

Essential Polymer Material Analysis Techniques for Scientists, Researchers, and Engineers

Proactively Characterize Polymers to Improve
Processibility and End-Product Performance

Waters™



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INTRODUCTION

Polymers are used in a diverse range of applications – from food packaging to automotive materials – due to their versatility and low cost making them an ideal replacement for traditional materials such as wood, metals, ceramics, and glass. The versatility of polymers is linked to their intrinsic properties dictated by their molecular weight, molecular weight distribution, and branching, which have a direct impact on processing and end-use performance.

For polymer scientists, researchers, and engineers, failing to comprehend how these properties impact processability, and ultimately end-product performance, can lead to time-consuming and expensive setbacks. Furthermore, the emergence of recycled plastics poses challenges in managing variability which can complicate material characterization.

Fortunately, various techniques like Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Rheology are available to quickly predict processing behavior and troubleshoot feedstock variation.

This e-Book showcases the various tools accessible to R&D and QA/QC environments for proactive characterization and troubleshooting processing issues while ensuring the consistency of their materials.

- **Introduction to Polymer Melt Rheology and its Application in Polymer Processing** Understanding the rheological properties of materials can help to identify and solve both processing and product performance problems early on
- **Semi-Crystalline Thermoplastic Analysis Using the Discovery X3 DSC** Test up to three different samples simultaneously under the same conditions to quickly detect differences that can impact performance.
- **Determination of Polymer Blend Composition** Rapid test for identification and verification of polymer blend composition.
- **Ash Testing of Formulated Products Using Thermogravimetric Analysis** Perform quick test, investigate composition mismatches, and identify processing issues.
- **Using Rheology and Thermal Analysis to help Optimize Processing Conditions of Recycled PET** Fingerprint molecular architecture, detect variability, and optimize processing conditions of recycled material.

Our commitment

While the polymer industry faces ever-growing challenges, leading polymer scientists and labs around the world rely on TA Instruments to support their innovation. Whether you are characterizing complex recycled resin feedstocks, improving operational efficiency, accelerating product innovation, implementing process improvements, or meeting sustainability goals, TA Instruments offers the reliability and ease-of-use you need to succeed.

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Introduction to Polymer Melt Rheology and its Application in Polymer Processing

Introduction

Polymer melts are viscoelastic fluids which can behave as viscous or elastic, depending on how fast they flow or are deformed in the process. A material which processed easily on a film blowing line twenty years ago may not run at all on today's lines, which operate at much higher draw speed. The process time could have become much shorter and the new conditions could have negative effects on the overall processibility. Another example is sub-optimal melt flow in the mold during the injection molding process caused due to changes in material chemistry, or process time, or both. These can induce orientation effects resulting in undesirable anisotropy in the mechanical properties of the finished parts. **Polymer melt rheology** aims to understand and quantify the viscous and elastic properties of a polymer so that the process parameters are aligned with the material's melt properties and vice-versa.

Viscosity and Elasticity

A typical characteristic of a polymer melt is that they are non-Newtonian fluids with viscosity decreasing with increasing shear rate. Viscosity measurements can be performed either through direct flow measurements or through oscillation measurements over a range of frequencies (and converted to flow measurements using the Cox-Merz transformation¹) can be used to gauge the rate of the viscosity changes with shear rate. This is important from the standpoint of processing ease, and for determining processing energy needs. The dynamic measurement also provides a simultaneous measure of melt elasticity, the main determinant of viscoelastic melt behavior, and the cause of such phenomena as die swell.

Low Shear

Low shear rate measurements in the melt's linear viscoelastic region are a key in material problem solving. While thermoplastic polymer processing operations such as extrusion and injection molding typically involve high shear rates, finished part quality is often controlled by the low shear rate behavior. For example, gauge variation can be caused by variable post-extrusion die swell, and warpage can occur from non-uniform relaxation during cooling of an improperly formulated injection molding compound. Also, by testing at low enough shear rates so that the measurements are in the melt's linear viscoelastic region, the data can be linked directly to the polymer's molecular structure such as molecular weight and molecular weight distribution- factors which control polymer process ability and product performance.

Time dependence and Deborah number

Thermoplastic polymers are viscoelastic materials and as such exhibit a pronounced time or frequency dependence. For convenience, thermoplastic melts are characterized with a representative material relaxation time (λ). In a similar way, individual steps in a manufacturing or transformation process can be described by a characteristic process time (see Figure 1).

The ratio of the material relaxation time and the characteristic process time; the De (Deborah) number; is an important process parameter. Increasing the take up speed in a film blowing process is identical to decreasing the process time: in order for the Deborah number, characteristic for the process to be constant, the material relaxation time has to be decreased as well, typically by increasing the viscosity by decreasing the temperature or increasing the molecular weight). Not adapting the characteristic material time would cause the material to behave more solid-like (high De number) under the new processing regime and lead to reduce performance and eventual breaking of the film due to reduced flexibility. A low De number stands for a predominately viscous behavior, a high De number for an elastic material response.

Shear and Elongation

Most **rheological tests** are done in shear using rotational or capillary rheometers, whereas most process flows are usually mixed flows with elongation deformations being important and dominant in processes like film blowing, blow molding, fiber spinning, etc. The elongation viscosity of elastic materials at large deformations can deviate significantly from the shear viscosity and therefore is an important parameter to predict processing performance or to design process equipment. Elongation properties at large deformations correlate with molecular structure. The elongation viscosity as such is a very sensitive indicator of long chain branching.

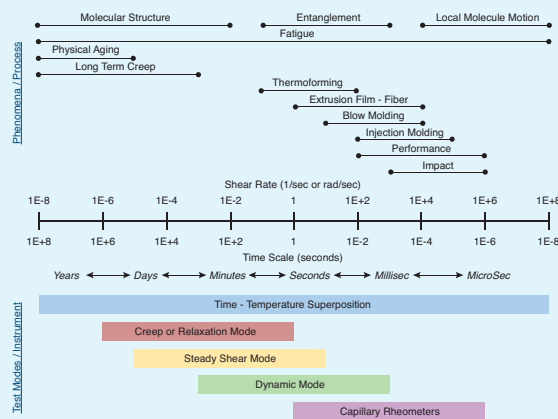


Figure 1

Effect of Molecular Structure and Morphology

Molecular Weight and Molecular Weight Distribution (MWD)

Molecular weight is a critical structural parameter of polymers' flow behavior at temperatures above the glass transition temperature (for an amorphous material) or the melting point (for a semi-crystalline polymer).

Melt viscosity does not change with changing shear rates at low shear rates or frequencies. The viscosity in this region is known as the zero shear, or Newtonian, viscosity η_0 . For low molecular weight polymers in which chain entanglement is not a factor, the zero-shear viscosity is directly proportional to the polymer's molecular weight.

However, above a critical molecular weight, chains begin to entangle, and the zero-shear viscosity depends much stronger on molecular weight, proportional now to about the 3.4 power of the molecular weight. This is shown in Figure 2. Rheological measurements are therefore ideal for studying the effects of molecular weight differences in resins as small differences in molecular weight are manifested in large changes in viscosity.

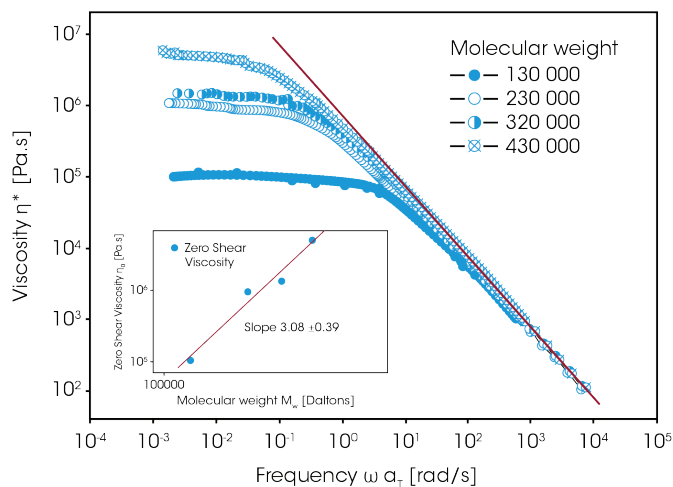


Figure 2. The zero-shear viscosity is a sensitive measure of polymer molecular weight. The relationship for flexible linear polymers is $\eta_0 \sim M_w^\alpha$ with $\alpha = 3.08 \pm 0.39$ in this example.

Molecular Weight Distribution

Beyond the Newtonian region, melt viscosity drops with increasing shear rate, a phenomenon called shear thinning. This behavior is considered the most important non-Newtonian property in polymer processing because it speeds up material flow and reduces heat generation and energy consumption during processing.

At constant molecular weight, the amount of energy required to process the polymer is directly related to the viscosity's shear rate dependence. The onset and degree of shear thinning vary among materials and qualitatively correlate with the molecular weight distribution. Polymers with a broader molecular weight distribution tend to thin more at lower shear rates than those with a narrow distribution at the same average Mw. (Figure 3).

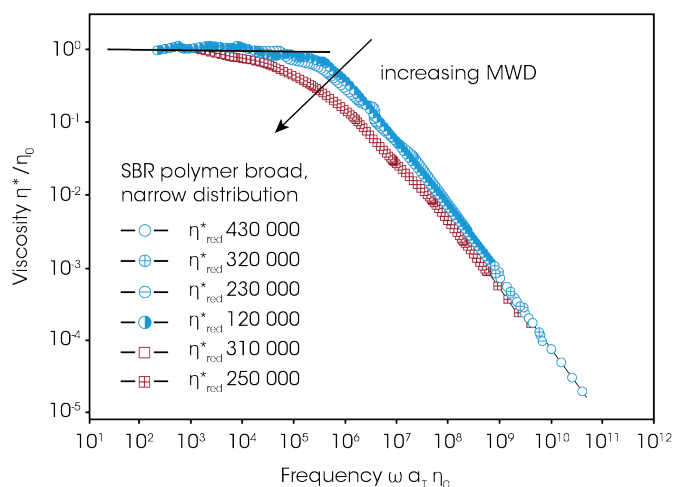


Figure 3. Molecular weight distribution differences in polymer melts are easily detected by measuring the complex viscosity η^* as a function of frequency.

Some important consequences of this: molding and extrusion can for example be made easier by broadening a polymer's molecular weight distribution. Finished product characteristics, such as sag and haze in blown LDPE films, surface smoothness in a variety of thermoplastic molded goods, can be altered by changing molecular weight distribution.

Polymer melts are viscoelastic materials. When subjected to oscillatory mechanical perturbations at different frequencies, $G' > G''$ at higher test frequencies. Depending on the material and the test conditions, the converse can also be observed on the same graph, where $G' < G''$ lower frequencies. This results in a crossover of the G' and G'' curves at a specific crossover frequency (ω_c) and a crossover modulus (G_c) at which $G' = G''$. The cross-over frequency is a measure of the longest relaxation time (λ) of the system, given by $1/\omega_c$. All other properties being comparable, a material with a higher average molecular weight can be expected to have a longer λ and consequently a lower ω_c .

As a result, comparisons of ω_c can often be used for relative comparisons of molecular weight. Similarly, the cross-over modulus can be used as a relative measure of the molecular weight distribution. This concept is shown schematically in Figure 4 below.

The slope of the modulus versus the frequency curve for a melt also mirrors changes due to molecular weight distribution. Isothermal measurements of the modulus at low frequencies show marked increases in the storage modulus as distribution is broadened. Such changes have been used to distinguish between good and poor performing products and guide subsequent product improvements through adjustments in molecular weight distribution (Figure 5).

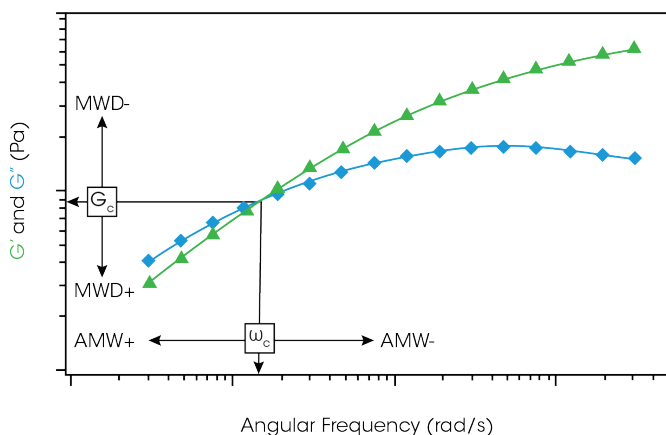


Figure 4. General representation of frequency sweep data depicting the elastic modulus, G' (green) and viscous modulus, G'' (blue) for a molten polymer.

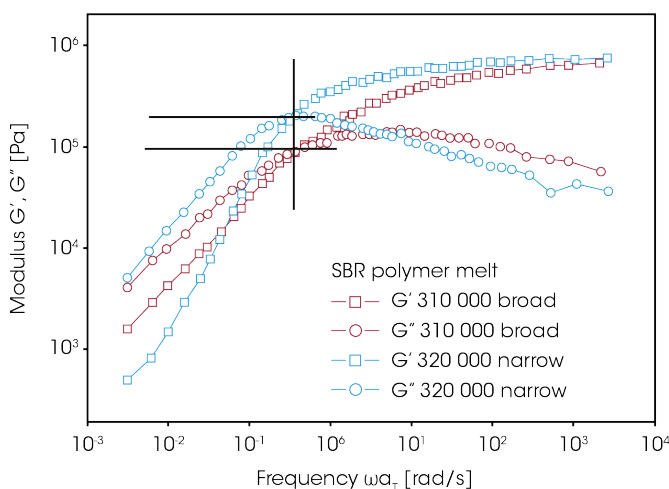


Figure 5. Molecular weight distribution differences in polymer melts. Note the storage modulus of the broad MWD SBR (red squares) are higher than the narrow MWD SBR (blue squares) at low frequencies near the terminal region. Also note the cross over modulus G_c is lower for the broad MWD SBR (red curve).

Branching

Polymer chain branches can vary in number, length and distribution along the main chain. Increasing the number, the size, or the flexibility of the branches changes the melt viscosity. But if the branches are few and long enough to entangle, melt viscosity will be higher at low frequency than that of a corresponding linear polymer of the same molecular weight (Figure 6). The viscosity of long-branched polymers is more shear rate dependent than is the viscosity of linear polymers and long chain branching affects the elasticity of the polymer melts which shows in the normal stress difference and the storage modulus.

The extensional viscosity at high strains increases strongly with long chain branches. Figure 7 compares the rheological responses of a long chain branched LDPE and a linear LLDPE in elongation. The pronounced viscosity increase at large elongation strains (strain hardening) is characteristic for long chain branching.

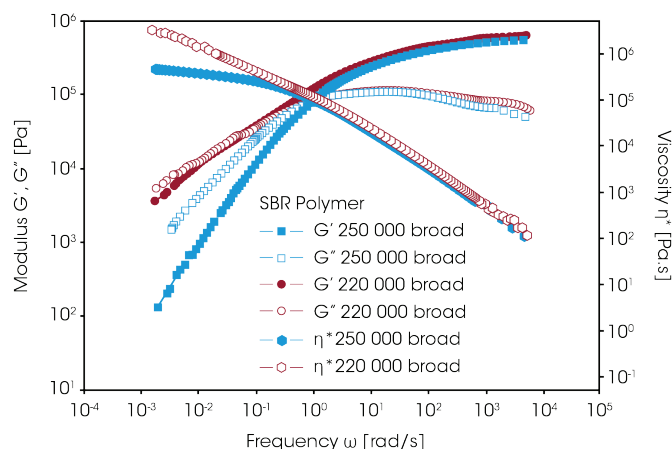


Figure 6. Effect of branching on the complex viscosity η^* and the dynamic moduli G' , G'' .

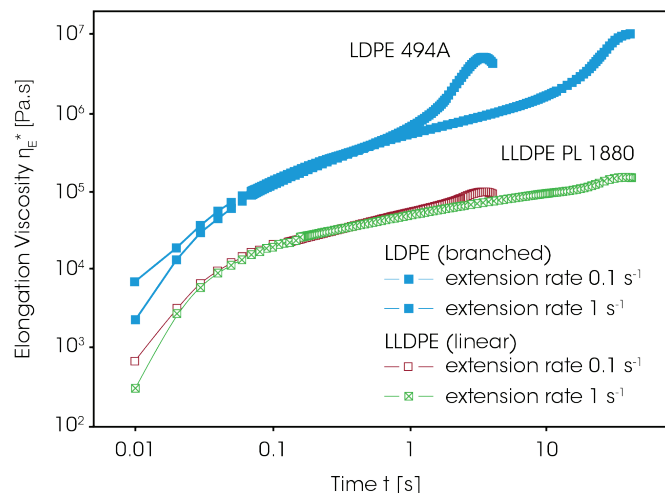


Figure 7. Elongation viscosity of LDPE (branched) and LLDPE (linear) show pronounced differences at high total strains. This strain hardening effect is a characteristic feature of long chain branching.

Fillers

Adding fillers to a neat polymer melt changes its rheology, influencing both the way the melt processes and the properties of the ultimate product. Key factors are filler size and shape, filler concentration, and the extent of any interactions among the particles.

The consequences of adding fillers are an increase in melt viscosity and a decrease in die swell. Moreover, particle interactions increase the non-Newtonian range and cause it to occur at a lower shear rate than for the unfilled polymer melt. Filled polymers have a higher viscosity at low shear rates, and yielding may occur with increased filler concentration (Figure 8). At higher shear rates the effect of the filler decreases and the matrix contributions dominate. Another effect of the filler is the reduction of the linear viscoelastic range, characterized by the onset of the strain dependent behavior.

Application Examples

Processing

Molecular structure and ability to process Rheological measurements are extensively used to study polymer melts. The parameters obtained describe the fundamental behavior of materials such as ABS, PVC, polyolefin, etc. In processes such as bottle blow molding, injection molding, sheet forming, cable jacket extrusion, fiber spinning, etc., rheological measurements correlate molecular structure, MW, MWD and LCB to such processing behavior as flow rate, die swell, melt stability, recoverable shear and frozen-in stresses.

Figure 9 shows melt viscosity and the first normal stress difference data, measured in cone plate. The two HDPE's M-1 and M-2, were found to be very similar by capillary viscometry and even GPC, yet they perform quite differently in a standard bottle blowing line. M-2 produced significantly heavier bottles. Although the viscosity and the molecular weight distribution (see Table 1) of these two materials are almost identical, the normal stresses reported differ significantly. The measured normal stress difference correlates well with the parison swell – a difference in long chain branching or a small amount of high molecular weight component may be the origin. Due to the increased die swell, the parison is thicker, therefore the increased weight of the bottle. In order to evaluate the effect of long chain branching, uniaxial elongation viscosity measurements in the melt can be performed. Data are shown in Figure 10 for three polyethylenes, an LDPE, a HDPE and an LLDPE. The LDPE shows a pronounced strain hardening, i.e. a significant increase of the viscosity with increasing Hencky deformation. This strain hardening stabilizes the parison – the wall thickness of the bottle during blow molding or the free film in a film blowing process becomes more uniform. Strain hardening with a minimum of die swell and enough viscosity to prevent sagging of the parison are the design criteria for a good blow molding compound. The HDPE does show much less strain hardening and the LLDPE follows closely the trace of 3 times the zero shear viscosity. The LLDPE also reaches steady state much faster than the HDPE and the LDPE.

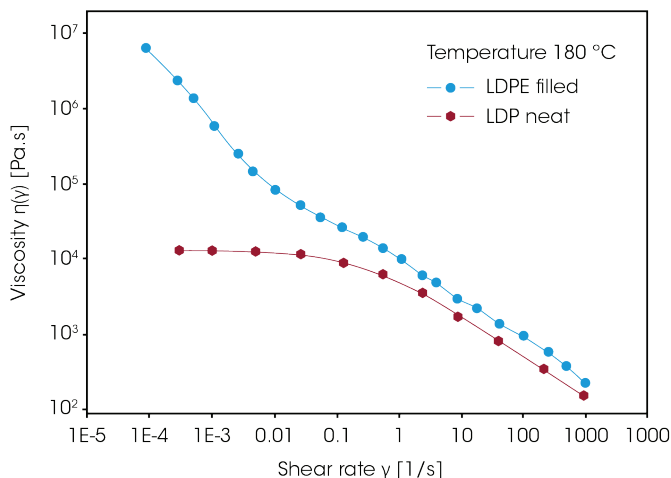


Figure 8. The viscosity of a highly filled LDPE exhibits yielding at low shear rates.

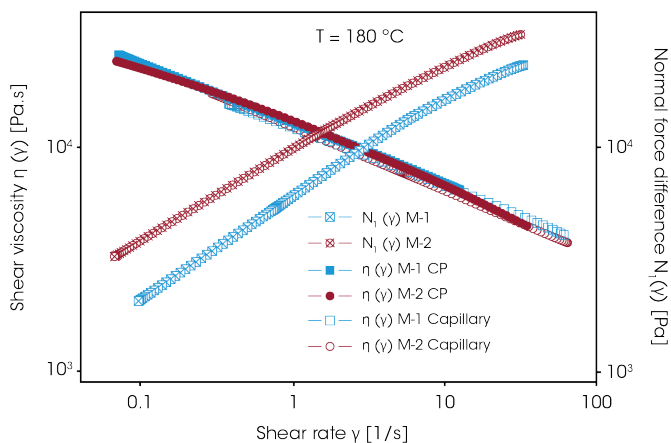


Figure 9. Shear viscosity and first normal stress difference of two blow molding polyethylenes M-1 and M-2 exhibiting significant process performance².

Table	M-1	M-3
MF1 (190; 2.16)	0.6	0.5
GPC (Mw)	131 500	133 600
(Mz)	907 000	1 035 000
η (@ 1s1)	84 000	83 000
η (@ 100s1)	10 200	9 500
Swell (%)	28	42

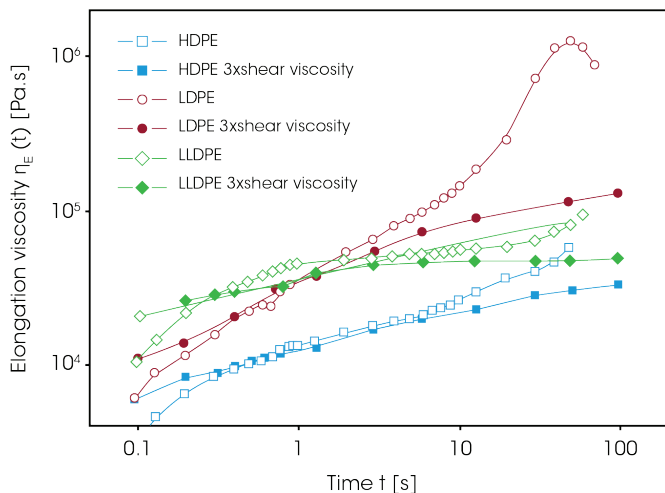


Figure 10. Shear and elongation viscosity for LDPE, HDPE and LLDPE4

Rheology during injection molding - effect on residual strains

For high viscosity melts such as filled thermoplastics or unvulcanized elastomers, cone plate measurements suffer from difficulties forming the sample prior testing as well as edge effects at higher shear rates during testing. Oscillation measurements, probing the material with a sinusoidal shear deformation using parallel plates instead of cone plate, are much easier to perform.

Figure 11 shows the rheological characterization of an injection molding grade ABS. Capillary viscosity data compare well with the absolute values of the complex viscosity, as suggested by Cox and Merz¹ and found by many others in unfilled systems.

In addition to the viscosity, an oscillation measurement provides also a measurement of the materials elasticity, represented by the storage modulus G' . G' correlates with the flow behavior in the mold and strongly influences the relaxation behavior and consequently orientation and frozen-in strains. Relative warpage effects and melt strength depend also on the elastic nature of the polymer melt and the resultant flow behavior in the mold.

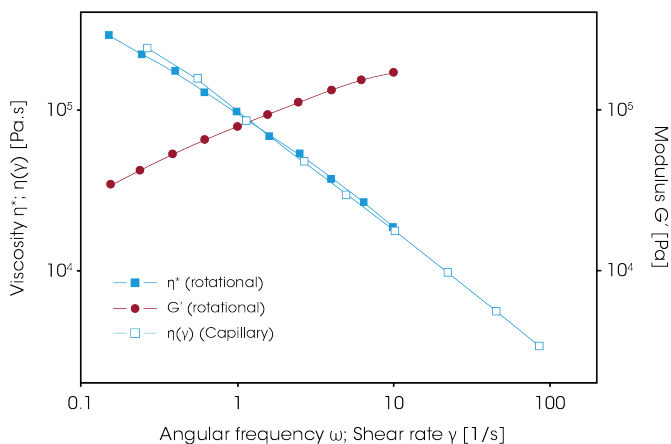


Figure 11. Oscillation and capillary data for an injection molding ABS compound. Cox-Merz $\eta^*(\omega) = \eta(\dot{\gamma})$ holds¹.

Melt degradation of PVC

Important in nearly all melt processing operations, melt degradation can readily be followed by recording the dynamic moduli at constant frequency continuously as a function of time at process temperature. PVC is particularly sensitive to process temperature, as shown in Figure 12 for the two injection molding compounds A and B. The two compounds differed in flame retardant additives and color concentrate. The effect on the thermal stability is dramatic. Sample A shows in comparison to sample B rapid degradation after 20 minutes at 215 °C, represented by a steep increase in viscosity.

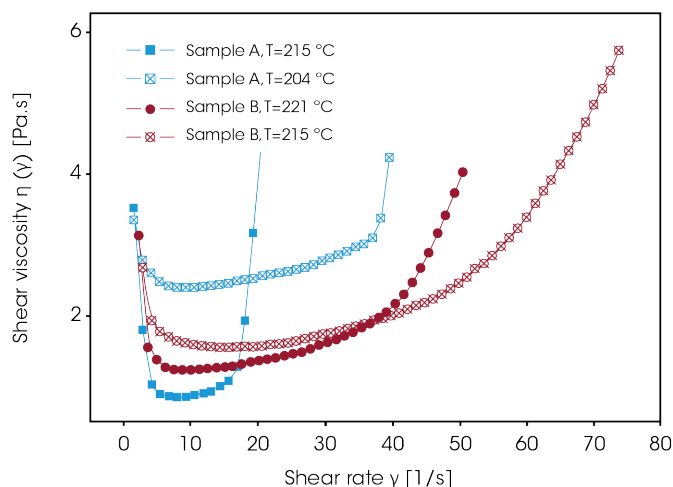


Figure 12. PVC melt stability followed in oscillation for sample A and B at different temperatures.

Extrusion problems of thermoplastic melts

The extrusion of thermoplastics is a high shear process. However, this does not mean that extrudate problems are associated with high shear rate phenomena. As soon as the extrudate emerges from the die, the shear rate declines considerably – the extrudate swell is a comparable low rate phenomenon. Figure 13 shows the storage modulus as a function of frequency, obtained from dynamic mechanical tests on two grades of polyurethanes, used for medical tubing. The specifications call for tight tolerances in diameter and wall thickness.

The material with the higher G' provides too thick, the one with the lower G' too thin tubing. Under identical processing conditions, the small difference in elasticity represented by G' is enough to cause the tubing to be off spec as a result of variations in die swell. During extrusion through the die, the polymer orients and builds up internal strains. As the polymer leaves the die, these strains recover and the polymer swells. The degree of swelling depends on the ability of the material to store deformation energy, the shear rate and the residence time in the die. In the material, the distribution of molecular weight and the degree of branching affects the degree to which internal strains form and recover. Because G' is related to the amount of stored energy during the deformation, it provides an estimate of to the degree of recovery of the PU resin. The greater G' , the higher the die swell, the thicker the tubing.

Pipe surface quality defects can also be traced back to small variations of the melt elasticity. Too high elasticity, measurable by the storage modulus at low frequency, (Figure 14) causes rough surfaces during extrusion of HDPE pipes. Reducing the elasticity by using an HDPE with a narrower molecular weight distribution eliminated the problem. Note that small variations of the molecular structure, caused by, for example, tiny amounts of a high molecular polymer may cause significant processing problems. These variations are usually not detectable in MI values or standard SEC analysis.

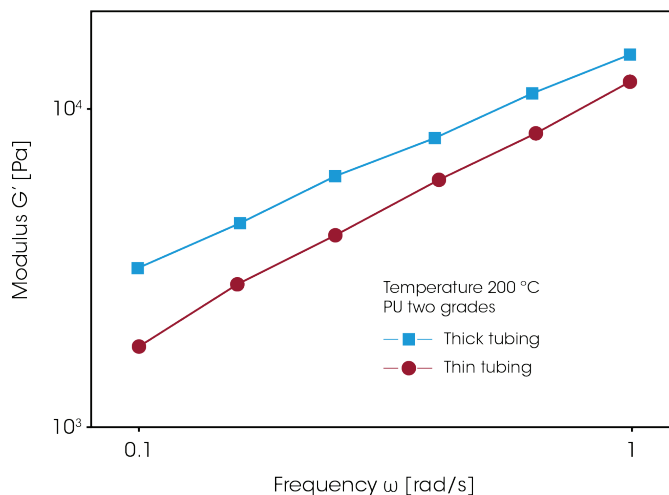


Figure 13. Two grades of extrusion polyurethane. The grade with the higher elasticity (G') produces the thicker tubing.

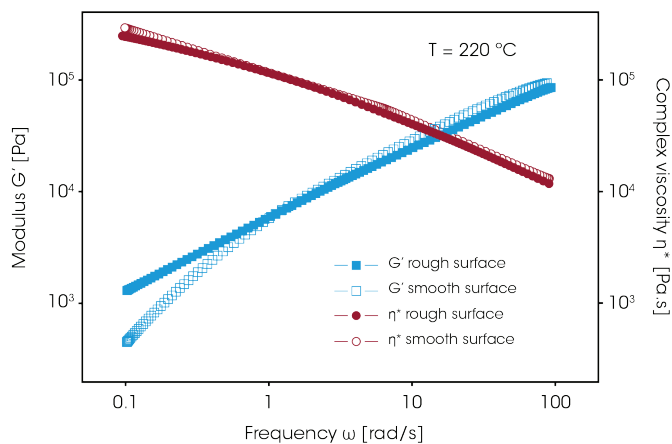


Figure 14. The elasticity, characterized by G' , correlates with the surface quality of HDPE during extrusion. A rough surface corresponds to a high G' .

Conclusion

Rheology is very sensitive to small changes of the material's polymer structure – thus ideal for characterization of polymers. The role of rheology in solving material, processing and performance problems can be illustrated schematically in figure 17.

The rheology of the melt provides direct information on the processability and relate it to the polymer structure. This rheology-polymer structure relation makes rheology the ideal tool to design materials with specific processing and end-use performance.

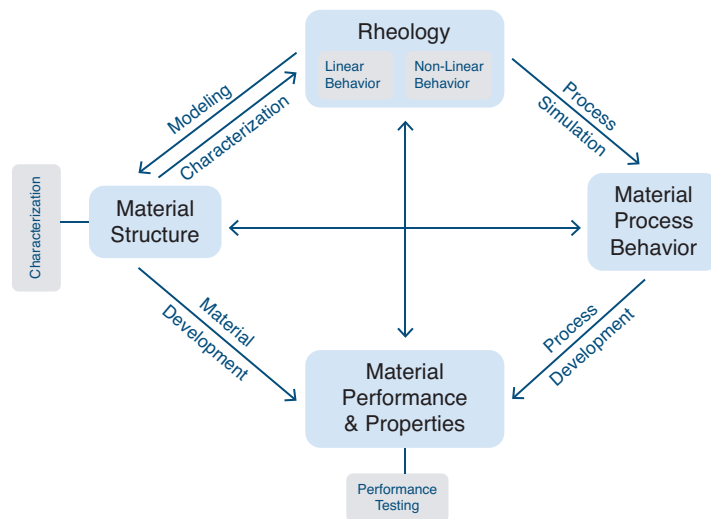


Figure 17. This diagram shows how rheology can be used to correlate end-use and processing performance to the polymer structure. Rheology is a key characterization technique for developing materials with the desired physical properties and for controlling the manufacturing process in order to ensure product quality.

References

- 1 Cox, W.P.; Merz, E.H. J. Polym. Sci., 28, 118 (1958)
- 2 Macosko, C.W.; Lorntson, J.M. private communication (1973)
- 3 Meissner, J. presented at Tezukayama College, Nara, Japan, October 1994
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Acknowledgement

Revised by A. Franck

Semi-Crystalline Thermoplastic Analysis Using the Discovery X3 DSC

Introduction

The Discovery X3 Differential Scanning Calorimeter

The **Discovery X3 Differential Scanning Calorimeter** features a multi-sample cell which can analyze up to three samples simultaneously. This arrangement enables a significant boost to productivity and sample throughput. This Applications Note discusses the advantages of the Discovery X3 DSC for thermoplastic analysis which includes the ability to identify potential differences in thermal properties as a function of thermal history. The Discovery X3 is a powerful tool for quality control. Up to three samples can be run at once under identical conditions and any differences can be readily identified. Research can also be improved through replicate testing and statistical analysis, a distinct advantage of the Discovery X3 multi-sample cell.

Semi-Crystalline Thermoplastics

Thermoplastic polymers can be semi-crystalline or amorphous. A polymer crystalline phase is a region wherein chains are aligned and oriented with long-range order. An amorphous region, by contrast, does not contain this long-range order. Many polymers have a blend of these two phases within their morphology and are identified as semi-crystalline. These polymers can be characterized by their "percent crystallinity." Differences in percent crystallinity can have a dramatic effect on the material properties of a thermoplastic. Some properties which can be impacted include strength, hardness, ductility, and thermal stability. A polymer must have crystalline regions to have a melt temperature. This does not mean that an amorphous polymer cannot flow, but if there are no crystallites there cannot be a melt. The morphology of a polymer can be controlled by many factors including thermal and mechanical processing and the use of additives. To understand the final properties of a material it is crucial to understand its morphology and how it may be controlled. DSC is a key tool in understanding thermal properties and morphology of a material.

Polyethylene terephthalate (PET) is an example of a ubiquitous semi-crystalline thermoplastic polymer. It is used all over the world in applications as different as packaging and clothing. To serve these varied industries, PET must have the required properties for those end uses. One of the key factors which affects the material properties of PET is percent crystallinity, which can be controlled by thermal processing conditions.

This Applications Note showcases the capability of the Discovery X3 DSC to simultaneously probe the thermal properties of three semi-crystalline PET thermoplastics, to gain information about the thermal history of those materials.

Experimental

Three PET samples were prepared for this work. All samples were cut from a commercially available plastic water bottle, which is known to be made of PET. All the samples were loaded into TA Instruments Tzero™ Aluminum pans. Two of the samples were heated to 300 °C and melted in a DSC (to remove preexisting thermal history) then cooled using different methods. The "PET Quench Cooled" sample was removed from the DSC and rapidly cooled to room temperature in seconds by placing the pan on a chilled surface. The second melted sample was cooled back to room temperature at a controlled rate of 20 °C/min in the DSC. The final sample was tested directly as it was taken from the bottle and is identified here as "PET As Received."

Three samples can be run at once under identical conditions in the Discovery X3 DSC. When designing an experiment in the TRIOS software with the equipped Autosampler the samples are identified as Sample A, B and C. The pan location from the Autosampler tray can be identified and programmed into the experiment along with the location of the reference pan. Figure 1 shows the interface in TRIOS when designing an experiment using all three available sample sensors. An illustration can also be observed of the four sensors of the Discovery X3 DSC cell; the sample sensors (A, B, and C) and the reference sensor (R).

The three PET samples with different thermal histories were run simultaneously in the Discovery X3 DSC. All sample masses were between 6.3 mg and 6.8 mg. A "Heat-Cool-Heat" experiment was performed in order to probe the effect of thermal history on the semi-crystalline PET samples. The samples were ramped at 20 °C/min from 40 °C to 300 °C (1st Heat), then cooled at a controlled rate of 10 °C/min back to 40 °C, and finally ramped again at 20 °C/min to 300 °C (2nd Heat).

By analyzing the 1st Heat, the thermal properties of the samples as they were initially loaded into the DSC can be studied. After a thermoplastic polymer goes through a melt (as these samples do during the 1st Heat step) all previous thermal history is erased. The 2nd Heat in this experiment is meant to identify the thermal properties of the thermoplastic samples after having the identical history of the 10 °C/min controlled cooling from the melt imparted onto them.

The screenshot shows the 'Sample' configuration window in the DSC software. It lists three samples: Sample A (PET Quench Cooled), Sample B (PET Cooled 20 °C/min), and Sample C (PET As Received). Below the list is a table with columns for Pan Number, Sample Mass, and Pan Mass. To the right is a diagram of a 4-pan DSC tray.

	Pan Number	Sample Mass	Pan Mass
Sample A	1	6.310 mg	51.590 mg
Sample B	2	6.710 mg	51.740 mg
Sample C	3	6.490 mg	51.440 mg
Reference	52	0.000 mg	51.937 mg

Additional options include 'Edit Tray Configuration' and 'Pan Type: Tzero Aluminum'.

Results

Three semi-crystalline PET samples were run simultaneously in the Discovery X3 DSC. By analyzing the thermograms much can be learned about the thermal properties of the materials as a function of their individual thermal histories. The thermograms presented in this note are shown with exothermic transitions moving upward on the y-axis ("Exo Up"). An endothermic step change in the heat capacity baseline indicates the glass transition temperature (T_g). The magnitude of this step change is proportional to the percentage of amorphous phase in a polymer. The endothermic peak in the data indicates the melt transition of the crystalline phase for these samples. For polymer samples, the temperature of the minima of the melt peak is taken to be the melt temperature (T_m) even though melting does not occur at one discrete temperature point. Semi-crystalline polymers can undergo a process during a thermal ramp known as "cold crystallization." Above the T_g , previously glassy polymer chains gain long range mobility which can result in those chains aligning and forming new crystallites which were not present at the beginning of the run. Cold crystallization results in an exothermic peak above the glass transition but below the melt T_m . Once all the crystalline region has melted thermal history is effectively erased.

Figure 2 shows the 1st heat for the three samples run in this experiment. Samples A and B were taken from the same source as Sample C (As Received) but were first melted and cooled back to room temperature at different rates. The quench cooling process results in a cooling rate much greater than the crystallization rate of PET, which results in the polymer existing predominantly in its amorphous state. The high degree of amorphous content of Sample A can be observed in Figure 1 by the relatively large cold crystallization peak. This indicates the large volume of amorphous polymer which was available to align and crystallize during the thermal ramp. Additionally, the magnitude of the step change in the baseline at the glass transition temperature is largest in the quench cooled sample. Sample B was cooled at a slower (but controlled) rate of 20 °C/min. A larger percentage of the sample was able to crystallize at this rate, but some crystallization was suppressed by this step. The As Received sample shows very little exothermic activity during the thermal ramp. This, along with the small magnitude of the T_g step change, indicates a highly crystalline morphology.

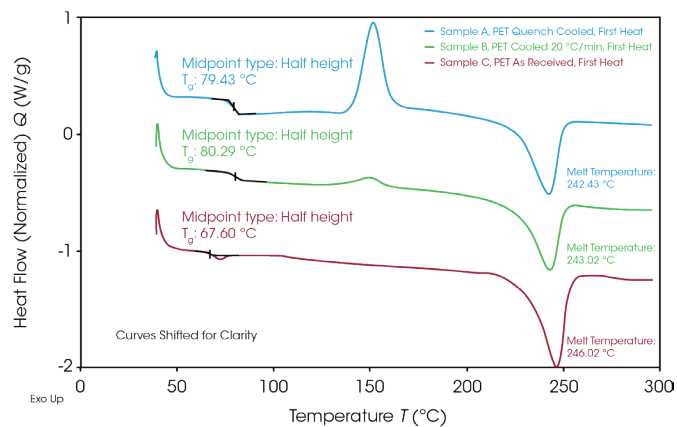


Figure 2. Three PET samples with different thermal histories run together in the same Discovery X3 DSC experiment (ramp from 40 °C to 300 °C at 20 °C/min).

It is interesting to note that the As Received sample has a lower T_g than either of the samples which were previously melted and cooled back to room temperature. It is not uncommon for commodity plastics to include low molecular weight plasticizers to control final material properties. Additionally, certain mechanical processes, such as drawing and stretching from a blow molding process, can affect semi-crystalline morphology. Some of these factors may be at play in the observed thermal properties of Sample C. Regardless of thermal history, the melt temperature of the crystalline region is consistent in all three samples.

All three samples were heated past their melt temperatures and cooled simultaneously under the same conditions. Figure 3 shows the 2nd heat of these samples. It can be observed that controlled cooling at 10 °C/min allowed for a large amount of crystallization to occur in the samples. The T_g of Sample C increases to match 80 °C to match the values observed in the other samples. In addition to the glass transition temperature, the onset of the melt and the melt temperature are all consistent. Additionally, the enthalpies of the melt transitions are very similar, which shows that the samples have very nearly the same percent crystallinity.

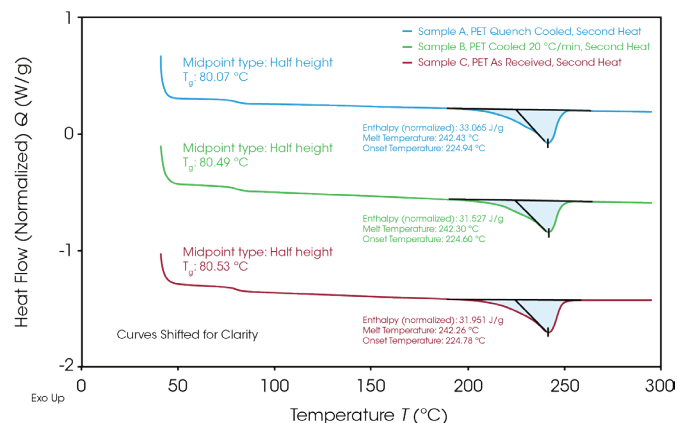


Figure 3. The second heat for the same three PET samples now with the same thermal history (cooled from the melt at 10 °C/min).

Conclusion

In this Applications Note, the Discovery X3 DSC was used to showcase the effect of thermal history on semi-crystalline PET. Samples from the same source were treated with different cooling profiles after the melt. The X3 DSC then allowed for the samples to be studied under identical conditions, simultaneously. The different thermal treatments were shown to affect the properties of the samples. After experiencing cooling from the melt under the same conditions the three samples, which were taken from the same source, treated with the same thermal histories, and then run together, show nearly identical thermal properties. The Discovery X3 DSC allows for samples to be directly compared against each other under the same conditions while also increasing throughput. It is an instrument with the potential to increase research output, decrease run times, and improve the overall efficiency of a lab without sacrificing any of the characterization capabilities of a traditional TA Instruments DSC.

Acknowledgement

This note was written by Andrew Janisse, Ph.D., Applications Scientist at TA Instruments.

Determination of Polymer Blend Composition

Problem

The blending of two or more **polymers** is becoming a common method for developing new materials for demanding applications such as impact-resistant parts and packaging films. Since the ultimate properties of blends can be significantly affected by what polymers are present, as well as by small changes in the blend composition, suppliers of these materials are interested in rapid tests which provide verification that the correct polymers and amount of each polymer are present in the blend. **Differential scanning calorimetry (DSC)** has proven to be an effective technique for characterizing blends such as polyethylene/polypropylene where the crystalline melting endotherms or other transitions (e.g., glass transition) associated with the polymer components are sufficiently separated to allow identification and/or quantitation. However, many blends do not exhibit this convenient separation and thus are difficult to accurately evaluate by conventional DSC.

Solution

DSC is a technique which measures the total heat flow into and out of a material as a function of temperature and/or time. Hence, DSC measures the sum of all thermal events occurring in the material. Modulated DSC (MDSC), on the other hand, is a new technique which subjects a material to a linear heating method which has a superimposed sinusoidal temperature oscillation (modulation) resulting in a cyclic heating profile.

Deconvolution of the resultant heat flow profile during this cyclic heating provides not only the "total" heat flow obtained from DSC, but also separates that "total" heat flow into its heat capacity-related (reversing) and kinetic (nonreversing) components. It is this separation aspect which allows MDSC to more completely evaluate polymer blend compositions. Figure 1, for example, shows the conventional DSC (total heat flow) result for an as received polymer blend containing polyethylene terephthalate (PET) and acrylonitrile-butadiene-styrene (ABS). Three transitions indicative of the glass transition, cold crystallization, and crystalline melting of the PET are seen at 67 °C, 112 °C, and 235 °C respectively. However, no apparent ABS transitions are observed. Upon reheating, after cooling at a controlled rate (10 °C/minute), the DSC result changes (Figure 2). Now only two transitions are observed – a glass transition at 106 °C and a crystalline melt at 238 °C. Explanation of these changes on reheating, particularly the apparent shift in the glass transition temperature, is difficult based on only these results. The MDSC results for the "as received" material shown in Figure 3 resolve these interpretation issues. Phenomena such as glass transitions and melting are predominately reversing under MDSC, while cold crystallization is nonreversing. Hence, separation of the total heat flow into its reversing and nonreversing components separates overlapping thermal events with different behavior. The nonreversing curve in this case shows only the exotherm associated with the PET cold crystallization. The reversing curve shows three transitions – the glass transition (69 °C) and crystalline melting associated with PET [this melting is not shown in Figure 3 since it's outside the temperature range chosen], as well as a second glass transition (at 105 °C) associated with the ABS. In DSC, this latter glass transition is hidden under the PET cold crystallization peak and only becomes visible on reheating after a less amorphous PET phase is produced. Figures 4 and 5 show another example of the improved interpretation provided by MDSC. The total heat flow (Figure 4) is the DSC result for a blend believed to contain PET, polycarbonate (PC) and polyethylene (PE). Obviously, interpretation of this curve is not straightforward.

The MDSC results (reversing and nonreversing heat flow in Figures 4 & 5), on the other hand, again facilitate interpretation. The total heat flow curve shows a glass transition, an overlapping group of transitions at 110 – 140 °C, and a crystalline melt. Separation of the total heat flow into its reversing and nonreversing components allows the following transitions to be resolved and assigned.

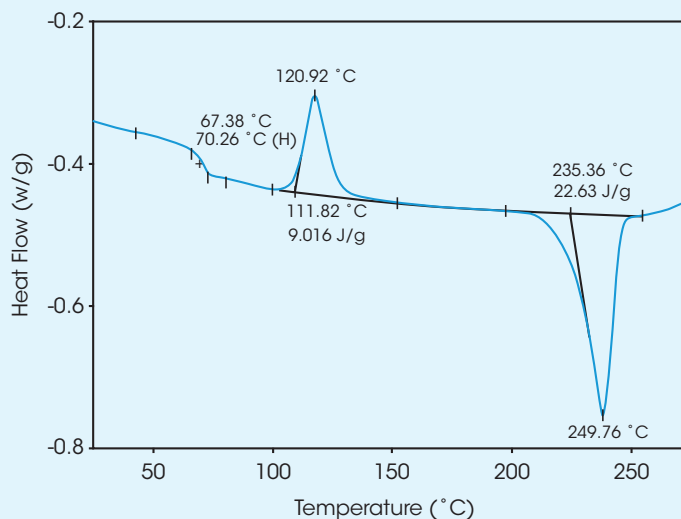


Figure 1. PET/ABS blend (as received) DSC

Curve	Transition	Assignment
Reversing	Glass Transition (73 °C)	PET
	Melt (116 °C)	PE
	Glass Transition (140 °C)	PC
	Melt (224 °C)	PET
Nonreversing	Relaxation (75 °C)	PET
	Cold Crystallization (120 °C)	PET

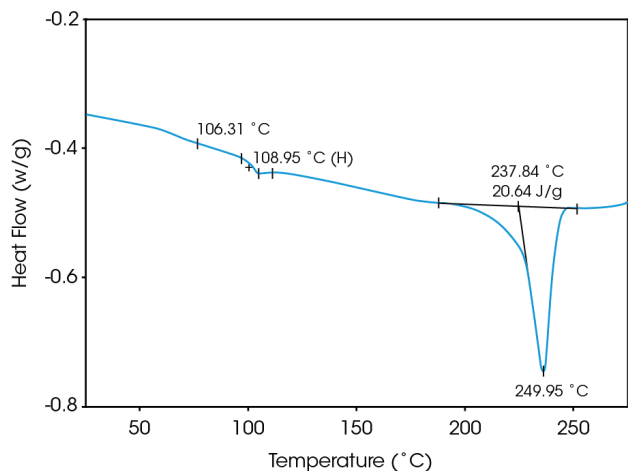


Figure 2. PET/ABS blend (reheat) DSC

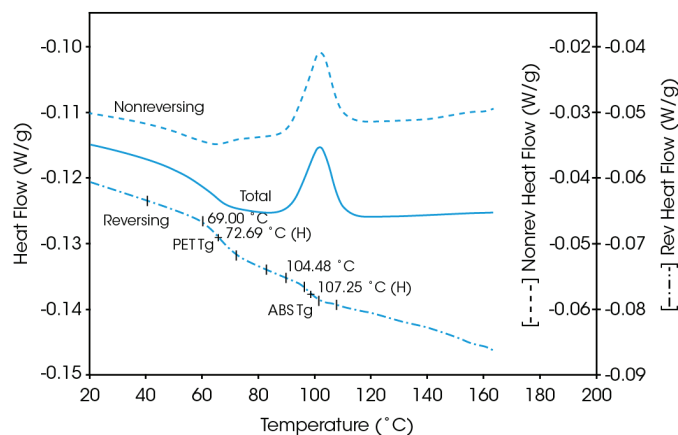


Figure 3. PET/ABS blend (as received) Modulated DSCTM

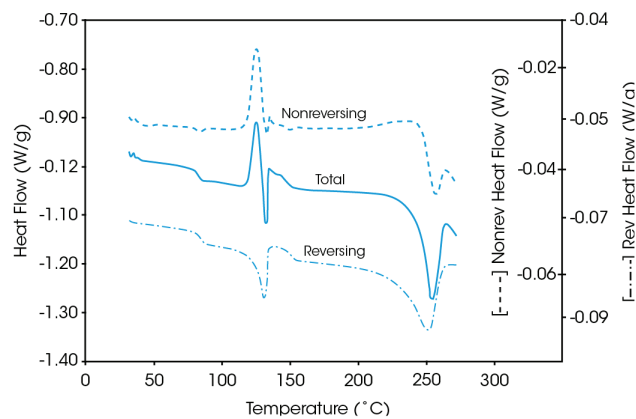


Figure 4. PE/PC/PET blend) Modulated DSCTM

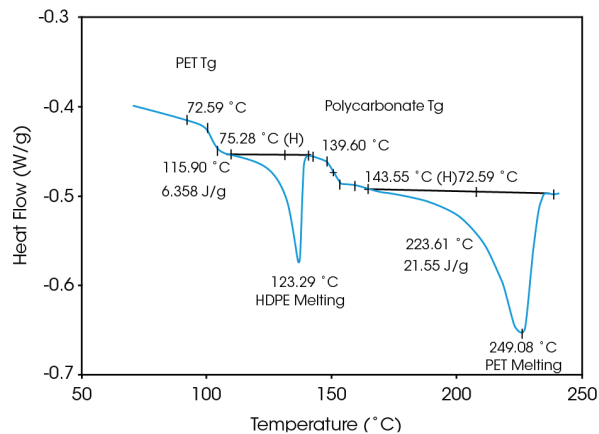


Figure 5. PE/PC/PET Blend MDSCTM Reversing Heat Flow

Ash Testing of Formulated Products Using Thermogravimetric Analysis

Background

Ash testing is a common technique used to determine the composition of materials. By heating a sample to high temperature in air all organic substances will pyrolyze leaving behind only inert and inorganic substances. This residue is then weighed to determine its weight percentage in the original material. **Thermogravimetric Analysis (TGA)** is commonly used for this purpose. The following Applications Note discusses this technique along with some typical examples of materials that are analyzed in this manner.

Ash Testing

The most basic form of ash testing involves placing material into a tared crucible and then into a furnace at high temperature. Weights are recorded before and after the sample is heated to determine inorganic weight percentage. ASTM D5630 and E1755 correspond to this furnace method for plastic and biomass samples, respectively. An advantage of this method is that relatively large samples can be tested, reducing error due to sample heterogeneity. Alternatively, TGA is an instrument designed to measure the weight of a sample vs. temperature, with the ability to easily and precisely reach temperatures needed to fully pyrolyze organic content. TGA is widely available in many industrial and research settings, making it convenient for ash testing. TGA instruments are also often equipped with autosamplers and record data electronically, which allows simple, high throughput, and real time ash data collection. The tradeoff with this method is smaller sample sizes (often only a few pellets vs. 2g-10g of material in the crucible method), however this is generally not an issue for homogenous materials and replicate testing can reduce error. Ash content by TGA is specified in the methods ASTM E1131 and ISO 11358.

Ash Testing of Reinforced Polymers

Polymers are often formulated with inert fillers to improve mechanical or other properties. One common example of this is glass reinforced thermoplastics. Thermoplastics are compounded using extrusion, with the filler content controlled by a feeder set to the appropriate rate. An important quality control check for these materials is ash testing to verify that the actual level of filler matches the set level. A mismatch between measured and set filler content indicates an issue in the process, such as a feeder not feeding material at the correct rate.

Figure 1 gives the results of a routine ash test on a glass filled polymer. Nylon 6 with 30% by weight glass fiber (PA6 + 30% GF) was tested using a TA Instruments **Discovery TGA 5500**. The following method was used:

- Set purge gas to air
- Ramp at 20 °C/min to 1000 °C

A final testing temperature of 1000 °C is not necessary for many materials, but the temperature should exceed the point where weight loss stabilizes and the weight signal reaches a plateau.

TA Instruments **TRIOS software** was used to analyze this data, using the "residue" analysis feature. The result of a representative TGA test of this material is presented in Figure 1, along with statistics for five total replicates. The measured residue at 1000 °C is about 2% lower than the stated value of 30% glass fiber loading. This may be within the process limits for this material but may also be a large enough deviation to affect mechanical properties.

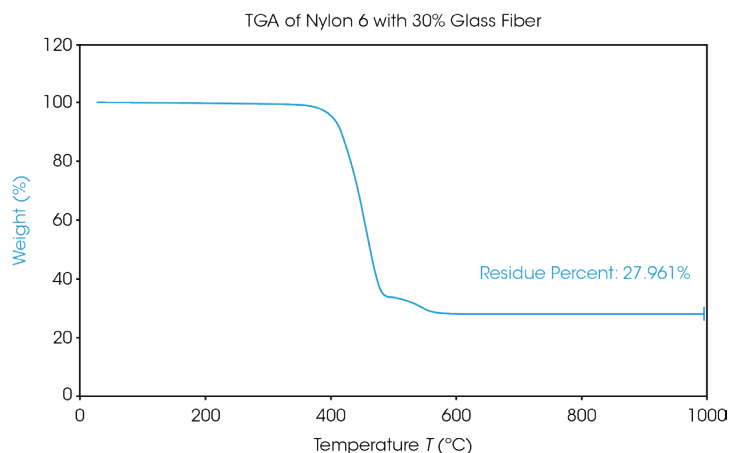


Figure 1. Ash testing residue of a commercially available sample of glass filled nylon.

1	2	3	4	5	M-3
28.124	27.961	27.864	27.889	27.798	27.927 ± 0.125

Ash Testing of Food Products

Ash level is also a commonly reported parameter for many food products, especially processed/formulated products such as pet food. This is often reported as a maximum ash level on a product's label. This number gives a non-specific indication of the inorganic content in the product. Depending on the context, this number can be important for understanding mineral nutrient content. It can also reflect the quality of food in some cases, as low-quality foods may be formulated with excessive amounts of inexpensive fillers such as bone and cartilage.¹

Figure 2 gives the results of ash testing of two commercially available pet foods, designated Pet Food A and Pet Food B. The packaging of both samples had ash content reported on the nutritional labels. The same method as above was used. Five replicates were performed on each pet food. The results aligned well with the nutritional labels, with both pet foods giving ash results below the maximum stated levels.

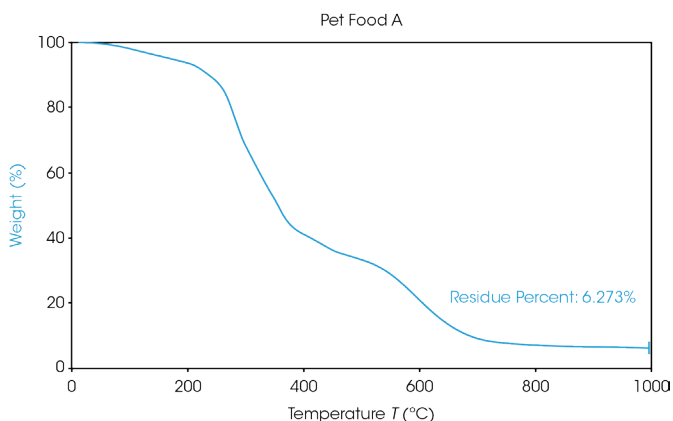


Figure 2. Ash residue results of two off-the-shelf pet foods.

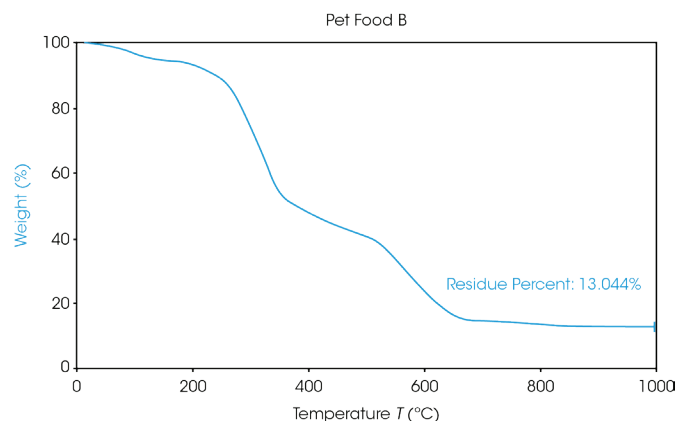


Figure 2. PET/ABS blend (reheat) DSC

Test Number	Pet Food A	Pet Food B
1	6.273	13.044
2	6.053	13.129
3	6.223	13.285
4	6.367	13.214
5	6.054	13.109
Average	6.194	13.156
Std. Dev.	0.138	0.094
Maximum Ash (from nutritional label)	7.66%	18%

Conclusion

Ash testing is a well-known application of TGA for measuring precise levels of inorganic content in materials. This technique is widely used as a quality control tool for formulated products, as well as in other applications where the level of filler/inorganic content must be quantified. This Applications Note demonstrated a simple TGA method that can be used to measure ash content of plastic and food products.

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2. ASTM E1131-20, "Standard Test Method for Compositional Analysis by Thermogravimetry"; <https://www.astm.org/Standards/E1131>
3. ISO Standard 11358-1:2014, "Plastics – Thermogravimetry (TG) of polymers"; <https://www.iso.org/standard/59710.html>

Acknowledgement

This paper was written by Jeffrey Marvin, Applications Engineer at TA Instruments.

Using Rheology and Thermal Analysis to Help Optimize Processing Conditions of Recycled PET

Abstract

Polyethylene terephthalate (PET) is one of the most commonly used plastics in our daily life. It is completely recyclable and is the most recycled plastic in the U.S and worldwide. However, recycled PET from different sources may have large variabilities, such as reduced molecular weight, broader molecular weight distribution, different crystallinity and with different impurity contents, which can affect their processing and application. This application note describes the importance of using thermal and rheological techniques to help fingerprinting the molecular architecture of the PET feedstocks. The melt stability of the feedstock is determined through monitoring the viscosity change at the processing temperature. Also, the feedstock processing conditions can be optimized by measuring the crystal melting and viscosity change as a function of temperature.

Introduction

Each year, large amounts of plastic waste release into the environment have causing widespread pollution from landfills to ocean water and negatively affecting marine wildlife. Today, consumers have realized this concern and manufacturers are working to make plastic products more sustainable. The push for **sustainable polymers** is supporting by governments and companies around the world who are setting targets on using recycled content in plastic products. Numerous recycling technologies such as mechanical recycling and chemical recycling have been developed to address plastic waste [1-4]. Among them, mechanical recycling is one of the most common methods employed to recycle some of widely used plastics such as polyolefins, PET, and polystyrene (PS). This process typically includes collecting, sorting, washing, regrinding, and extruding to make new products. However, compared to virgin resins, the post-consumer recycled (PCR) feedstocks are more complex with significant variability from different sources, which create big challenges to the processing engineers.

Among all of the common plastic wastes, PET is the most recyclable polymer. More than 1.5 billion pounds of used PET bottles and containers are recovered in the United States each year for recycling. Recycled PET (rPET) has been used for numerous applications such as carry bags, roofing materials, and sandwich honeycomb panels for automotive and aerospace insulation use. One of the biggest challenges in rPET application is feedstock variability and contamination. PET collected from different sources may have differing molecular weight (MW), molecular weight distribution (MWD), and impurity contents. These can cause batch-to-batch variation in their crystallinity, crystal melting, and resin melt viscosity. Differential Scanning Calorimetry (DSC) can provide sensitive measurements on PET's crystallinity and crystal melts, while a rotational rheometer can help fingerprint the molecular architecture of the rPET feedstocks. Through melt viscosity measurement as a function of time and temperature, the rheological analysis can also help determine the thermal stability of the feedstock at their processing temperature and optimize the processing conditions. In this application note, the **DSC** and **rheology** characterization techniques are utilized to guide the melt extrusion of rPET feedstocks from different sources.

Experimental Setup

Four batches of recycled PET samples labeled as rPET -1, -2, -3 and -4 are kindly provided by EconCore N.V in Belgium. These samples are collected from difference sources and are reported to have big differences in their intrinsic viscosity. EconCore uses these rPET feedstocks in manufacturing of sandwich honeycomb panels for insulation applications. The commonly used processing (i.e. extrusion) temperature is reported to be at 280 °C.

A TA Instruments **ARES-G2 rheometer** with forced convection oven (FCO) and 25 mm parallel plate geometry was used for the rheological analysis. To identify the linear viscoelastic region of the molten polymer, a dynamic amplitude sweep test was performed at 280 °C with a frequency of 10 rad/s. The dynamic frequency sweep measurements were conducted at a frequency range from 1-600 rad/s using a 5% strain, which is within the linear region of the sample. The time sweep test was setup at 280 °C at a constant frequency of 10 rad/s and strain at 5%. Finally, the dynamic temperature ramp test was programmed from 265 °C to 280 °C with a heating rate of 2 °C/min. The DSC temperature scans were performed using TA Instruments Discovery DSC 2500. A 10 °C/min heating rate was used to heat the sample from 10 °C to 300 °C. More detailed DSC analysis results are reported in reference [5].

Results and Discussions

Determine Linear Viscoelastic Region

Figure 1 shows an example amplitude sweep testing result of rPET-2 at 280 °C. This amplitude sweep test is used to determine the linear viscoelastic region of the polymer sample at its processing temperature. Within the linear viscoelastic region, the sample's oscillation stress and strain follow a linear relationship, where the measured moduli (G' and G'') are independent of the testing stress and strain. Based on this test result, an oscillation strain of 5% is selected to use for the rest of the dynamic measurements including frequency sweeps, time sweeps and temperature ramps.

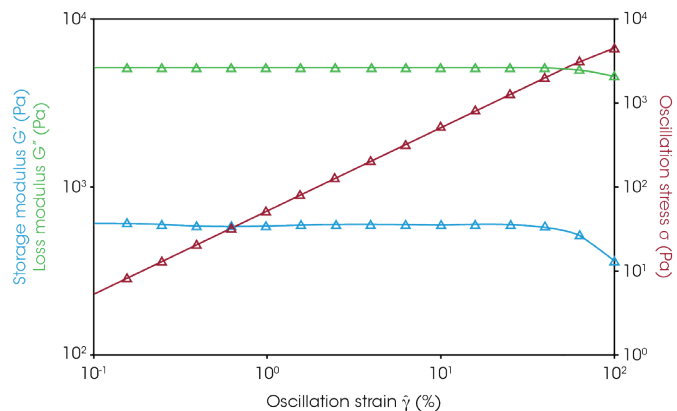


Figure 1. Amplitude sweep test result of rPET-2 at 280 °C

Fingerprint the Molecular Architecture

Figure 2 shows the dynamic frequency sweep test result of rPET-2 at 280 °C. Dynamic frequency sweep test is commonly used in polymer melt analysis as a nondestructive alternative to flow viscosity testing. The measurement results correlate to the polymer molecular architecture, such as molecular weight (MW) and molecular weight distribution (MWD). At 280 °C, rPET-2 is fully molten. Within the measurement frequency range, loss modulus (G'') is greater than storage modulus (G'). No G'/G'' crossover is observed. In the terminal low frequency regime, the slope of G'' curve is at -1, and the slope of G' curve is approaching to -2 as expected. The complex viscosity curve reaches to the plateau regime, and the zero-shear viscosity, which is the plateau viscosity extrapolate down to shear rate (frequency) of zero, is observed at 430Pa.s.

The zero-shear viscosity measured in frequency sweep experiment directly correlates with the molecular weight of the polymer. As shown in Equations 1 below, the factor K depends on the polymer molecular structure, and alpha equals to 3.4 to 3.6 when the molecular weight of the polymer is greater than the critical entanglement molecular weight.

$$\eta_0 = k \cdot M_w^\alpha \quad (1)$$

The frequency sweep test results on the four different batches of rPET samples are plotted in Figure 3. The measurement results clearly show that the zero-shear viscosities of these four batches of rPET are significantly different, which means they have different molecular weight.

The zero-shear viscosity of rPET-1 is high and close to the viscosity of virgin PET. But rPET-2, -3 and -4 have much lower viscosity, indicating a significant reduction in MW due to feedstock processing such as grinding. While rPET-3 and rPET-4 have similar zero shear viscosity, but rPET-4 seems to be more shear thinning. This indicates that the batch feedstock for rPET-4 may have a broader MWD. Polymers with wider MWD always show an earlier shear thinning compared to narrow MWD. This is due to the increased molecular mobility caused by low MW fractions in polymer, which leads to the polymer to shear thin earlier at lower rates.

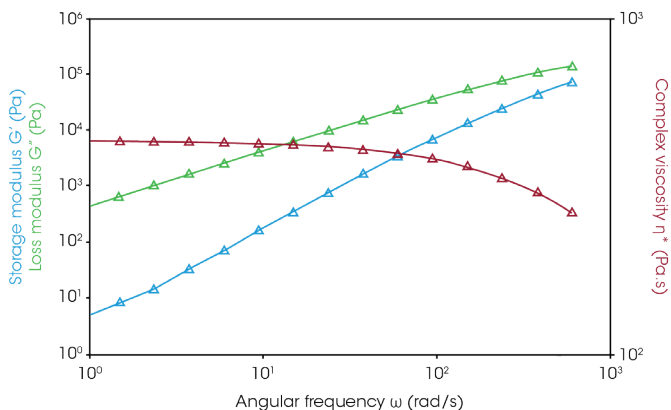


Figure 2. Frequency sweep test result of rPET-2 at 280 °C

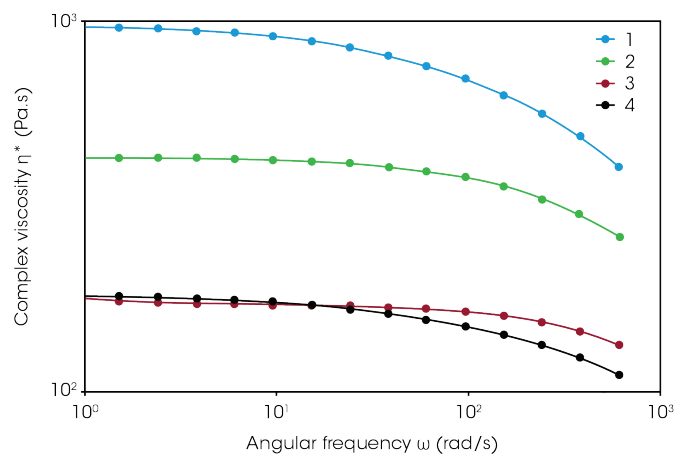


Figure 3. Frequency sweep results of four rPET samples at 280 °C

Process Optimization

The most commonly used extrusion temperature for processing virgin PET is at 280 °C. However, because the recycled PET has reduced molecular weight, and also have differences in their crystallinity [5], they may have different thermal stability and lower melting temperature. Among the industry, it is well known that PET polymer undergoes a slow crosslinking reaction under its molten state. The higher the processing temperature, the more crosslinking is observed. If the resin is not properly dried before processing, the residual moisture could also accelerate this crosslinking reaction.

A dynamic time sweep experiment can be used to evaluate the thermal stability of polymers at a given processing temperature. Figure 4 shows the time sweep test result of rPET-2 at 280 °C. The measurement result shows that the melt viscosity of rPET-2 increased about 10% within the first 10 minutes of equilibration, and 24% within 20 minutes equilibration at 280 °C. These results suggesting that properly reducing the processing temperature could be beneficial for improving the thermal stability.

Using thermal and rheological characterization techniques can help optimize the polymer processing temperature. First of all, a quick DSC scan on the feedstock helps to determine at what temperature the polymer crystals can fully melt. Figure 5 shows the overlay results of the DSC first heat scans on these four rPET resins. These results indicate that all 4 batches of rPET resins can get fully molten at temperature above 265 °C. The endset of melting peaks are observed at 246 °C-263 °C. During melt extrusion processing, the high shear rates experienced by the polymer can cause the PET crystals to break down and melt at temperatures even below the end of melting point, which is observed in the DSC testing. Therefore, a temperature of 265 °C can be selected as a reasonable starting temperature for further rheological investigation.

Based on the DSC results, a melt rheology temperature ramp experiment from 265 °C to 280 °C was conducted to monitor the viscosity change of the molten polymers versus temperature. Figure 6 shows the overlay temperature ramp test results of the four rPET resins, and the viscosities of these polymers at temperature between 265 °C and 280 °C are summarized in Table 1. After melt, the viscosity of rPET-1 remains high within the measurement temperature range, showing that this particular batch rPET may require a higher processing temperature of 280 °C. Because rPET-2, -3 and -4 have much lower molecular weight, their melt viscosities are low and do not have significant increase with decreasing measurement temperature. Therefore, these three rPET resins can be processed under lower temperatures.

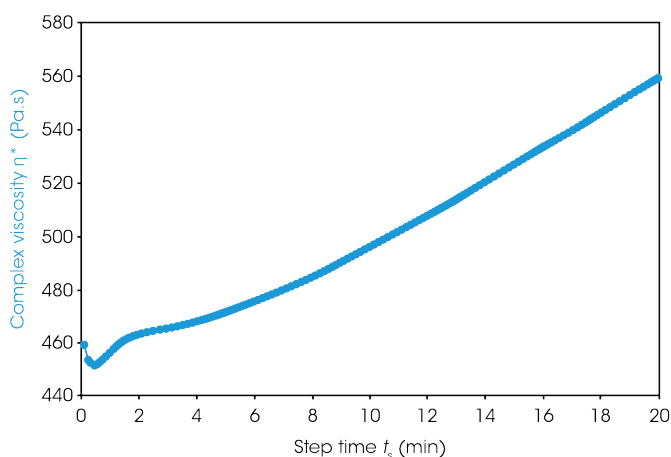


Figure 4. Time sweep test result of rPET-2 at 280 °C

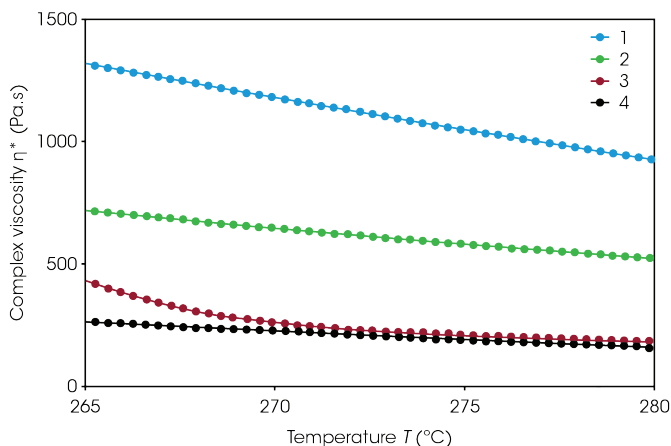


Figure 6. Overlay of temperature ramp test results on four rPET

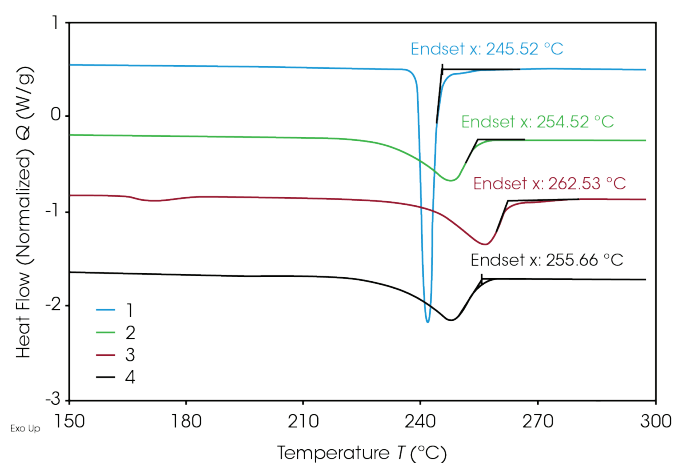


Figure 5. DSC first heat temperature scan results on four rPET

Viscosity @ Temperature	265 °C (Pa.s)	270 °C (Pa.s)	275 °C (Pa.s)	280 °C (Pa.s)
Sample 1	1318	1180	1050	983
Sample 2	722	646	581	430
Sample 3	436	266	206	176
Sample 4	264	229	192	186

Table 1. The melt viscosity summary of four rPET resins at different temperatures

Conclusion

Recycled PET has been widely reused in different applications. However, as the raw feedstocks are collected from different sources, the polymer resins may have significantly reduced molecular weight, wider molecular weight distribution and with different crystallinity. The processing conditions, which commonly used for processing the original virgin resins may not be optimum for their recycled products. Thermal and rheological characterization techniques can help fingerprint the polymer molecular architecture, providing useful guidance to the optimization of processing conditions:

- A dynamic frequency sweep analysis can help fingerprinting the molecular architecture (MW, MWD) of the feedstock resins
- A time sweep test can monitor the polymer stability at their processing temperatures
- The DSC temperature scan and the rheology melt viscosity measurement at different temperatures help guide and optimize the processing temperature

Supporting Resources:

- Webinar: Fingerprinting Recycled Thermoplastic Resins for Process Optimization
<https://register.gotowebinar.com/register/3909935239496367883?source=CW+webvision>
- White paper on Chemistry World website: Characterization and process optimization of recycled resins for the polymer industry
<https://www.chemistryworld.com/sponsored-content/characterisation-and-process-optimisation-of-recycled-resins-for-the-polymer-industry/4016082.article>

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Acknowledgement

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