



Time-resolved rheology as a tool to monitor the progress of polymer degradation in the melt state – Part II: Thermal and thermo-oxidative degradation of polyamide 11/organo-clay nanocomposites



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ABSTRACT

Thermal and thermo-oxidative degradation of nanocomposites based on polyamide 11 (PA11) and organo-modified clay (Cloisite[®] 30B) are studied in the melt state ($T = 215\text{ }^{\circ}\text{C}$) via time-resolved mechanical spectroscopy (TRMS). The goal is assessing the potentiality of rheological analysis for studying polymer degradation in complex systems such as polymer nanocomposites, whose rheological response stems from the combination of the contributions of polymer and nanoparticles. We prove that a thorough analysis grounded on TRMS allows to isolate the effect of degradation of the polymer matrix, whose progress can be hence profitably monitored. Essentially the same degradation mechanisms as in neat PA11 are identified for the nanocomposite, but the kinetics of the thermo-oxidation processes are much faster in the presence of organo-clay. In particular, rheology promptly identifies cross-linking reactions since the early stage of the treatment in air. Matrix-assisted laser desorption/ionization and oxidative induction time measurements corroborate the conclusions drawn on the basis of rheological analyses, shedding light on the chemical aspects of PA11 degradation. Overall, rheological analysis confirms to be a valuable tool for monitoring polymer degradation even in case of inherently complex systems such as nanocomposites. In this case, however, the analysis can be difficult if the dynamics of the nanoparticles prevail over those of the polymer matrix, which is the case of nanocomposites at high filler contents.

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1. Introduction

Materials undergoing fast changes of their properties require specific experimental protocols able to elude the time evolution of the properties while testing. Polymer melts experiencing rapid degradation phenomena fall in this category of “transient materials”, hence measuring their rheological properties can be challenging. In Part I we have shown how time-resolved mechanical spectroscopy (TRMS) can be profitably used for eluding changes in

the rheological properties of polyamide 11 (PA11) due to degradation [1]. As a result of the high accuracy of data collected in this way, we have been able to relate the time evolution of rheological properties to the progress of thermal and thermo-oxidative degradation. Specifically, different reaction mechanisms have been conjectured solely based on the analysis of rheological data. The hypotheses have been corroborated through size exclusion chromatography and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. The issue that we are going to address now is assessing the potential of rheological analysis to study polymer degradation in systems more complex than neat polymers. In particular, we focus our attention on polymer nanocomposites (PNCs). This class of materials has attracted huge interest in the last decades, and is finding application in many

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fields of modern technology [2]. Apart from this, the reason why we selected PNCs is that nanoparticles remarkably affect the flow behavior of the host matrix, possibly masking the polymer degradation phenomena to be studied via rheology. In particular, nanoparticles are well-known to move and rearrange in polymer melts, causing a gradual change over time of the rheological functions [3–5]. At the same time, alterations in the polymer rheology due to degradation in turn affect the nanoparticle dynamics; this adds further complications to the interpretation of rheological data. Additionally, nanoparticles can play an active role in the degradation pathways of the polymer matrix. This is the case of many organo-modified fillers, which are commonly used for producing PNCs due to their better dispersibility compared to bare nanoparticles. The organo-modifier can partially degrade during processing, and the degradation products can promote specific reactions involving the matrix [6]. To sum up, the overall rheological behavior of PNCs is the result of a complex interplay among various actors, who influence each other making particularly difficult the analysis of rheological data. Indeed, rheological methods are seldom used to study PNC degradation, which is more commonly investigated by means of analytical techniques, such as IR/UV spectroscopy, chemiluminescence, size exclusion chromatography, gas chromatography, matrix-assisted laser desorption/ionization (MALDI) [7]. Here we test the potential of rheology for studying polymer degradation in PA11-based nanocomposites containing commercial organo-modified clay. This kind of nanoparticles is among the most used for producing PNCs because the starting clay materials are easily available, and their intercalation chemistry has been studied for a long time [8]. The rheology of PNCs based on organo-clays has been the subject of intensive research in the last decades. As far as we are concerned, the selected nanoparticles substantially alter the viscoelastic behavior at low frequencies [9,10], which is the regime in which polymer degradation is more plainly detectable. Another reason that led us to select organo-modified clay is its renowned interference with the degradation pathways of host polymers [11–14]. This makes the effect of nanoparticles on the rheology of PNCs not merely additional, and this is in line with our purpose of dealing with rheologically complex systems. The objective was pursued by means of a comparative analysis performed using neat PA11 as reference material. In more detail, profiting from the knowledge acquired in *Part I*, TRMS was used to monitor the viscoelasticity of PNCs during time. The hypotheses about the degradation mechanisms of PA11 in the presence of nanoparticles were corroborated through analytical techniques, namely oxidative induction time (OIT) measurements and MALDI-TOF mass spectrometry. The latter allowed to detect chain scission reactions deriving from hydrolysis and/or α -CH Hydrogen abstraction processes [15]. Finally, the effect of nanoparticle loading was studied to critically discuss the limits of rheology when the flow behavior is dominated by the filler.

2. Experimental

2.1. Raw materials and sample preparation

The PA11 (Sigma–Aldrich) has $\rho = 1.026 \text{ g cm}^{-3}$ at $T = 25 \text{ }^\circ\text{C}$, glass transition temperature $T_g = 46 \text{ }^\circ\text{C}$ and melting temperature $T_m = 198 \text{ }^\circ\text{C}$. The filler is an organo-modified clay supplied by Southern Clay Products with trade name of Cloisite[®] 30B; it is a montmorillonite modified by 0.09 equiv. per 100 g of bis(2-hydroxyethyl)methyl tallow alkylammonium cations. 2-(4-hydroxyphenylazo)benzoic acid (HABA) and hexafluoroisopropanol (HFIP) were purchased from Aldrich Chemical CO (Italy) and used as supplied.

Nanocomposite samples at 3 and 9 wt.-% of organo-clay,

hereinafter referred as PA11-C3 and PA11-C9, respectively, were prepared by using a co-rotating twin-screw extruder (DSM Xplore) equipped with a cylindrical capillary die (diameter 1.5 mm, length 30 mm). The polymer and the filler, both dried overnight under vacuum at $T = 80 \text{ }^\circ\text{C}$ for 18 h, were simultaneously loaded inside the mixing apparatus. The extrusions were performed under gaseous nitrogen at $T = 215 \text{ }^\circ\text{C}$ and screw speed 80 rpm, corresponding to average shear rates of $\sim 50 \text{ s}^{-1}$. The residence times, carefully controlled owing to an integrated back-flow channel, were set to 2 min. Preliminary investigations indicated that such conditions represent a good compromise to get adequate filler dispersion while preserving the stability of polymer matrices and clay organo-modifier.

Rheological, TEM and calorimetric (OIT) analyses were performed on as-extruded pellets. The samples for MALDI investigations were prepared by dissolving in HFIP pellets treated under either N_2 or air atmosphere at $T = 215 \text{ }^\circ\text{C}$ for 30, 60, 90, 120 and 150 min. The solutions were filtered and dried before the analyses. Insoluble fractions of dry solid, if any, were dried under vacuum and weighed. WAXD analyses were performed on compression-molded films prepared by means of a laboratory press (LP-20B by Lab. Tech. Eng. Company Ltd.).

2.2. Characterization

Wide angle X-ray diffractometry (WAXD) was performed using a Siemens D-500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). Scans were taken from $2\theta = 2\text{--}10^\circ$ with a step size of 0.02° .

Transmission electron microscopy (TEM) was performed using a Philips CM 200 TEM. The samples were thin slices (thickness $\sim 100 \text{ nm}$) randomly cut from the extruded pellets using a diamond knife at room temperature.

Rheological analyses were carried out using a stress-controlled rotational rheometer (AR-G2 by TA Instruments) in parallel plate geometry (plate diameter 40 mm). The as-extruded pellets, dried for 18 h at $T = 80 \text{ }^\circ\text{C}$ under vacuum, were compacted between the plates of the rheometer by means of a containment ring just before running the rheological tests. Repeated frequency scans were performed at $T = 215 \text{ }^\circ\text{C}$ from frequency $\omega = 10^{-1}$ up to 10^2 rad s^{-1} , and the elastic (G') and viscous (G'') shear moduli were recorded as a function of time at strain amplitude low enough to be in the linear regime. The latter was preliminarily estimated for each sample through strain scan experiments. Measurements were carried out both in air and gaseous nitrogen atmosphere.

Thermogravimetric analysis (TGA) was carried out using a Seiko EXSTAR 7200 TGA/DTA instrument. Analyses were carried out on 5–10 mg samples under either nitrogen or air flow (200 ml/min) from room temperature up to $700 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C/min}$.

Oxidation induction time (OIT) measurements were performed using a differential scanning calorimeter DSC 400 (Perkin Elmer) according to the testing procedure of ISO 11357-6-2008. Samples of approximately 5 mg were heated up to $215 \text{ }^\circ\text{C}$ at a rate of $20 \text{ }^\circ\text{C/min}$ under nitrogen flow (50 ml/min) and kept at this temperature for 15 min to ensure complete melting and to attain thermal equilibrium. After, the gas was switched to pure oxygen. The OIT represents the time at the onset of the exothermic oxidation process, whose rate can be inferred by referring to the time at the oxidation peak (see Fig. S2, Supplementary data). Each measurement was repeated at least three times on different portions of sample.

MALDI-TOF mass spectra were recorded in reflector mode using a Voyager-DE STR (Applied Biosystems) mass spectrometer equipped with a nitrogen laser emitting at 337 nm with a 3-ns pulse width and working in positive ion mode. The accelerating voltage was 20 kV; the grid voltage and the delay time were optimized for

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