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Rheological Behavior of Blends of Metallocene Catalyzed Long-Chain Branched Polyethylenes

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# Abstract

Abstract text (normal)

# Keywords

Polyethylene, blend, long-chain branch, thermorheological complexity, activation energy spectrum

# Introduction

Polyolefins account for ca. 50% of the synthetic polymers produced worldwide which are mainly used for packaging, cable insulation and household goods. The most commonly used polyolefin is polyethylene (PE), chemically correct also known as polyethene, comprising ca. 30% of the world polymer production, which to a very large extent to make films and cable insulations. Both processes include strong elongational deformations, for which strain hardening has proven to be essential for obtaining a stable process and a homogeneous film or layer thickness.*[1,2]* Strain hardening, in the rheological sense, refers to an increase of the elongational viscosity above the triple shear viscosity, usually for Hencky strains εH>0.7, i.e. a stretch ratio of 2.*[3-9]* This ratio is known as the Trouton ratio*[10]* and commonly defined as Tr or χ=ηe+(t)/3 η0(t), where ηe+(t) is the time-dependent shear viscosity at constant Hencky strain rate$ \dot{ϵ}$ and η0(t) is the shear viscosity at infinitely low shear rate $\dot{γ}.$

The strain hardening for classical long-chain branched polyethylene, the well-known low density polyethylene (LDPE), is established to be very good, while for the Ziegler-Natta polyethylene (linear low (ZN-LLDPE) or high (ZN-HDPE)) usually no strain hardening, at least at high Hencky strain rates*[11]* $\dot{ϵ} $is found.*[1,2,8,12]* LCB-mPE, shows weak strain hardening, predominantly at low strain rates$\dot{ ϵ}$, making these materials potentially better processable. However, in general the strain hardening of LCB-mPE is not very high, so that the processing behavior is still not quite on par with LDPEs.

In the past attempts have been made to blend LDPE with LLDPE (ZN-LLDPE, mostly), which has led to a mix of the properties of both, i.e. the processing improved in comparison to LLDPE, while the mechanical properties degraded.

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In the field of analytical characterization of polymers with respect to their branching topography, a lot of attempts were made to characterize the branching structures, which, however, has always suffered from the ambiguity that the effects of long-chain branching and molar mass distribution are very similar to each other in shear rheology, so that primitive approaches to characterize samples with respect to understanding their long-chain branching topography will not deliver reliable results for polydisperse materials. Classically, the relation between zero shear-rate viscosity *η*0 and weight average molar mass Mw (*η*0~*Mw*3.4) for linear polymers was found to be molar mass distribution (MMD) independent.*[13-15]* However, this relation requires the determination of Mw by analytical means and when taking a ±%5 error of Mw-determination into account, only deviations by more than 20% with respect to *η*0 can be considered reliable. Further, for many materials determining an accurate Mw is far from straightforward. Furthermore, especially for samples with very broad molar mass distribution the determination of the true Mw is far from obvious, so that it is not 100% clear whether for some “exotic molar mass distributions” the relation *η*0~*Mw*3.4 would have to be amended with some MMD-dependent terms,*[16-19]* although the authors believe that it is more likely that this is not the case.

However, there is one rheological quantity that is not dependent on the molar mass distribution, while it reacts to long-chain branching – the thermorheological behavior, as long as it follows an Arrhenius temperature dependence.*[20-26]* For materials following a WLF-temperature dependence, long-chain branching does not lead to changes in temperature dependence.*[27]*

However, as already pointed out by Carella, Gotro, and Graessley in 1986,*[28]* the increase of Arrhenius activation energy is accompanied by the occurrence of thermorheological complexity, i.e. the failure of the time temperature superposition. Thus, for analyzing the temperature dependence of LCB-materials with an Arrhenius temperature dependence, the simplest possible way would be to ignore the thermorheological complexity and make a best fit, which, however, would be scientifically incorrect and would lead to ambiguous results.*[29]* E.g. the results would depend on the frequency range, for which they were calculated. First attempts for a proper analysis of the thermorheological complexity were presented by Carella et al.*[28]* and Laun*[30]* who did not analyze the temperature dependence globally but locally, namely by determing the shift factors from specific values of G” and the shear stress σ21 (which would be called τ in today’s terms), respectively. For LCB-mPE, the thermorheological complexity was first described by Wood-Adams and Costeux through determining activation energies derived from storage modulus G’, loss modulusG”, the relaxation spectrum and *η*0.*[22]* Based on these initial reports, the authors started analyzing the thermorheological complexity systematically, by determining the rheological spectra with high precision methods*[31-33]* and shifting them slicewise.*[34-36]* However, while shifting the relaxation spectrum (and potentially also the retardation spectrum, although to the best of the authors’ knowledge that has not been done systematically) is the fundamentally most meaningful way of analyzing such a complicated behavior, it is very cumbersome to do so, as the calculation of a rheological spectrum is a highly difficult undertaking, being easily influenced by various artefacts. Thus doing so is the best but practically rather difficult method.

Instead, research has shown that shifting G’, G” and phase angle δ can provide insight into different aspects of the thermorheological complexity of branched LCB-mPE.*[36,37]* However, at this point the determination still suffered from the fact that the determination of the shift factors as a function of the rheological quantity (e.g. G’, δ) still had to be done manually. For this reason, the authors developed a script, which does that task automatically and more precisely and classified the resulting types of thermorheological complexity.*[38]*

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The thermorheology of polymer blends was investigated for ZN-LLDPE/LDPE and mLLDPE/mVLDPE (very low density PE) blends by Dordinejad et al..*[25,39]* In case of mLLDPE/mVLDPE-blends, the absence of long-chain branches leads to a small transition between the Ea of each sample, which essentially not thermorheologically complex. However, the LDPE/LLDPE blends show a clear thermorheological complexity, which is systematically changing as a function of composition in a way that at a first glance it is possible to interpolate between the Ea-spectra with respect to G’ and δ for each blend by using the pure blend components and a linear mixing rule.

In this paper, we will analyze the rheological behavior of different combinations of blends of long-chain branched mPE, where four different low molar mass LCB-mHDPEs with different molar mass distribution are blended with a high molar mass LCB-mHDPE at different blending ratios. The paper focuses on understanding the interactions in such blends with respect to the thermorheological behavior and the elongational properties, especially the strain hardening.

# Experimental

## Materials and sample preparation

**Table 1. molecular data of the basic materials.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Materials | Mw [g/mol] | MZ [g/mol] | Mw/Mn [-] | LCB from SEC-MALLS |
| HDPE A | 87 000 | 320 000 | 4.2 | Medium |
| HDPE B | 105 000 | 1400 000 | 15.8 | Medium-strong |
| HDPE C | 180 000 | 5400 000 | 14.1 | none |
| HDPE D | 310 000 | 1300 0000 | 18.1 | none |
| HMW-HDPE 1 | 470 000 |  |  |  |

**Table 2. Designation of the blending materials.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Proportion of HMW-HDPE 1 added | HDPE A | HDPE B | HDPE C | HDPE D |
| 1% | A1 | B1 | C1 | D1 |
| 3% | A3 | B3 | C3 | D3 |
| 6% | A6 | B6 | C6 | D6 |
| 9% | A9 | B9 | C9 | D9 |
| 12% | A12 | B12 | C12 | D12 |

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## Samples.

## The basic materials used in this paper are commercial materials produced by SABIC (Saudi Basic Industries Corporation). For these five HDPEs, Table 1 lists MW, MZ, MW/MZ and LCB from SEC-MALLS. The blending materials used in this paper are prepared by blending the above four HDPEs and the HMW-HDPE 1 respectively. Table 2 gives the designation of the blend materials.

## After calculation, the corresponding proportions of HDPEs and HMW-HDPE 1 samples were weighed respectively each time, a total of 5g, and added into a round bottom flask containing 85ml of p-xylene (GC grade). The reflux condensation device was set up and the flask was placed in an oil bath at 120 ℃ for stirring. The samples were gradually dissolved and disappeared within 30 minutes. After stirring for 2 hours, the blending solution was prepared. Next, the high-temperature blending solution was slowly poured into a beaker containing 1.5L deionized water, which was continuously stirred at room temperature for 30 minutes to obtain HDPE polymer flocs. The solvent of p-xylene was removed twice by washing with ethanol in a Buchner funnel, and then washed with deionized water for 3 times. Following this, the blending particles were dried in a vacuum oven at 80℃ and -1 bar for 48 hours, afterwards the milky white powder blending samples were obtained.

## The samples were pressed on Beijing Future Mterial vacuum mould pressing machine with different moulds. The diameter and thickness of the samples used for shear rheological test are 25mm and 1-1.5mm respectively, while those for shear tensile test are 20mm long, 3.5-4.5mm wide and 1- 1.5mm thick, both samples are laboratory specifications.

## Rheology

The rheological characterization was carried out on an Anton Paar MCR 702 rheometer (Graz) equipped with a forced convection oven. All shear rheological experiments were carried out in nitrogen atmosphere.

The shear rheological experiments consisted of frequency sweeps in the range of ω=100 … 0.1 rad/s and a deformation γ0 of 5%, which is in the linear range of deformation for all samples. These experiments were carried out at 150°C, 170°C, 190°C, 210°C, 230°C, and finally repeated at 150°C to confirm that no thermal degradation had taken place. Prior to each experiment the temperature was equilibrated within ±0.5K of the desired temperature and followed by a waiting time of 300 s to ensure proper temperature equilibration in the sample.

The obtained data were analyzed in particular for their thermorheological complexity, which was done by the automated method developed by the authors previously.*[38]* In this method selected rheological quantities, in our case, storage modulus G’, loss modulus G”, and phase angle δ are not shifted globally but slicewise to determine the Arrhenius activation energy Ea, i.e. e.g. the activation energy Ea is determined at G’=10000, 5000, and 2000 Pa.*[22,34]* Practially, a Matlab® script is used to perform the following steps: 1. Fit logG’(logω), logG”(logω), and δ(logω) with 4th or 5th order polynomials, 2. Find the intersection points of these polynomials with a list of constant values of logG’, logG”, and δ, 3. Determine the Ea for each of those constant values, 4. Plot the data, save the plots and the determined data.

The elongational experiments were carried out using a Uniaxial Elongational Fixture (UXF, Anton Paar, Graz) at 150°C. The sample was loaded in the fixture and secured by clamps. Then the temperature was equilibrated for usually 7 minutes but at least 3 minutes. The equilibration time was reduced if the sample viscosity was so low that sagging of the sample became problematic. Typically, for zero shear-rate viscosity *η*0<100000 Pas the sagging has to be carefully observed. In order to reduce the time of equilibration, the temperature after the test was set to 160°C, which compensates for the temperature loss during sample unloading and loading the next sample, thus, reducing the required time to increase the temperature to 150°C. Following temperature equilibration, a constant Hencky strain rate*[11]* $\dot{ϵ}$ of 10 s-1, 1 s-1, 0.1 s-1, or 0.01 s-1 was applied and maintained until a Hencky strain εH of 4 was reached.

The elongational data were primarily analyzed with respect to two parameters: 1. Elongation at break εB, which was determined from the point when the elongational viscosity ηe+(t) rapidly decreased and 2. The strain hardening coefficient χ(εH), which is determined as the ratio of the elongational viscosity ηe+(t) in relation to the triple linear viscoelastic envelope.

# Results

# Conclusions

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# Acknowledgements

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# Conflict of interest

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# Author contributions

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# Author biographies

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