Polymer Testing 45 (2015) 12–19

Contents lists available at ScienceDirect

Polymer Testing

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

Material behaviour

# Influence of polymer reprocessing cycles on the microstructure and rheological behavior of polypropylene/mineral oil oleogels

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ARTICLE INFO

*Article history:*
Received 23 March 2015
Accepted 30 April 2015
Available online 19 May 2015

*Keywords:*
Polypropylene
Mineral oil
Oleogels
Reprocessing
Degradation
Viscoelastic properties

ABSTRACT

The overall objective of this work was to study the effect of reprocessing cycles of isotactic polypropylene (PP) on the rheological behavior and microstructure of gel-like dispersions in mineral oil. PP was subjected to 10 reprocessing cycles and oleogel samples were further prepared by using the mixing rheometry technique and characterized from a rheological point of view and polarized light optical microscopy (PLOM). Recycled polymer samples were also characterized by means of rheological measurements, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to evaluate the property changes induced by reprocessing. The values of different linear viscoelastic functions (elastic modulus and complex viscosity) of recycled PP decrease with the number of reprocessing cycles, which influences oleogel rheological response. An empirical exponential correlation between the storage modulus (G′) of PP samples and the plateau modulus ($G_N^0$) of oleogels has been proposed to predict the rheological behavior of oleogels. Results were explained considering the scission of PP chains induced by the thermomechanical reprocessing treatment applied.



## 1. Introduction

Isotactic polypropylene (PP) is a commodity polymer characterized by a wide range of advantages such as low cost, low density, high melting temperature, good mechanical properties, easy processing, recyclability and excellent resistant to many chemicals [1]. With the increasing environmental concern and growing interest in waste minimization, a variety of techniques for recycling/reusing waste PP are being developed. Among them, the most interesting for economic and environmental reasons is mechanical recycling, where the end-of-life plastics are mechanically crushed and reprocessed to obtain new structural parts [2]. It is well known that mechanical reprocessing, also called primary recycling, is extensively carried out in the plastics industry. It usually involves grinding the scrap from molding processes and blending with virgin material in appropriate proportions. Properly blended, the recycled/virgin material is then molded into new parts [3]. However, due to the highly aggressive shear conditions at high temperature and the presence of oxygen and impurities, reprocessing may lead to thermo-oxidative and thermomechanical degradation, altering the structure of the polymer backbone and, consequently, yielding loss of properties [4]. Therefore, the impact of PP degradation is given by structural changes such as a reduction in molecular weight and polydispersity occurring during reprocessing, resulting in a significant modification of the functional properties, i.e. increase of melt flow index and decrease of complex viscosity and elasticity [5,6].

Oleogels are generally considered complex soft matter systems comprised of a liquid oil as continuous phase that is physically entrapped in a three-dimensional network of a dispersed thickener agent. Physical and rheological properties of oleogels basically depend on the colloidal network structure achieved, linked to the chemical composition, in particular to the thickener/oil ratio [7]. The development of PP oleogel formulations may create new approaches with interesting perspectives for different industrial applications such as synthetic binders and lubricants. This work is focused on the impact of reprocessing cycles on the properties of oleogels based on isotactic polypropylene and

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http://dx.doi.org/10.1016/j.polymertesting.2015.04.016
0142-9418/

mineral oil. In order to understand the impact of recycling on oleogels, recycling was simulated by multiple extrusion of the virgin PP sample. Previous works [7–9] reported a detailed study of the rheological properties of oleogels using recycled polypropylene as thickener agent for a range of polymer concentrations. Considering the rheological properties, these oleogels were proposed as alternative lubricating grease formulations, exhibiting enhanced viscoelastic properties (e.g. elastic modulus) with respect to industrial standard lithium greases. However, to the best of authors' knowledge, the influence of PP thermomechanical degradation on the rheological and microstructural properties of PP oleogels has not been investigated. Hence, the overall objective of this work was to study the effect that thermomechanical degradation, i.e. the number of reprocessing extrusions cycles, has on the morphology and rheological properties of oleogels based on isotactic polypropylene (PP) and mineral oil, aiming to establish a relationship between the structural changes in the polymer and the mechanical properties of resulting oleogels.

## 2. Experimental

### 2.1. Materials

A high isotactic grade Isoplen PP 070 homopolymer from Repsol S.A. (Spain) was used as received. This polymer is characterized by the following physical properties and molecular parameters: $M_w = 5.71\ 10^4$ g mol$^{-1}$; $M_w/M_n = 1.97$; $\rho = 0.905$ g/cm$^3$ and melt flow index of 12 g/10 min (230 °C/2.16 kg). A commercial naphthenic oil (SR-10) from crude distillation (110 cSt at 40 °C), kindly supplied by Verkol Lubricantes (Spain), was used as the base oil for oleogel formulation.

### 2.2. Extrusion

PP reprocessing cycles were carried out with a co-rotating Thermo Scientific twin-screw extruder Prism Eurolab 16 (40:1 L/D ratio, 16 mm barrel diameter), equipped with Brabender gravimetric feeders. Throughput and screw speed were kept constant at 1.6 kg/h and 130 rpm, respectively, generating a value of torque corresponding to 40–50% of the maximum torque allowed by the device design specifications. The extruder was equipped with a single 4 mm diameter strand die. Polymer was extruded by applying a temperature profile between 200 and 240 °C (zone 2–zone 10) in the barrel of the extruder and 200 °C at the die. All extrusions were done in air, without the use of blanketing gas. The screw configuration and details of screw elements are shown in Fig. 1 and Table 1. Extruded material was cooled on line in a water bath and pelletized to be eventually used for further reprocessing or oleogel preparation. PP was reprocessed up to ten times. After each extrusion cycle, a sufficient sample was taken in order to carry out the characterization measurements.

### 2.3. Preparation of oleogel formulations

Oleogels were prepared using the mixing rheometry technique, with an experimental setup consisting of a cylindrical vessel (40 mm diameter, 71 mm height) and a stirrer (four-blade propeller, 30 mm diameter) coupled to the transducer of a controlled-stress Haake RS600 rheometer (Germany). This experimental configuration allows monitoring of the evolution of torque with time and studying the kinetics of mixing. PP/mineral oil blends were prepared at 170 °C. Approximately 30 g of mineral oil was thermostated and stirred for around 10 min at 400 rpm with the four-blade stirrer placed at 12 mm above the bottom of the cylindrical vessel, until a homogeneous value of temperature was attained. After that, the polymer was carefully added to the mixing device and the blend stirred for 2 h under the processing conditions previously established. Once a fine dispersion and constant torque values were obtained, the sample was cooled to room temperature on a 3–5 mm steel sheet in order to induce gelation. All blends contained 9 wt% polymer.

### 2.4. Characterization tests

The thermal stability of reprocessed PP was investigated, by thermogravimetric analysis (TGA) using a Q-50 TA Instrument (New Castle, USA). Approximately 10 mg of sample was placed on a Pt pan and heated from 35 °C to 600 °C at a rate of 10 °C/min, under nitrogen gas flow of 100 mL/min. The temperature corresponding to a 5% weight loss (considered $T_{onset}$), temperature at which decomposition rate is maximum ($T_{max}$) and residue percentage were obtained from weight loss curves. Every system was tested at least twice in order to ensure the reproducibility of the results.

Differential scanning calorimetry (DSC) tests were conducted in a Q-100 TA instrument (USA) using 6–8 mg samples sealed in hermetic aluminium pans. The heat history of the samples was eliminated by heating them at a rate of 10 °C/min and holding them for 5 min at 200 °C. Subsequently, the samples were cooled to 5 °C at a rate of 10 °C/min and the crystallization temperature and heat of crystallization were recorded. At least two replicates of each test were done. Melting temperatures and heats of fusion were determined during a second heating sequence. Degree of crystallinity in each sample was calculated as follows:

$$\chi_c = \frac{\Delta H_f}{\Delta H_{100}} \times 100\% \quad (1)$$

where $\Delta H_f$ is the integrated melting enthalpy from the DSC endothermic curve and $\Delta H_{100}$ is the melting enthalpy for a neat crystalline isotactic polypropylene equal to 209 J/g [10].

Rheological measurements on PP polymer samples were carried out by means of small-amplitude oscillatory shear (SAOS tests) in a controlled-stress Physica MCR-301 (Anton Paar, Austria) rheometer, equipped with a parallel plate geometry (25 mm diameter, 1 mm

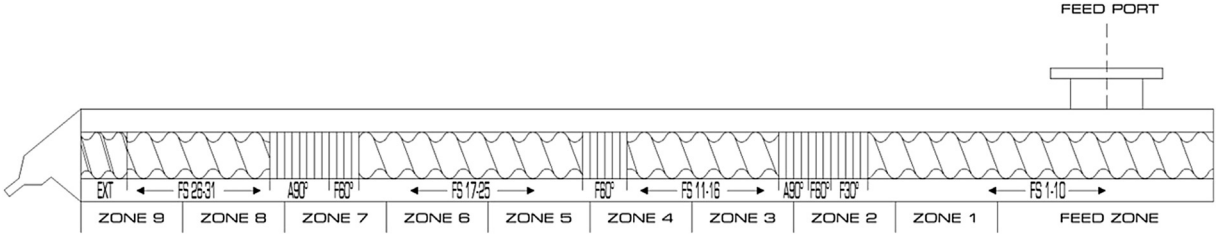


**Fig. 1.** Screw profile scheme of co-rotating intermeshing twin-screw extruder (L/D = 40, D = 16 mm).