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Short communication: test method

## A simple rheological method for the assessment of susceptibility of thermoplastic polymers to radical reactions under dynamic conditions



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### ABSTRACT

The purpose of the work is to present a simple test method for assessment of the susceptibility of thermoplastics to reactions under dynamic conditions. It is based on measurements of torque values with the use of a batch mixer. It is well-known that the torque values are strictly related to polymer melt viscosity. On the other hand, temperature changes in the batch mixer due to friction and thermal effects of chemical reactions are restrictions precluding measurements in isothermal conditions. However, it was established that the temperature spontaneously changing in a chamber of the batch mixer may be seen as the opportunity to evaluate the changes of torque induced by chemical processes. For radical modification of eleven ethylene copolymers, it was shown that results obtained according to the method provide valuable information for insight into changes taking place in the reacting system.

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## 1. Introduction

Nowadays, polyolefins are the most important group of synthetic polymers due to their beneficial price to performance ratio. Contemporary achievements in the fields of catalytic systems and copolymerization methods open up possibilities for making new materials from simple monomers [1]. Ethylene copolymers with short  $\alpha$ -olefins, such as butene or hexene, and especially octene, are of great commercial importance. Their macromolecules are in general linear, and are composed of a hydrocarbon backbone to which short chain branches (SCBs) are attached. The number of SBCs in the macromolecule significantly affects its reactivity as it determines the number of reactive tertiary carbon atoms in the polymer backbone. The length of the SCBs is two carbon atoms shorter than the length of

their original monomers. The number and length of the SBCs, as well as their distribution along the macromolecule, e.g. the most common random or block-like configurations, as is the case for olefin block copolymers (OBCs) synthesized according to chain shuttling catalyst technology (CSCT) [2], all together influence the polymer properties. However, in some cases in ethylene copolymers macromolecules, apart from SCBs, long chain branches (LCBs) may occur [3]. The presence of LCBs, even at very low concentration, e.g. one LCB for several tens of thousands of carbon atoms in the polymer backbone, has a great influence on rheological properties of the polymer melt [4]. In the case of LCBs, even more than for SCBs, their length is crucial, which can be in a very broad range. In some situations, the length of LCB can be comparable to the length of polymer's main chain. In that case, there is a certain probability of additional branching appearance, leading even to branch-on-branch structure. It is clear that the above-mentioned features of the molecular structure of polymers must be taken under consideration, keeping also

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in mind a phenomenon of the polymer molecular weight distribution (MWD). It should be also taken into account that some unsaturation can occur in macromolecules, at their ends or inside, which play a very important role during reactive processing [5,6]. In conclusion, it can be stated that ethylene copolymers with short  $\alpha$ -olefins are quite complicated structures.

A broad range of ethylene-short  $\alpha$ -olefin copolymers, supplied by many producers using different catalytic systems, is available on the market. Copolymers produced according to Ziegler-Natta technology are commonly described as conventional LLDPEs, while polymers synthesized with the use of metallocene, or most recently post-metallocene catalysts, are described differently by their manufacturers. The latter are typically linear polymers with excellent properties but, in the case of thin-walled products, such as in the film or foam industries, their linear structure is not highly desirable, as it implies low strength of polymer melts. As a result, much research effort has been put into intentional incorporation of LCBs into linear macromolecules, as the presence of LCBs is responsible for beneficial phenomenon known as strain hardening [7]. The LCBs can be introduced into macromolecules by the use of free radical reactions, and this procedure is one of the main aspects of the paper.

There is a vast amount of information published on radical modification of ethylene copolymers. Most of it concentrates on cross-linking processes [8–10], however there are a few papers devoted to incorporation of LCBs without gel phase formation [11,12]. Because of the small number of LCBs formed, problems with their analytical determination arise. The only analytical method suitable for the direct measurement of LCBs quantity is NMR, by the use of which the number of tertiary carbon atoms can be precisely determined. The technique is, however, time-consuming and, what is more important, it is suitable only for side chains not longer than six carbon atoms. Another analytical technique, SEC coupled with a MALLS detector, can be used to obtain valuable information, however it fails at very low LCBs concentrations. The most sensitive, but indirect, analytical method is rheometry [13–15]. Using the results of rheometrical measurements conclusions on the molecular structure of polymers can be drawn. The insight into processes taking place during polymer modification is possible by the use of special rheometers known as rubber process analyzers or torque rheometers [8,16]. Results obtained from the latter group of rheometers are typically presented as dependence of torque on time at constant temperature and, therefore can be used for kinetic calculations. The measurements made with the use of the rheometers are precise, however, they require expensive equipment, skilled personnel and considerable time.

The idea of a simple batch mixer used as a measuring device is not new [9,10,17–19]. The main problem is spontaneously rising temperature, which makes results of torque measurements hardly useable. According to [19], the problem may be solved by using temperature compensation, i.e. by lowering its initial value proportionally to predicted thermal effect. As a result, similar temperature profiles were obtained for processes conducted at

different rotor speeds. However, no information on measurements of torque values for reacting polymer system as a function of temperature can be found. As a result, there are no methods of using rheological measurements for quantitative description of changes taking place “in situ” as a function of temperature during reactive processing of polymers.

## 2. Experiment

### 2.1. Materials

Eleven ethylene –  $\alpha$ -olefin copolymers were used in the experiments. Each of them belongs to the group of random butene or octene copolymers or block octene copolymers (OBCs). Melt flow index (MFI) values for all the polymers were in the range of ca. 0.5 to 3.0 g/10 min. and their commercial names and selected properties are shown in Table 1. The values of density and melting temperature are given according to producers' specifications, whilst MFI values were determined independently. Engage and Infuse polymers are products of The Dow Chemical Company, LLDPE 0209AA - Iran Petrochemical Commercial Co., Flexirene FF25 - Polimeri Europa SpA, and Exact 1001 - Borealis Plastomers v.o.f.

As the source of free radicals, dicumyl peroxide (DCP), CAS 80-43-3, 98%, Aldrich Chemistry, was used.

### 2.2. Methods

The experiments were performed in a batch laboratory mixer, Haake PolyLab QC with PolySoft OS software. Process parameters were always the same: rotor speed 60 rpm, time 15 min., no temperature change programmed. The initial concentration of DCP was in the range of 0 to 0.6 wt.%. The mixer was pre-heated to 180 °C, and then 45 g of polymer or polymer impregnated with DCP in acetone solution was put into the mixer chamber, while the rotors were turning. After closing the chamber, the temperature of the raw materials dropped to ca. 130 °C, and then increased up to 150 °C in no longer than 50 s. After that, analytical data were collected every 1 second.

The measurements of MFI values were carried out on a Zwick/Roell model BMF-001 plastometer at 190 °C, under a load of 2.16 kg or 10 kg.

## 3. Results and discussion

### 3.1. Virgin polymers

According to literature information, it can be supposed that all polymers under investigation are essentially linear. Moreover, it can be stated that both butene copolymers produced by Ziegler-Natta catalysts have considerably broader MWDs than octene copolymers synthesized by (post)metallocene catalysts, since for the last group the MWD values are known to be close to 2.0.

According to [4,20], the ratio of MFI under a load of 10 kg to MFI under a load of 2.16 kg ( $I_{10}/I_2$ ) is a good measure of susceptibility of a given polymer to shear-thinning. Consequently, it can be used as an indirect measure of

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