

Effect of stress and temperature on the thermomechanical degradation of a PE-LD/OMMT nanocomposites^{*)}

Francesco Paolo La Mantia^{1), **)}, Marco Morreale²⁾, Manuela Ceraulo¹⁾, Maria Chiara Mistretta¹⁾

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Abstract: Thermomechanical degradation of nanocomposites is a topical issue that has not been fully investigated as demonstrated by the low number of papers available in the literature regarding this specific aspect. In particular, with regards to low density polyethylene/clay nanocomposites, the degradation behavior is very complex since it involves the degradation paths of both the polymer matrix and the organomodified nanoclay. In the present work, the effects of mechanical stress and temperature on the thermomechanical behavior of PE-LD/organomodified clay nanocomposites and the degradation paths were investigated by rheological, FT-IR and mechanical methods. The results have shown that the thermomechanical degradation mechanisms are very complex, involving several phenomena such as chain scission, branching, recrystallization and crosslinking, degradation of the organomodified clay and interaction between the degradation products of both system components. These interactions between the degradation products of the organomodifier and the polymer matrix can deeply influence the final behavior of the nanocomposite in a way which is similar to what usually happens in polymer blends.

Keywords: nanocomposites, thermomechanical degradation, melt flow rate, rheology, mechanical properties.

Wpływ naprężeń i temperatury na termomechaniczną degradację nanokompozytów PE-LD/OMMT

Streszczenie: Zbadano wpływ naprężeń mechanicznych i temperatury na przebieg termomechanicznej degradacji nanokompozytów polietylenu małej gęstości (PE-LD) i organicznie modyfikowanej glinki montmorylonitowej (OMMT). Zdegradowane nanokompozyty oceniano na podstawie wartości wskaźnika szybkości płynięcia (*MFR*), widm FT-IR oraz właściwości mechanicznych. Wyniki badań wskazują, że mechanizm termomechanicznej degradacji kompozytów PE-LD/OMMT jest procesem złożonym, obejmującym: rozerwanie łańcucha polimeru, rekrytalizację i sieciowanie, degradację organicznie modyfikowanej glinki, a także interakcje między produktami degradacji, a składnikami kompozytu — glinką modyfikowaną organicznie i matrycą polietylenową. Interakcje mają duży wpływ na przebieg procesu i na właściwości końcowego produktu degradacji.

Słowa kluczowe: nanokompozyty, degradacja termomechaniczna, wskaźnik szybkości płynięcia, reologia, właściwości mechaniczne.

In the last decade, a large number of papers have been published on many different kinds of polymer based nanocomposites [1–3]. However, this number becomes very low as far as the thermomechanical degradation (degradation due to the contemporary action of stress

and heat) of these new class of materials is concerned; the available literature data are basically on the reprocessing of nanocomposite systems [14–19].

In these works, it was found that the degradation was strongly dependent on the polymer used, as well as the nanosized filler and the processing conditions. In particular, with regards to PE-LD/clay nanocomposites, the degradation behavior is very complex since it involves the degradation paths of both the polymer matrix and the nanoclay, in particular the degradation of its organic modifier, which gives rise to the formation of radicals according to the well known Hofmann's elimination reaction [20, 21]. The degradation of clay nanocomposites depends, like in polymer blends, on the interactions between the degradation products of the two components.

¹⁾ University of Palermo, Department of Civil, Environmental, Aerospace, Materials Engineering, Viale delle Scienze, 90128 Palermo, Italy.

²⁾ Kore University of Enna, Faculty of Engineering and Architecture, Cittadella Universitaria, 94100 Enna, Italy.

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^{**)} Corresponding author; e-mail: francescopaolo.lamantia@unipa.it

More specifically, polymer based organomodified clay nanocomposites show very interesting features since the filler particles do not behave inertly, which is different to all of the conventional polymer composites. Actually, the layered clay particles change their shape and size while being subjected to the flow because of the action of both temperature and mechanical stress, giving rise even to an exfoliated morphology [19, 22]; it has also been shown that the reaction products from the degradation of the organo-modifier can interact with the radicals from the polymer by changing the degradation behavior of the polymer matrix [19]. This behavior is similar to that of polymer blends where the dispersed polymeric particles change shape and size when subjected to a flow and the degradation products interact among them to give unforeseen degradation paths [23]. Furthermore, when a low density polyethylene (PE-LD) is used as matrix, the degradation can undergo two paths: branching or cross-linking [24].

In a previous paper [19], some of the authors reported the effect of repeated processing steps in an extruder on the rheological, morphological and mechanical properties of a polyethylene/organomodified montmorillonite. The properties did not change significantly under the adopted processing conditions. On the contrary, the properties and morphology can strongly change if the processing conditions (temperature, mechanical stress and time) are much more severe than those adopted in extrusion. The aim of this work is to understand better the complex degradation paths of this system considering the effect of applied stress and temperature. In particular, the aim is to map the effect of temperature and stress on the final molecular structure of the polymer matrix and of the morphology of the nanocomposite by using only a simple viscosimetric characterization, i.e. the melt flow rate.

EXPERIMENTAL PART

Materials

The materials used in this work were a sample of film grade ($MFR = 0.26$ g/10 min) polyethylene (Riblene FC39 from Versalis, Italy) that does not contain any antioxidant or stabilizer, and an organomodified clay sample (Cloisite[®] 15A from Southern Clay Products). Cloisite 15A, (CL15A) is a ditallowdimethylammonium modified montmorillonite, with an average diameter of 8 μm ; the organomodifier concentration is 125 meq/100 g clay.

Methods of testing

— Thermomechanical degradation tests were carried out in a Brabender batch mixer (one hour processing time) at three different temperatures (160, 210 and 280 °C) and two speeds (3 and 60 rpm).

— MFR (melt flow rate) values were measured with the aid of a Instron[®]'s CEAST melt flow indexer at 190 °C under a weight of 2.16 kg. The MFR is the amount of material flowing out through the die, under specific temperature and pressure conditions, in ten minutes.

Compression molded sheets were thus prepared by using a Carver (USA) laboratory press operating at 190 °C.

— Tensile tests were performed using an Instron (USA) mod. 3365 universal machine on specimens (90×10×0.5 mm) cut off the compression molded sheets, with an initial testing length of 30 mm.

— FT-IR spectra were measured by a Spectrum One spectrometer manufactured by Perkin-Elmer (USA), using the SpectrumOne software. Spectra were obtained with 16 scans and a 4 cm^{-1} resolution. Measurements were obtained from the average of triplicate samples.

— Calorimetric data were obtained by DSC analysis using a Perkin Elmer (USA) DSC7 apparatus performing runs from 30 °C to 180 °C at 10 °C/min. Only the heating step was performed since the aim was to analyze the actual situation of the materials as obtained from its processing step.

— Gel content determination (in order to assess the occurrence of crosslinking phenomena) was performed by Soxhlet extraction tests using boiling xylene.

RESULTS AND DISCUSSION

As reported in the previous paper [19], the morphology of the nanocomposite produced under standard conditions is quite unsatisfactory, with relatively large particles showing low adhesion to the matrix and a small intercalation degree, as revealed by a standard XRD analysis (Fig. 1) with a peak at 3.65 nm while the typical peak of Cloisite 15A is at 3.15 nm.

This morphology is typical of the poorly optimized polyolefin-clay systems [25] because of the poor compatibility between the two phases and the consequent low stress transmission from the matrix to the clay particles. Although the small intercalation effects, no compatibi-

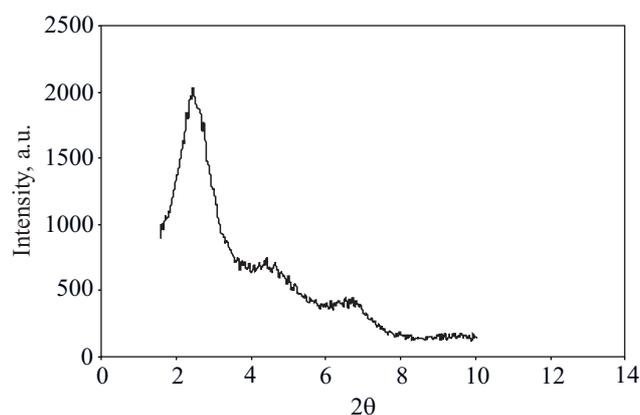


Fig. 1. XRD trace of clay-polyethylene nanocomposite

lizer was used to improve the intercalation or to produce the exfoliation. Indeed, the presence of a third polymeric phase can make the degradation paths of this system significantly more complex [22], while the aim of this work is investigate the thermomechanical degradation and the interactions between polyethylene and organomodified clay.

Table 1. *MFR* of all the investigated samples

Sample		Temperature		
		160 °C	210 °C	280 °C
PE-LD	low speed	0.24	0.046	0.12
	high speed	0.42	0.24	0.35
PE-LD + CL15A	low speed	0.28	0.056	0.065
	high speed	0.47	0.26	0.27

The *MFR* values of all the samples processed under different conditions of temperature and rotational speed are reported in Table 1. For comparison purposes, the value of the neat, unprocessed matrix (PE-LD) is 0.26 g/10 min.

All of the values present a minimum at intermediate temperatures and the curves of the pure matrix are higher than those of the nanocomposites, except for the higher temperature (280 °C). Furthermore, the values of the *MFR* are higher upon increasing the rotational speed and therefore the mechanical stress applied to the melt. Since the *MFR* values are related to the inverse of the viscosity, this means that increasing the stress applied to the melt leads to an increase in the viscosity, while the opposite is true when the shear stress decreases. In particular, taking into account the values of the pure PE-LD, it is possible to draw additional information from the results. Upon increasing the stress (low temperature and high rotational speeds), the viscosity decreases with respect to the initial value and this means that chain scission is predominant over chain branching. On the contrary, chain branching prevails over chain scission at low shear stress values (high temperature and low rotational speed). At high temperature and low mechanical stress, the *MFR* tends to flatten and this means that the two degradation paths counterbalance each other.

A different situation is shown by the nanocomposite sample. Indeed, the behavior is the same as already described, with chain scission prevailing over chain branching at low temperatures, while at higher temperatures the values of the *MFR* rise in all of the processing conditions. Furthermore, the values of the *MFR* are lower than those of the matrix except for those at higher temperature.

The lower values of *MFR* at the lowest processing temperatures are easy to explain because the viscosity of the nanocomposite is higher than that of the matrix; on the other hand, it is more difficult to interpret the unexpected rise of the *MFR* at higher temperatures.

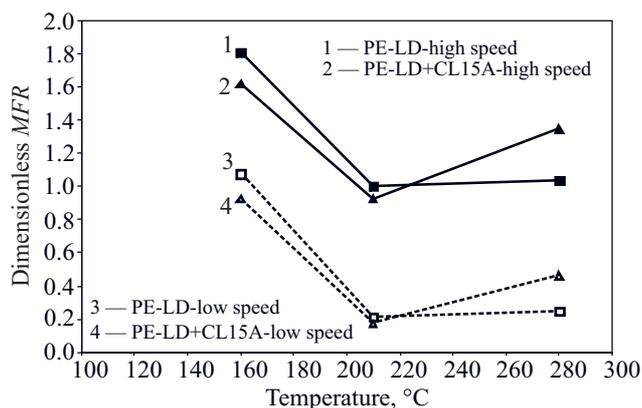


Fig. 2. Dimensionless *MFR* of the investigated systems

In Fig. 2, the dimensionless values of *MFR* of the nanocomposite samples are reported. These values have been obtained by dividing the single values of the nanocomposites' *MFR* by the values of the matrix *MFR* processed in the same conditions. In this way, it is possible to separate and determine the effect of the clay particles and that of the polymer matrix.

It is evident that, at 160 °C, the *MFR* of the nanocomposite is lower than that of the matrix, whilst it approaches a similar value at 210 °C and becomes higher at 280 °C. The decrease of the viscosity of the filled material with respect to the matrix can be interpreted only by assuming that some extra degradation of the matrix, caused by the presence of the second phase, has occurred. At high temperatures, indeed, the organomodified clay can undergo degradation of the organic modifier [19, 22] giving rise to radicals that, in their turn, can react with the radicals coming from the degradation of the macromolecules or with the macromolecules themselves. In order to confirm this hypothesis, the organomodified clay was subjected to a one hour treatment at the three temperatures. After one hour at 160 °C, the clay does not undergo any macroscopic change, while after the same time at 210 °C the clay becomes brownish and then almost black at 280 °C.

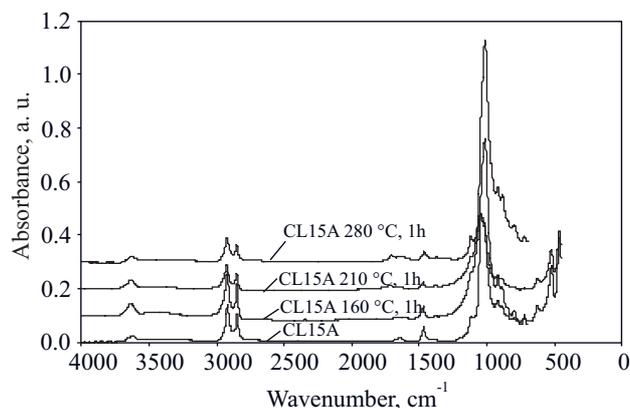
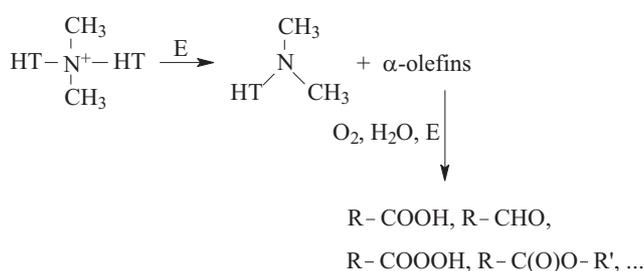


Fig. 3. FT-IR traces of the organomodified clay treated at three temperatures

The FT-IR traces of the three samples, Fig. 3, indicate that the one hour, 160 °C treated nanoclay does not undergo any significant modification.

On the other hand, the one hour, 210 °C treated one shows some changes: in fact, new peaks begin to appear in the 1600–1900 cm^{-1} range. This region corresponds to carbonyl groups such as carboxylic acids, ketones, aldehydes, esters, therefore it is a complex region since these multiple peaks are overlapped. Upon increasing the annealing temperature, the carbonyl peak area gradually increases.

We have therefore hypothesized the degradation path of the nanoclay's surfactant, as shown in Scheme A.



Scheme A

As reported in the literature [20, 21, 26], the organic modifier degradation starts according to the Hoffmann's elimination where, due to the high temperatures, it decomposes into α -olefins and amines. The α -olefins, in the presence of oxygen or water and high temperatures initiate oxidation reactions that lead to the formation of several carbonylic compounds. In particular, clay decomposition starts at 250 °C, whereas decomposition of the organic modifier starts at 220 °C [20, 21].

The increase of the *MFR* at this temperature with respect to that of the matrix processed under the same conditions clearly suggests that the interactions between the radicals coming from the two components provokes an increase of the chain branching kinetics.

These interactions hardly occur at 160 °C since the clay does not undergo degradation, are small at 210 °C, a temperature at which the clay's organomodifier starts to degrade and becomes very relevant at the highest temperature (280 °C).

This behavior is very similar to that shown by polymer blends where the degradation kinetics depend on the degradation kinetics of the two components, but also on the interactions between the two phases or between the species coming from the degradation of the components [23]. Furthermore, in previous papers, it has been demonstrated that these nanocomposites can show a „blend-like“ behavior even during processing under elongational flow [27–29]. Indeed, the OMMT particles are not just oriented by the flow but, like a polymer particle in a blend, they change size and shape when subjected to this flow.

As for the behavior under high mechanical stresses, where the nanoparticles undergo deformation and change size and shape like the dispersed particles in a polymer blend, also for the degradation path the polymer/clay nanocomposites show a behavior similar to that of polymer blends.

Obviously, polymer based clay nanocomposites are not polymer blends since the dispersed particles are not a molten polymer like in blends but the analogy between polymer blends and polymer nanocomposites with organomodified clays concerns the fact that, in the latter systems, the dispersed phase can be not only dispersed (like other inert fillers) but also „disaggregated“, depending on the applied stress, thus giving rise to particles (e.g. exfoliated platelets) with different shape and dimensions in comparison to the initial particles [28].

The change of molecular structure and morphology modifies, of course, the mechanical properties of these materials. In Figs 4 to 6, the elastic modulus (*E*), tensile strength (*TS*) and elongation at break (*EB*) are reported for both the samples at the lowest and highest stress, as a function of temperature.

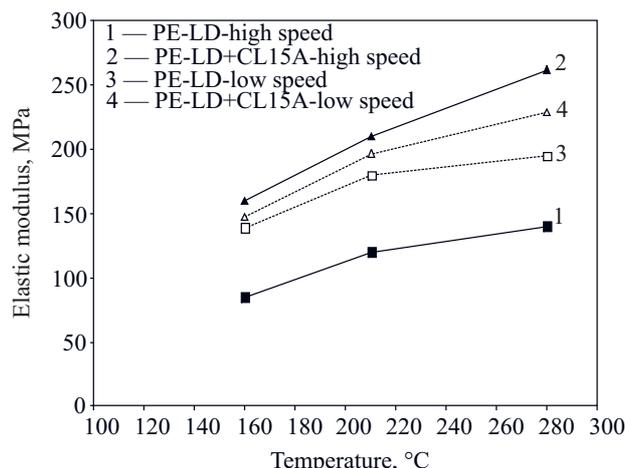


Fig. 4. Elastic modulus of the investigated samples

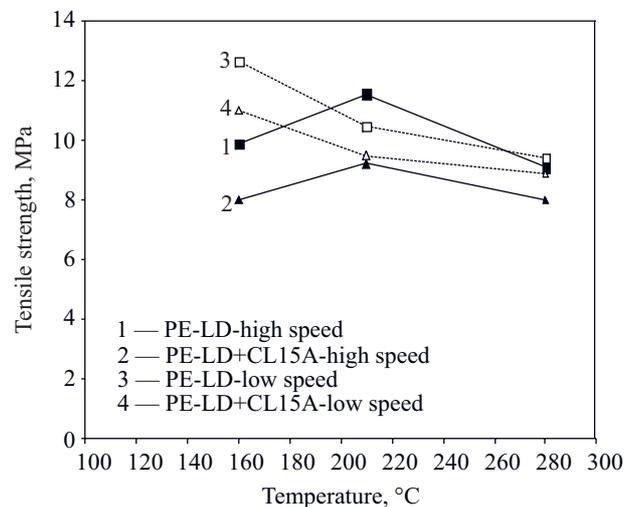


Fig. 5. Tensile strength of the investigated samples

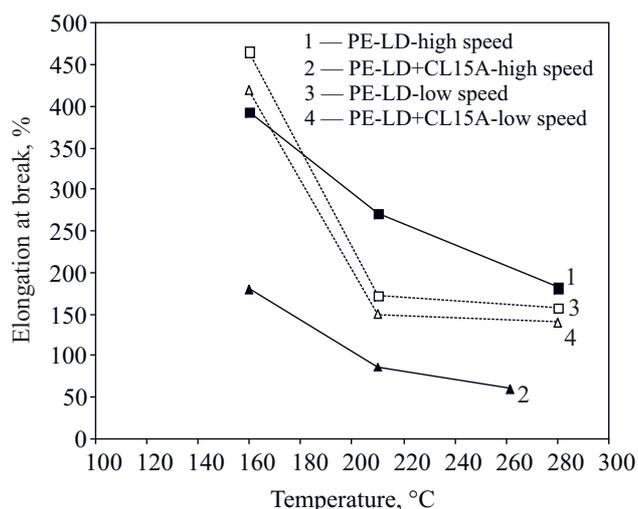


Fig. 6. Elongation at break of the investigated samples

For both the matrix and the nanocomposite, the elastic modulus increases upon increasing the processing temperature. As already discussed, the degradation paths lead to chain scission or chain branching. In the first case, the lower molecular weight increases the crystallinity degree of the materials, while the opposite is true for chain branching. This means that chain scission causes an increase of the modulus while chain branching, leading to a decrease of crystallinity, should lead a decrease in the rigidity. However, if the chain branching turns to crosslinking this causes an increase of the modulus. The monotonic increase of the modulus with the processing temperature would suggest that the effect of the chain scission on the crystallinity is larger than that of the chain branching or that this chain branching goes towards crosslinking. In both cases, a rise of the modulus should be expected. The decrease of the elongation at break can be interpreted in the same way. Both the rise of the crystallinity and of the crosslinking provokes a decrease of the ductility. The tensile strength curves show different trends. A possible explanation is connected with the increase of both crystallinity and crosslinking and then with the decrease of the elongation at break that hinders the increase of the tensile strength because of the premature breaking of the sample.

Table 2. Enthalpy of fusion and gel content

Material	ΔH_f , J/g	Gel content
PE-LD — high speed, 280 °C	91.7	yes
PE-LD — low speed, 280 °C	99.4	yes
PE-LD — high speed, 210 °C	92.1	yes
PE-LD — low speed, 160 °C	99.3	no

These hypotheses are confirmed by the calorimetric data and by the gel content, reported in Table 2. The samples with low values of elongation at break underwent crosslinking as demonstrated by the presence of gel residues after Soxhlet extraction.

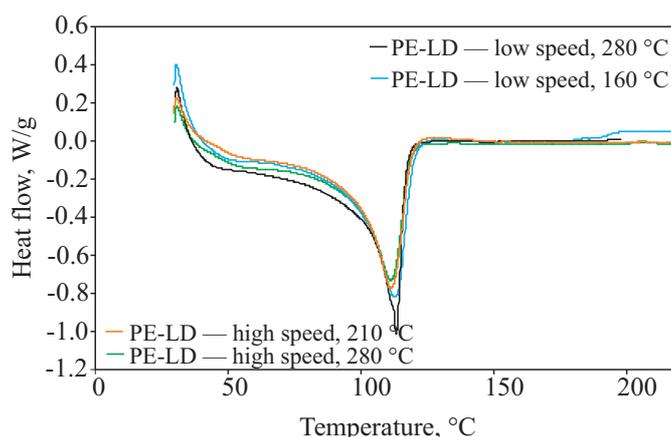


Fig. 7. DSC curves of some of the investigated samples

Some of the DSC curves are shown in Fig. 7, which further show the above described experimental evidence.

CONCLUSIONS

In this work, the effects of mechanical stress and temperature on the thermomechanical behavior of PE-LD/organomodified clay nanocomposites were thoroughly investigated. The complex degradation paths were deepened by using rheological and mechanical characterization methods. The results showed that the thermomechanical degradation mechanisms are very complex, involving several phenomena such as chain scission, branching, recrystallization and crosslinking, degradation of the organomodified clay and interaction between the degradation products of both the system components. In particular, with regard to the neat PE-LD, the viscosity decreases upon increasing the stress (i.e. low temperature and high rotational speeds) while chain branching prevails over chain scission at low shear stress values (high temperature and low rotational speed); at higher temperature and low mechanical stress the two degradation paths counterbalance each other. With regard to the nanocomposite, the situation is much more complex because in this case the degradation of the organomodifier of the nanofiller must be taken into account. It can be stated that at low temperatures, the overall degradation behavior (and therefore the rheological and mechanical properties) is ruled by the degradation of the matrix, while at higher temperatures, the degradation of the organomodified clay gains importance and the interactions between the degradation products of the organomodifier and the polymer matrix determine the final behavior of the nanocomposite, in a way that is similar to what usually happens in polymer blends between the degradation products of the two polymer phases.

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