APPLICATION**NOTE**

Polymers – DMA/DSC

Protect Your Plastic Products: Why Cars Can Be a Risk on Hot Summer Days

Part 1 – Influence of Repeated Extrusion Processing on the Creep Behavior of PE-HD Polymers

Sascha Sebastian Riegler, Applications Laboratory Ahlden/Selb, and Martin Rosenschon, Customer Training

Introduction

Polymers have become indispensable in many areas of our lives including the packaging industry, offering versatile solutions such as films, sheets, bottles and foam containers. Their light weight, durability, and adaptability make them ideal for transporting, protecting and preserving products across various sectors. One such application is the use of bi-modal high-density polyethylene (PE-HD) in detergent bottles, as its unique molecular structure provides an excellent balance of strength, durability, and environmental stress crack resistance, ensuring reliable performance during storage and handling. Currently, most industries are facing increasingly stringent restrictions on recycling quotas and CO_2 emission targets. In the European Union, the so-called "Green Deal" sets a target that 55% of all plastic packaging waste should be recycled by 2030 [1]. Polymer product engineers are therefore facing the challenge of manufacturing with the required portion of recyclates while still fulfilling the quality standards of their customers.

Among the polymers most commonly used as post-consumer recycled (PCR) polymers are thermoplastics such as polyethylene (PE), polypropylene (PP) or polyethylene terephthalate (PET) [2]. Thermoplastics allow for easy recycling by remelting the material and repeatedly processing it into the desired final shape. However, the use of PCR polymers does not come without any disadvantage. During processing (e.g., injection molding), materials such as PE exhibit two distinct degradation processes [3]: Chain scission and crosslinking due to recombination of polymer chain parts. Furthermore, a thermo-oxidative degradation can occur.

Importantly, the effect of these degradation mechanisms may not affect the relevant mechanical properties in the same way. Depending on which of these reactions dominates during reprocessing, the changes in mechanical properties will be different for each specific situation. For example, an increase in Young's modulus or a decrease in elongation at break is observed when crosslinking reactions dominate. Likewise, a scission reaction may produce the opposite outcome. Therefore, the individual properties must be studied separately, depending on the application of the final product [3].

In the following, the creep behavior of a bi-modal PE-HD polymer typically used in detergent bottles was investigated using the DMA 303 *Eplexor®*.

A static stress of 1 MPa was chosen for these experiments. This simulates a real-life scenario where your plastic product is placed under the weight of your other purchases and left in a hot car on a summer day. Temperatures of 50°C and above are not uncommon when your car is left in the hot summer sun for extended periods of time.

The difference between each of the three PE-HD samples is the number of extrusion cycles the material has undergone. Here, PE-HD polymers that have been extruded once (x1), three times (x3) and seven times (x7) are compared.

Creep

Creep is the permanent, time-dependent deformation at elevated homologous temperatures, which is the temperature, T, normalized on the melting point, T_m, of the material,

$$T_{hom} = \frac{T}{T_m}$$

caused by a constant applied stress below the elastic limit. Because semicrystalline polymers have rather low melting points, their homologous temperature in service, even at room temperature, is relatively high compared to other material classes such as metals or ceramics. This fact requires designers of polymer products to be aware

NGB · Application Note 365 · EN · 0225 · Technical specifications are subject to change.

of this deformation mode, as it can lead to undesirable consequences if the creep behavior of the material is not well understood. An illustrative example is shown in figure 1, which displays the bottom of a PET plastic bottle. Here, the polymer deformed under the increasing pressure of the air trapped inside the bottle due to the elevated temperatures that occur in a car in summer. Both factors resulted in permanent deformation of the reusable plastic bottle, rendering it unusable for its intended reuse.
During creep, materials undergo three distinct stages, referred to as primary, secondary or steady-state and tertiary creep.

When stress is applied, the material will immediately deform elastically according to the Young's modulus of the material. As time increases, the strain rate decreases until it reaches the second stage, where the strain rate remains constant. Once a threshold strain is reached, the material tends to start necking. This causes a local increase in stress that further accelerates the strain rate until the material fails [4].

Tensile creep measurements, such as those performed here, are covered by the ASTM D2990 and ISO 899-1 standards.

The creep experiments were performed according to the Stepped Isothermal Method presented in [5], where the load is kept constant and the temperature is increased stepwise. This method is important for the accelerated testing of the long-term creep behavior of polymer samples.

Experimental

The Material

The PE-HD samples used for these creep experiments exhibit a bi-modal molecular structure. The bi-modal molecular structure of PE-HD is particularly relevant for detergent bottles due to its ability to provide an optimal balance of high strength, toughness, and environmental stress crack resistance. This structure consists of a combination of short-chain and long-chain molecules, enhancing the material's rigidity and impact resistance while maintaining flexibility. These properties make bimodal PE-HD ideal for packaging aggressive chemicals and heavy liquids, such as detergents, that require durable and leak-proof containers.

The polymer samples were manufactured by twin screw extrusion as the initial step, followed by a drawing process resulting in sheets with a thickness of about 0.75 mm. From these, dog-bone-shaped samples were cut out along the machine direction, i.e., along the extrusion direction of the sheets. The thickness and width of the reduced section of the samples were approx. 0.75 mm and 4 mm, respectively. The length of the samples was controlled by the clamping length of the tension sample holder and was set to approx. 20 mm for all experiments.

1 Image of a reusable plastic bottle left for too long in a hot car in summer.

DMA Measurements

The definition of the measurements was performed in the NETZSCH *Proteus®* DMA software. All parameters are summarized in table 1.

DSC Measurements

Before the measurement series, a correction measurement was performed with empty crucibles to subtract from the sample measurements the heat-flow contribution and baseline effects stemming from the crucibles. The temperature and heat flow sensitivity calibration were performed with adamantane ($C_{10}H_{16}$), water, indium, bismuth and tin. All necessary parameters used for this experiment series are summarized in table 2.

Measurement Results

Table 1 Overview of the measurement parameters used for the DMA creep experiments

Parameter	Value
Instrument	DMA 303 *Eplexor®*
Measurement mode	Tension
Sample dimensions	≈0.75 mm × ≈3.9 mm × 20 mm
Atmosphere	Static air
Creep Measurement	
Temperature	Isothermal at 25 ... 120°C (5°C steps, each step for 1 h)
Conctact stress	1 MPa
Statical load type	Stress
Target value	1 MPa (100 % limit)

Table 2 Overview of the measurement parameters used for the DSC experiments

Parameter	Value
Instrument	DSC 214 *Polyma*
Sample mass	≈10…12 mg
Crucible	Al *Concavus®*, 30 µl (pierce, cold welded)
Temperature interval	-160°C ... 190°C
Atmosphere	N_2 40 ml/min (purge 2) N_2 40 ml/min (protective)
Cooling device	CC200 LN_2 cooling
Heating rate	10 K/min
Cooling rate	10 K/min

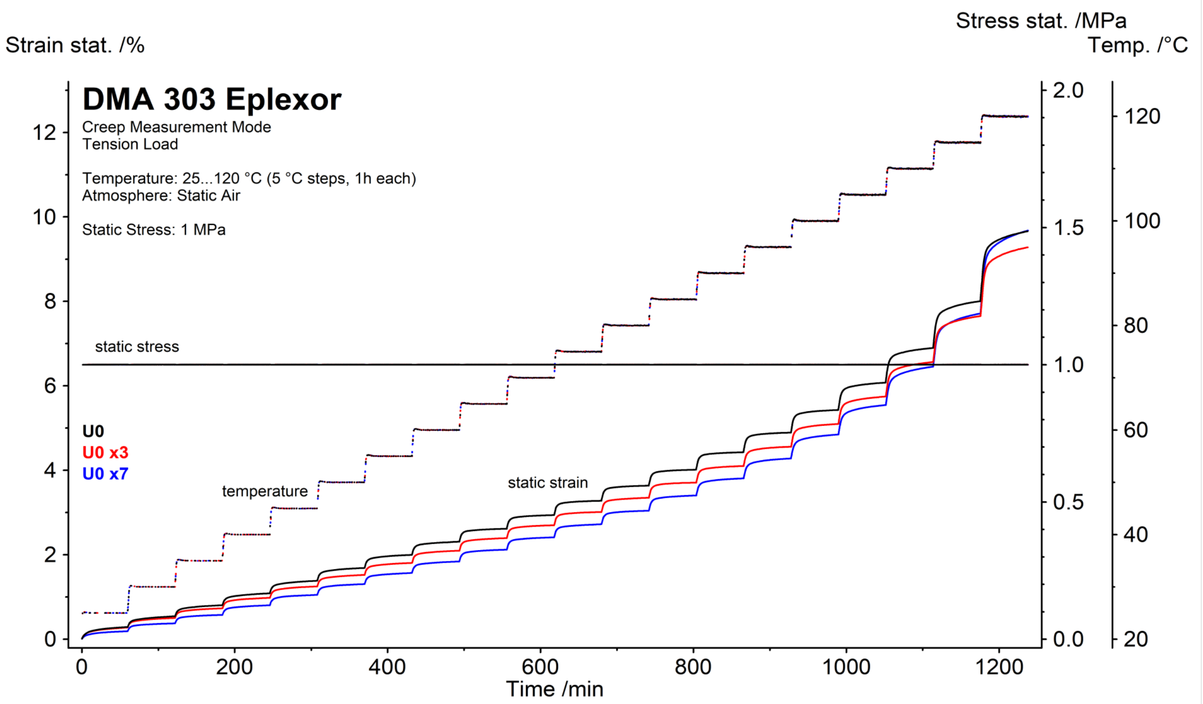
DMA Creep Experiments

The results of the creep experiments for all three PE-HD polymers extruded for different numbers of cycles are summarized in figure 2. The black, red, and blue curves represent the data for the samples extruded one, three and seven times, respectively. The solid curves show the elongation of the sample as static strain; the corresponding temperatures are displayed as dash-dotted curves.

In general, it can be observed that the strain rate increases with increasing temperature for all investigated polymers. In particular near the onset of the melting point, the strain rate increases significantly.

Far below the melting point of PE-HD, which is around 125°C to 135°C [7], there is a clear relationship between the creep resistance and the number of extrusion cycles. The more cycles the material has been through, the higher its creep resistance. At high temperatures, close to the melting point of PE-HD, the strain rate for U0 x7 (blue curves) accelerates more with increasing temperature compared to U0 (black curves) and U0 x3 (red curves)

At the end of the isothermal step at 85°C (48000 s), the U0 sample shows a total strain of 4.01%, the U0 x3 one of 3.70%, and the U0 x7 one of only 3.40%. At the end of the creep measurement at 120°C, the total strain is nearly identical for the U0 x7 and U0 samples, with a total strain of 9.68% and 9.66%, respectively. The U0 x3 sample shows the best creep performance over the entire time/temperature program with a total strain of 9.28%. It should be noted that the thermal expansion plays a role in these stepwise temperature protocols as well. Thus, this factor needs to be taken into consideration when comparing the total strains for each of the samples at a given temperature.



2 Static strain (solid curves), temperature (dash-dotted curves) and static stress (dashed curves) as a function of time. The black, red and blue curves represent the data for the sample extruded one (U0), three (U0 x3) and seven times (U0 x7).

DSC Experiments

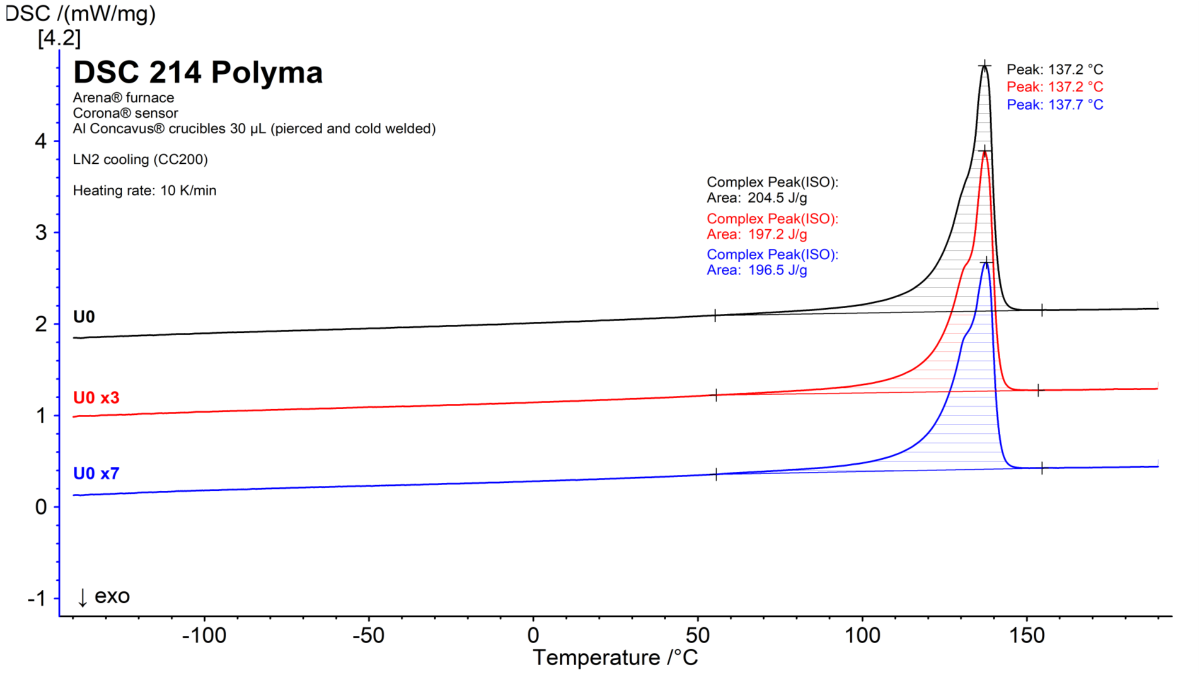
The results of the DSC measurements are shown in figure 3. All three samples display similar melting behavior. The average peak temperature of the melting event is at 137.4°C±0.3°C. However, there are minor differences that can be observed in the melting enthalpy and the shape of the melting event. As the amount of extrusion cycles increases, the total melting enthalpy drops from 204.5 J/g to 196.5 J/g. These values are in good agreement with the values of semicrystalline PE-HD [7]. Correspondingly, a lower crystalline fraction has been determined; it drops from 69.78% to 67.07%. The most striking difference is the shape of the melting event. All three samples show a convolution of two different distinct melting events. This manifests as a shoulder on the left side of the melting peak. With increasing extrusion cycles, the left shoulder appears to become more pronounced as the low molecular weight fraction increases.

Discussion

Two mechanisms are discussed in literature that can lead to a change in mechanical properties for scissoring and crosslinking reactions. Regarding creep, polymers with a higher degree of crosslinking usually exhibit better creep resistance [3]. The results obtained here suggest that the improved creep resistance stems from crosslinking that is the dominant mechanism during repeated extrusion cycles. However, the sample extruded seven times, demonstrating optimal performance in the creep tests, showing lower creep resistance above 100-105°C compared to the other two samples. This might be related to the crystalline fraction within the samples. A lower melting point raises the homologous temperature.

In this regard, the DSC measurements reveal no change in the melting temperature of any of the samples. However, distinct minor changes such as the lower melting enthalpy of U0 x7 and U0 x3 as well as the change in the shape of the melting event might account for the observed change in the creep behavior of the sample. The two overlapping endothermic melting events indicate a bimodal size distribution of the crystallites present in the polymers.

Above the glass transition, but below the melting point of the polymers, the volume fraction of the amorphous microstructure determines the creep behavior. Based on the DMA creep results, it is possible that the polymer chains within the amorphous volume increasingly become more crosslinked with higher extrusion cycles.



3 Heat-flow curve of the three PE-HD samples as indicated. Only the first heating runs are shown. The curves have been shifted vertically along the DSC axis for better clarity.

With increasing temperature, the volume fraction of the crystallites plays an increasingly important role in terms of the creep behavior. The DSC results suggest a lower volume fraction of crystallites present for the U0 x3 and U0 x7 samples. However, this depends on the size distribution of crystallites for each sample. Smaller crystallites tend to melt earlier than larger crystallites. Based on the melting events observed, the fraction of the lower-melting crystallites present in the samples increases with a higher number of extrusion cycles. Thus, at higher homologous temperatures, the low-melting crystallites have a growing influence on the creep behavior.

But an exact interpretation must be treated with caution, as it is difficult to draw certain conclusions without knowledge about the microstructure and the additives used within the polymer.

Conclusion

Most common thermoplastic polymers have a low melting point. This makes them susceptible to creep effects at ambient and elevated temperatures. When elevated temperatures occur, such as those in cars on hot summer days, one must be careful not to expose these products to such high temperatures for extended periods of time. Static forces from heavy weights (e.g., other consumer products) placed on the plastic products, combined with elevated temperatures, can cause creep in a short period of time. In the worst case, plastic bottles or other plastic products may lose their primary use function due to permanent deformation. It should be noted that creep also occurs at lower temperatures, but on a longer time scale.

Literature

1] “Plastic waste and recycling in the EU: facts and figures”. [Online]. Available at: https://www.europarl.europa.eu/topics/en/article/20181212STO21610/plastic-waste-and-recycling-in-the-eu-facts-and-figures
[2] “What Plastics Can and Cannot Be Recycled?” [Online]. Available at: https://www.slrecyclingltd.co.uk/what-plastics-can-and-cannot-be-recycled/#:~:text=The%20most%20commonly%20recycled%20plastics,milk%20cartoons%20and%20shampoo%20bottles
[3] Mendes, A.A., Cunha, A.M., and Bernardo, C.A., “Study of the degradation mechanisms of polyethylene during reprocessing”, Polym. Degrad. Stab., Bd. 96, Nr. 6, S. 1125–1133, 2011.
[4] W. Korte, “Simulation of the Long-Term Behavior of Plastic Components”. [Online]. Available at: https://www.partengineering.com/en/blog/article/simulation-of-the-long-term-behavior-of-plastic-components
[5] F. Achereiner, K. Engelsing, and M. Bastian, “Accelerated Measurement of the Long-Term Creep Behaviour of Plastics”.
[6] “Polyethylen”. [Online]. Available at:
https://de.wikipedia.org/wiki/Polyethylen
[7] “PE-HD: Polyethylene high density”. [Online]. Available at:
https://polymers.netzsch.com/Materials/Details/8

NGB · Application Note 365 · DE · 0225 · Technische Änderungen vorbehalten.