Final report on the project

Rheologische Charakterisierung und Modellierung von mit Chain-Extendern modifiziertem Polyethylenterephthalat

Rheological characterization and modeling of Polyethylene terephthalate modified by chain extenders

Kennziffer: 2979

Dr. Víctor Hugo Rolón-Garrido

EXPERIMENTAL

Materials

The three grades of polyethylene terephthalate (PET) investigated are T49H, 6020 and 4048, which were selected because all of them are homopolymers. The influence of chemical and physical synthesis routes can be studied, because two types (T49H and 6020) are synthesized from dimethyl terephthalate (DMT) and ethylene glycol, and the third one (4048) from purified terephthalic acid and ethylene glycol. PET T49H has additionally been treated by the so-called "Solid State Polymerization (SSP)", consequently the influence of initial intrinsic viscosity (IV) can be analyzed since T49H has a higher IV (0.82-0.88dl/g) compared to IV of 4048 (IV: 0.643-0.647dl/g) and 6020 (IV: 0.664dl/g ± 0.012dl/g). The three grades were used as received from the producer (Invista).

To minimize hydrolysis and decomposition by high thermal exposure, the pellets were dried in a vacuum oven for 24h at 130°C. Differential scanning calorimetry was used to identify the melt temperature of the PET samples: T49H: 257.08°C, 4048: 258.54°C and 6020: 258.01°C.

Rheological Measurements

The dynamic rheological tests were performed with plate-plate geometry on a stress-controlled rheometer (Anton Paar MCR 301) at 280°C. To investigate the thermal stability and to determine the linear viscoelastic regime, amplitude sweeps were conducted for all PETs and found to be constant up to a strain of γ=10% for the three grades. Thermal stability tests were conducted up to 24h. Frequency sweep tests were conducted bidirectional, i.e. from angular frequency ω=0.05rad/s to 500rad/s (increasing mode), and subsequently from 500rad/s to 0.05rad/s (decreasing mode), or starting with the decreasing mode followed by the increasing run. The measurements were performed at least three times to verify reproducibility.

The impact of the atmosphere was tested by using nitrogen or air. The samples were loaded as pellets or compression molded sheets into the rheometer. The residence time between loading and the start of the measurements was always recorded.

Multiwave and time controlled measurements were tested to reduce the time necessary for a frequency sweep. Unfortunately these settings were not able to decrease the measurement time significantly without affecting the accuracy of the measurement. Therefore, these results are not presented here.

RESULTS AND DISCUSSION

Thermal Stability

To evaluate the thermally stability for the PET samples used, the storage modulus was followed due to its sensitivity to structural changes. Fig. 1 illustrates the behavior of PET T49H, 6020 and 4048 in N_2, and Fig. 2 presents the corresponding data for measurements in air. As seen in Fig. 1, the measurements in nitrogen increase G´ of the three PETs revealing chain extension. After some $3 \cdot 10^4$s (500min), the curves in Fig. 1 tend to a steady state, and seem to indicate a balance between polymerization and decomposition. Actually the enhancement of molecular weight (MW) is not surprising since SSP is performed under nitrogen and thermal exposure.

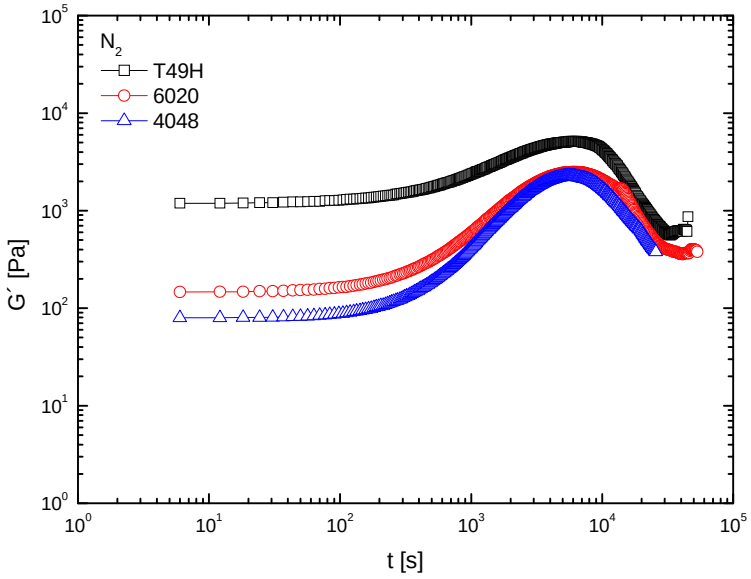

Fig. 1. Storage modulus at 280°C of PET T49H, 6020 and 4048 in nitrogen atmosphere as a function of alteration time at ω=10rad/s and γ=10%.

In contrast to that, the measurements in air decrease of the modulus in air for all three PET samples (Fig. 2). This is due to the possible hydrolysis (in spite of thorough drying of PET) and random chain scission. After the decrease of the modulus in air atmosphere, G´ starts to increase after roughly $6 \cdot 10^3$s (PET 4048 and 6020) or $2 \cdot 10^4$s (PET T49H), respectively. In this case the chain scission reaction is then overcompensated by a polymerization reaction.

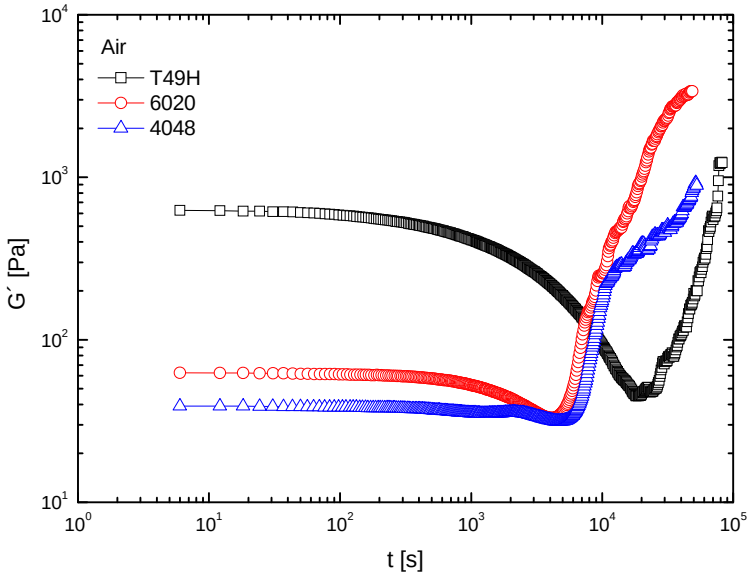

Fig. 2. Storage modulus at 280°C of PET T49H, 6020 and 4048 in air atmosphere as a function of the alteration time at ω=10rad/s and γ=10%.

It should be noted that T49H, which has already undergone SSP, shows the lowest increase of G´ in N_2 atmosphere (Fig. 1). SSP pre-treatment also explains the massive decrease of the storage modulus for T49H in air, while the low MW sample 4048 features still 80% of the initial value of G´ at the minimum (Fig. 2). The loss modulus G´´ present similar tendencies to G´.

Based on the initial moduli measured in N_2, it was also realized already the loading of the sample results in a substantial alteration of the polymer. Fig. 3 compares the elastic moduli of PET T49H, as example, in both atmospheres. The axes are linear and the abscissa comprises the range from minus 600s to plus 600s. The N_2 and air curves do not intercept at zero time in agreement. In order to take into account the effect of the loading time, the data are extrapolated to the actual initial time, i.e. the beginning of loading. Due to the varying duration of the heating time before the start of the measurements at time *t=0*, the actual initial time ranges from *-540s* to *-420s* and is denoted in Fig. 3 as transverse striped area. The intersection of each N_2 and air extrapolated curve is corresponding to the actual loading time. This extrapolation method constitutes a reasonable measuring routine that reveals the contrary performance in both atmospheres. This method was applied for the other two PET grades too.

Frequency Sweep

The variations tested are: atmosphere (air or nitrogen), preparation of the sample (pellets or compression molded plate) and the frequency mode (increasing: 0.05rad/s to 500rad/s or decreasing: 500rad/s to 0.05rad/s). All measurements were performed with the three PET grades. Only some results are shown as representative for the others. The experiment reported in Fig. 4 was performed first by the decreasing mode and then followed immediately by the increasing mode. Thus the first 10 to 15 points in the decreasing mode were recorded in a few minutes. The elastic modulus can be separated into three regions: i) a region from ω=500rad/s to 80rad/s, where the G' is not in the terminal regime and the slope is less than 2, ii) a region from 80rad/s to 1rad/s where the slope is approximately 2, and iii) the region from 1rad/s down to 0.05rad/s. The first region at high ω features the characteristics as observed before, i.e. the increasing run is shifted to lower values due to degradation. In the second region, and

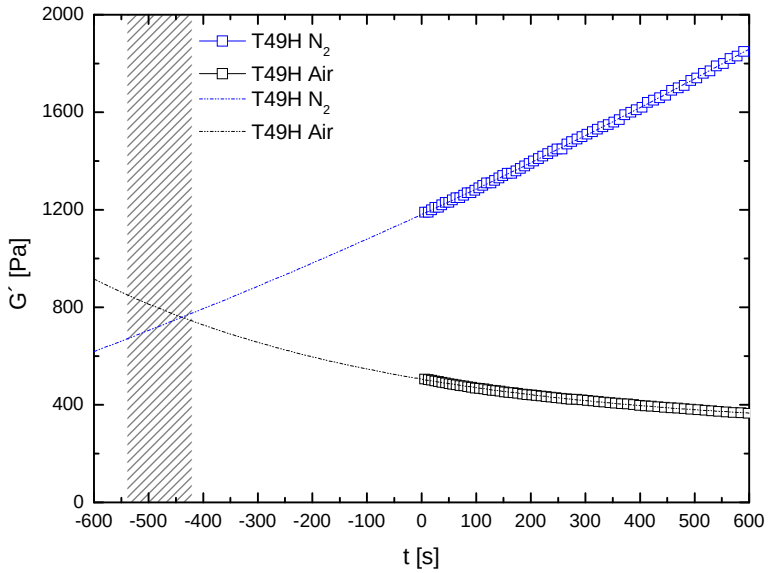

Fig. 3. Extrapolation G´ of PET T49H to the actual initial loading time.

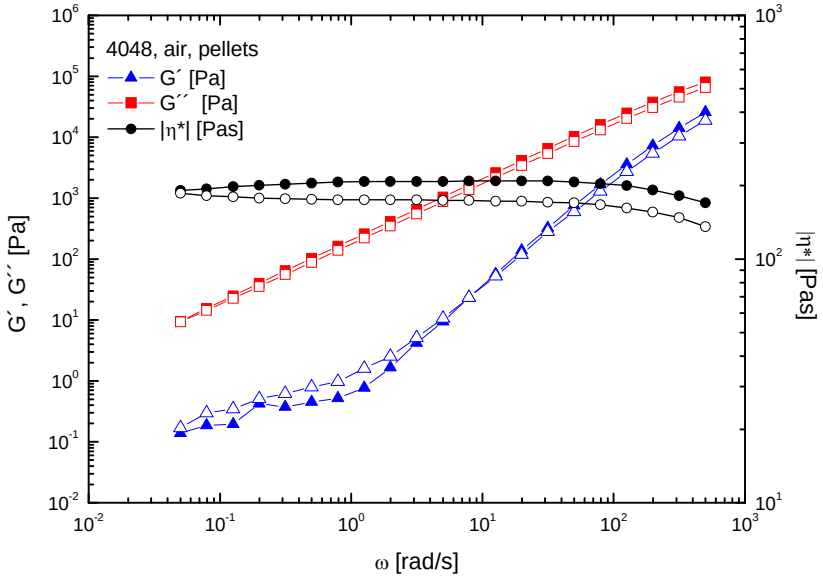

Fig. 4. Storage modulus (triangles), loss modulus (squares) and complex viscosity (circles) for an initially decreasing (500rad/s to 0.05rad/s, closed symbols) and subsequently increasing (0.05rad/s to 500rad/s, empty symbols) frequency sweep for PET 4048 pellets in air.

in particular for the decreasing run, G´ follows the terminal behavior with $G' \sim \omega^2$. In the third region (1rad/s to 0.05rad/s) G´ seems to approach to a plateau. A comparison of the increasing with the decreasing run indicates no decomposition in this region in contrast of what is expected from the thermal stability measurements. Assuming only chain scission, the G' values of the second run should lie below the values of the first run. However, as the G' values of the second run lie clearly above the values of the first run, the G´ data indicate an increasing content of molecular species with long relaxation times, such as a high molecular weight tail or long-chain branched molecules or even cross-linking.

As the complex viscosity and the loss modulus data illustrate, there is an overall decrease of the viscosity and hence of MW with time. But besides the decomposition of PET chains, also polycondensation reactions occur.

The results of frequency sweep tests in nitrogen are presented for PET 6020 (Fig. 5). The applied modes were firstly decreasing and secondly increasing. The plot clearly indicates the overall effect of polycondensation of PET in N_2 in contrast to measurements in air. The viscosity shows at first a shear thinning effect (decreasing run, i.e. starting from ω=500rad/s), and then after a short indication of a steady state, it increases strongly at lower frequencies and longer measurement times. This enhancement of the viscosity continues in the second (increasing) run, reaches a maximum and then transits in a strongly shear thinning behavior. Thus while the enhancement of the viscosity seen at lower frequencies is due to polycondensation reactions and the formation of higher molecular weight species, the enhanced shear thinning behavior indicates that at the same time shorter molecules are created due to chain scission. This can also be discussed in terms of G´, which shows a nearly terminal slope of 2 in the decreasing run between 80rad/s and 1rad/s, while the slope is significantly smaller in the increasing run, and indicates that thermal treatment in the melt state under nitrogen leads to an increase in polydispersity.

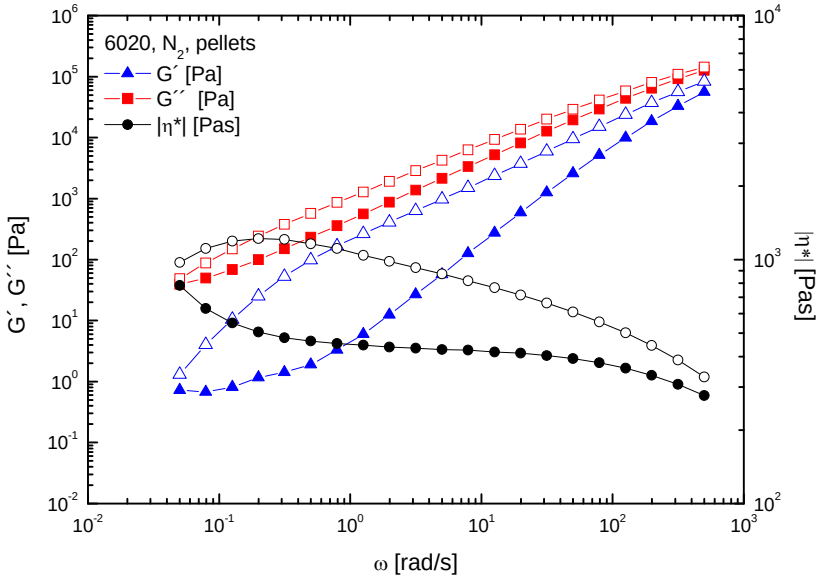

Fig. 5. Storage modulus (triangles), loss modulus (squares) and complex viscosity (circles) for an initially decreasing (500rad/s to 0.05rad/s, closed symbols) and subsequently increasing (0.05rad/s to 500rad/s, empty symbols) frequency sweep for PET 6020 pellets in nitrogen.

Effect of chain extenders

The chemically abbreviated PMDA and TPP were the two different type of chain extenders tested. PMDA was used in concentrations of 0.15%, 0.3%, 0.4%, 0.5%, 0.8% and 1.2%, meanwhile TPP at 0.5%, 1%, 2% and 3%. Those low concentrations have the objective of avoiding gel formation. The only characterization method discussed here is the reactive processing of PET in the presence of TPP, which was carried out in a Brabender that is a torque rheometer operating with a mixing chamber equipped with roller rotors. During mixing, the torque and temperature were monitored as a function of time. The chain extender was added to the chamber with a pipette after 3 minutes of mixing. The choice of this time for TPP addition was aimed to be a compromise of a good mixing condition and to avoid excessive chemical degradation of the material.

The Fig. 6 summarizes the effect of TPP content on the PET 4048 processed at 270°C and 60 rpm. It is noticed that the torque decreases continuously in the experiment performed without TPP, due to a combination of mechanical, thermal and chemical degradation during processing. An extreme increase in the torque can be noticed after addition of chain extender up to a maximum value. The rate of increase becomes stronger, the higher the TPP content is. The torque increment reflects that chain extension reaction dominates over the degradation processes. After the maximum torque has been achieved, the torque decreases steadily. In fact, the maximum value corresponds to the transition from the predominance of the chain extension reaction over the degradation processes to the predominance of the degradation over the chain extension. In this region, also the rate of change of the torque is dependent on the TPP content. Similar results were obtained when PMDA was used as chain extender.

The reactive extrusion has been also performed in a co-rotating twin-screw extruder and the material so produced characterized in capillary rheometer and through oscillatory measurements. Although the results are consistent with those presented in Fig. 6, further characterization is in process.

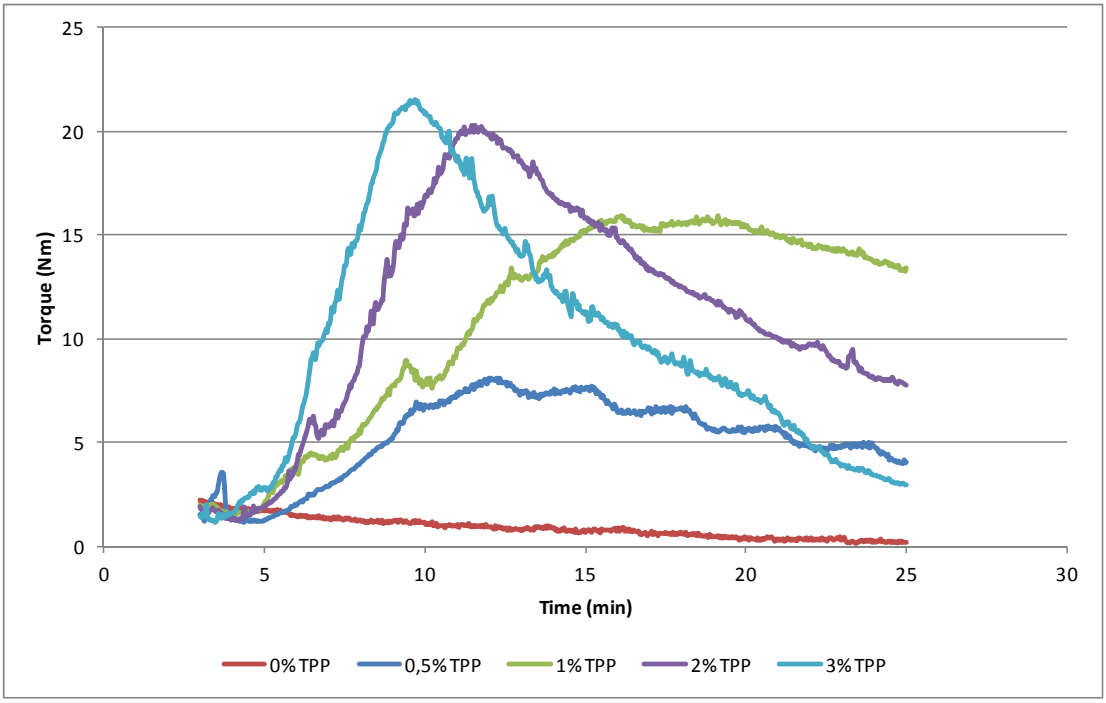

Fig. 6. Effect of TPP content on the PET 4048 processed at 270°C and 60 rpm.

CONCLUSION

The present project allowed:

- The selection of the three homopolymer PET grades, which allows comparing results between grades with different chemical and physical preparation and different starting molecular weights.
- The thermal stability analysis under different atmospheres (N_2 vs. air) and preparation conditions (pellets vs. compression molded samples) and determination of the actual loading time.
- The frequency sweep study of the alterations due to the rapid changes of the molecular structure, confirming the effects of the atmosphere applied, air or nitrogen, causing degradation and condensation, respectively.
- The reactive extrusion of PET through a Brabender and a co-rotating twin-screw extruder and the respective characterization of the material in capillary rheometer and through oscillatory measurements.

It is concluded that an optimal characterization of pure PET is obtained only through proper drying of pellets, avoiding the preparation of plates, considering the real loading time and taking into account that during frequency sweep experiments in cyclic mode should be performed to follow structural modification.

Already low concentrations of chain extender result in drastic structural modification. Samples prepared through reactive extrusion in a Brabender and a co-rotating twin-screw extruder were characterized by capillary rheometer and by oscillatory shear measurements, and the success of the application of chain extender was shown. However, more experiments are in progress in order to determine the molecular origin of the detected modifications.