the Presence of O_2



melt, or the orientation of such moieties. The rate of the migration step is not determined in the present study. It is however believed that this rate can be determined by suitably designed experiments in which the four preceding steps are omitted. Such experiments should be carried out on exfoliated nanocomposites annealed above the melting point without oxidation.

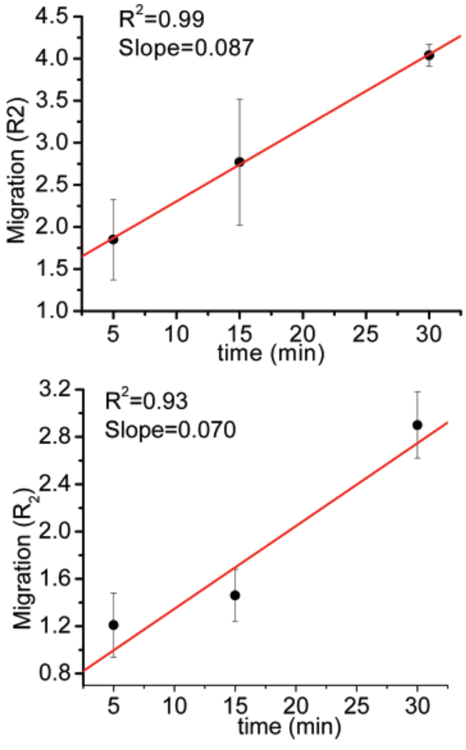


Figure 3. Migration (R_2) vs time: (a) 190 °C and (b) 180 °C.

In summary, the present communication provides evidence to the effect that a dispersion of clay in pristine PP, without compatibilization, is possible by oxidation with air. It also provides evidence that the migration of exfoliated platelets to the surface of molten nanocomposites hinders the penetration and diffusion of oxygen into the melt thus creating a barrier that slows down further oxidation, which indicates the possibility of increasing the aging and storage stability of nanocomposites and increasing their shelf life. In addition, this communication includes first data on the rate of migration and its energy of activation in molten nanocomposites. A mechanism by which oxidative annealing of polymer organically layered silicate nanocomposites brings about the migration of exfoliated platelets to the surface is suggested.

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