Polymer 72 (2015) 134–141

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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

G. Filippone [a, *], S.C. Carroccio [b, *], R. Mendichi [c], L. Gioiella [a], N.Tz Dintcheva [d], C. Gambarotti [e]

[a] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale (INSTM Consortium - UdR Naples), Università di Napoli Federico II, Piazzale V. Tecchio 80, 80125 Napoli, Italy
[b] Consiglio Nazionale delle Ricerche, CNR-IPCB UOS Catania, Via P. Gaifami 18, 95126 Catania, Italy
[c] Istituto per lo Studio delle Macromolecole (ISMAC) Consiglio Nazionale delle Ricerche (CNR), Via E. Bassini 15, 20133 Milano, Italy
[d] Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy
[e] Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

ARTICLE INFO

Article history:
Received 3 May 2015
Accepted 30 June 2015
Available online 14 July 2015

Keywords:
Rheology
Thermal degradation
Thermo-oxidative degradation
Polyamide 11
MALDI- TOF-MS
SEC

ABSTRACT

Thermal and thermo-oxidative degradation of polyamide 11 (PA11) in the melt state ($T = 215$ °C) are studied by resorting to time-resolved mechanical spectroscopy. Such an approach allows to elude the changes in the rheological properties occurring while testing, thus enabling the rigorous study of polymer degradation in the melt state. Different concurrent degradation reactions in oxidative (air) and non-oxidative (N_2) environment are promptly guessed by studying the time evolutions of rheological functions. In particular, changes in the zero–frequency complex viscosity reflects changes in the average molecular weight, while the appearance of a yield stress in the complex viscosity curve is identified as the rheological fingerprint of cross-linking reactions. Size exclusion chromatography corroborates the hypotheses based on rheological analyses, and matrix assisted laser desorption/ionization mass spectrometry sheds light on the chemical aspects of degradation. Specifically, post-condensation (in N_2), chain scission, hydrolysis and cross-linking reactions (in air) are identified as the dominant degradation mechanisms of PA11 in the melt state. Overall, our study demonstrates that rheology is a valuable tool to detect and discriminate among different degradation mechanisms in polymer melts. In particular, rheology promptly identifies cross-linking reactions, which can be difficult to be detected through common analytical techniques that envisage the solubilization of the polymer sample.

1. Introduction

Rheology is very sensitive to changes in the molecular architecture of polymeric materials. Any change in the molecular architecture, e.g. chain extension/scission, branching, cross-linking, affects the mobility of the entire chain or of a fraction of it, with immediate, clear repercussions on the polymer relaxation spectrum. This makes rheology a useful tool for studying degradation phenomena in the melt state. Compared to common steady-shear rheology, linear viscoelastic analysis (LVA) is preferable for this purpose, as it involves small amplitude oscillations that do not alter the evolving molecular structure while testing. In principle, a simple frequency scan can provide information on the polymer dynamics over different length scales, from few repeating units up to the sizes of the entire chain. Studying the latter, however, may be challenging. The reason is that the larger is structural unit to be probed, the longer is its characteristic relaxation time, and, hence, the lower is the mechanical frequency to be used. On the other hand, low frequency means long experimental times. More precisely, the minimum time required to collect viscoelastic data at a frequency ω is $t_{ext} = 2\pi/\omega$. In other words, the duration of common LVA measurements can exceed the characteristic time of the degradation phenomenon to be studied. This is one of the reasons which prevented a systematic employ of rheological techniques for monitoring and studying degradation of polymer melts. Speeding

---

* Corresponding authors.
E-mail addresses: gfilippo@unina.it (G. Filippone), sabrinacarola.carroccio@cnr.it (S.C. Carroccio).

http://dx.doi.org/10.1016/j.polymer.2015.06.059

the analyses without renouncing to probe low frequencies is hence crucial. To conciliate these two opposite requirements, we resort to time-resolved mechanical spectroscopy (TRMS) [1]. TRMS essentially consists in studying the viscoelastic properties as a function of time rather than in terms of the mechanical frequency. As such, TRMS allows determining frequency-dependent data and relaxation time spectra at intermediate states of transient materials. Many polymer systems belong to this category, e.g. polymer blends [2–4], gels [5,6], thermosets [7–9], nanocomposites [10]. Here we discuss the benefits of TRMS in the study of polymer degradation in the melt state. Besides the scientific interest, this matter is also relevant from a technological point of view. Indeed, the overwhelming majority of the transforming technologies of polymeric materials entails melt processing steps that can alter the polymer structure and, through it, the final material performances. Moreover, changes in the molecular architecture have a direct impact on the material processability, possibly inducing flow instability phenomena [11–13].

The polymer selected for this study is nylon 11 (PA11). It is a bio-based polyamide often used in flexible pipe applications for offshore oilfield exploration or, blended with polyolefins, for diesel and gasoline fuel tanks. Degradation of polyamides is a complex process that has been the subject of many studies, which differ among them for the analytical techniques employed and the conditions in which degradation has been investigated [14–21]. In this regard, it is worth noting that the literature on polyamide degradation in the molten state is pretty scarce [22–24]. Referring to specific papers for the chemical aspects, here we simply observe that PA11 degradation in the melt state can lead to chain scission, chain extension and/or cross-linking, and that these reactions can occur singly or in combination depending on the amount of water and the presence of oxygen. This makes PA11 a challenging test-bed for our study, which consists in a critical discussion about the potentiality of rheological analysis for the study of polymer degradation in the melt. The work is divided in two distinct papers. In *Part I* we deal with pure PA11, which has been subjected to rheological measurements in both N_2 and air environment aiming at studying the effects of thermal and thermo-oxidative degradation. In more detail, the first part of the paper is devoted to prove the advantages of TRMS techniques when the goal is studying fast degradation phenomena. Accurate viscoelastic data are collected and correlated to the changes in the molecular architecture. The conclusions drawn on the basis of rheological analysis are supported by means of size exclusion chromatography (SEC), while matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry is employed to shed light on the structural changes due to degradation. Like any other analytical techniques based on the analysis of polymer solutions, SEC and MALDI-TOF cannot provide direct information about cross-linking reactions, which results in insoluble gel fractions. On the contrary, we show that rheology promptly detects even small amounts of cross-linked polymer. Overall, our analysis provides useful guidelines for a profitable use of rheological techniques in the field of degradation of polymeric materials in the melt state. The study continues in *Part II*, where the implications stemming from the presence of nanoparticles, which are able to remarkably alter the rheology of the host polymer, are critically discussed [25].

2. Experimental

2.1. Materials and sample preparation

The PA11 (Sigma–Aldrich) has $\rho = 1.026$ g cm^{-3} at $T = 25$ °C, glass transition temperature $T_g = 46$ °C and melting temperature $T_m = 198$ °C. 2-(4 hydroxyphenilazo)benzoic acid (HABA) and hexafluoroisopropanol (HFIP) were purchased from Aldrich Chemical CO (Italy) and used as supplied.

Rheological tests were performed directly on the pellets of PA11. The samples for the SEC and MALDI analyses were prepared by treating the polymer under either nitrogen or air atmosphere at $T = 215$ °C for 30, 60, 90, 120 and 150 min. Then the materials were dissolved in HFIP, and the solutions were filtered and dried before analyses. Fractions of insoluble gel, if any, were dried under vacuum and weighed.

2.2. Characterization

2.2.1. Rheological tests

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 pellets of PA11 were compacted between the plates by means of a containment ring, which was removed before running the tests. The measurements were carried out after drying the polymer for 18 h at $T = 80$ °C under vacuum. Frequency scans were performed at $T = 215$ °C from frequency $\omega = 10^{-1}$ up to 10^{2} rad s^{-1}. This range represents a compromise to meet two opposite requirements: (*i*) the need to investigate timescales long enough to provide information on the behavior of large portions of the polymer chains, and (*ii*) the necessity of containing as much as possible the experimental times so to accurately detect degradation phenomena. The latter were monitored during time by means of repeated frequency scans. The elastic (G') and viscous (G'') shear moduli were recorded at strain amplitude low enough to be in the linear regime, which was preliminarily estimated for each sample through strain scan experiments.

2.2.2. Molecular characterization by a SEC-MALS chromatographic system

The molar mass distribution (MMD) of polymers was determined by a multi-detector size exclusion chromatography (SEC) system using two on-line detectors: (*i*) a multi-angle light scattering (MALS); (*ii*) a differential refractometer (DRI) as concentration detector. The SEC-MALS system consists of an Alliance 2695 separation module from Waters with a serial setup Alliance-MALS-DRI. Experiments were carried out at $T = 40$ °C using two PLgel Mixed C columns (5 μm particle size) from Polymer Laboratories. Hexafluoro-2-Propanol (HFIP) + 0.02 M Tetraethylammonium Nitrate salt was used as mobile phase. The flow rate was 0.5 mL/min of flow rate, and the sample concentration was ~3 mg/mL.

The MALS on-line detector uses a vertically polarized He–Ne laser (wavelength 632.8 nm) and measures simultaneously the intensity of the scattered light at 18 fixed angular locations ranging 14.0°–166.0°. An on-line MALS detector coupled to a concentration detector allows to obtain the absolute molar mass and the radius of gyration of each fraction of eluting polymer. The calibration constant was calculated using toluene as standard, assuming a Rayleigh factor of 1.406×10^{-5} cm^{-1}. The angular normalization of the different photodiodes was performed by measuring the scattering intensity of a poly(methyl methacrylate) standard. The use of a multi-detector SEC-MALS system was described in more detail in the literature [26,27].

2.2.3. MALDI-TOF analysis

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 each sample to achieve the higher molar mass values and the best