

Thermo-Plastic Elastomers (TPE) have gained considerable interest in the past 10 to 20 years. They offer interesting properties such as rubber-like final properties coupled with easy plastic processing. They do not require curing and therefore reduce energy and processing costs. TPE is a family of different products such as TPR (Thermo-Plastic Rubber), TPV (Thermo-Plastic Vulcanisate), TPU (Thermo-Plastic Urethane) and more. This paper will deal exclusively with TPR block co-polymers.

The TPR product family includes block co-polymers such as SBS (Styrene-Butadiene-Styrene) and SEBS (Styrene-Ethylene-Butylene-Styrene). SEBS is a fully-saturated specie of SBS to improve weather-ability and stability. To optimize TPR room temperature properties, average molecular weight (AMW) are often very high. This characteristic prevents the material from flowing easily and therefore viscosity measurements with instrument such as capillary rheometers are difficult to perform.

An oscillatory rheometer with a closed cavity test chamber is among the most appropriate test instruments for such material. Suitable instruments for such experiments include the RPA *elite* and RPA *flex*. TPR's, especially those with high to very high AMW do not flow when melted. Instead, they can be somehow "sintered" above melt temperature to prepare a repeatable test piece. Pressure is therefore essential and can be directly achieved in closed cell oscillatory rheometers.

Once the test sample is ready in the instrument, several tests can be performed. The traditional viscosity versus shear rate (frequency) can be performed but may prevent the collection useful information. Even in the melt, those materials behave almost is a purely elastic materials. This somehow surprising characteristic is enabled by their very high molecular weight and is illustrated in Fig. 1 below. When taking into account the viscosity power law model, $\eta = k \cdot \dot{\gamma}^{(n-1)}$, the pseudo plasticity index "n" is close to zero, $(n-1) = -0.87$ which is a characteristic of quasi-purely elastic materials. As a reminder, the "viscosity" of steel as measured by dynamic means has $n=0$ so the power law model returns a value for $(n-1) = -1$.

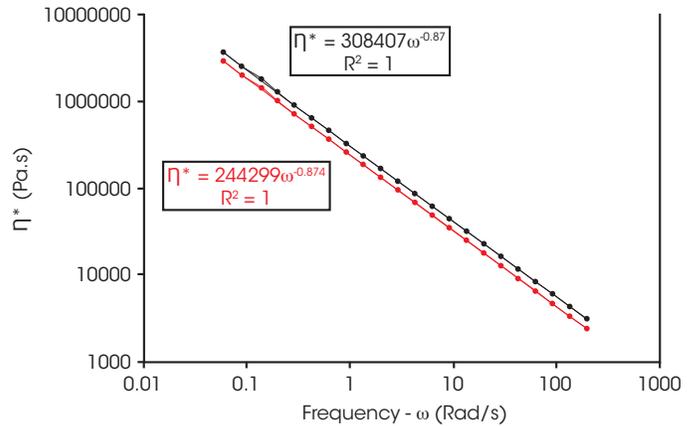


Figure 1

In addition, there is no way of seeing a Newtonian viscosity plateau. Due to their very high AMW, this plateau occurs only at frequencies well below frequencies that are directly measured by oscillatory rheometers ($\approx 10^5$ to 10^8 Rad/s).

Nevertheless, dynamic testing can also be used in testing mode similar to a DSC (Differential Scanning Calorimeter). This type test consists of monitoring the viscoelastic properties of the material when continuously varying temperature. This method enables the measurement of phase (δ), Tangent δ , and complex modulus (G^*), which provides useful information on transitions and hardness. The main transition as illustrated in Fig 2 is provided by the main tangent δ peak around 95° C. This transition is the PS glass transition temperature (TG). The graph illustrates some variation in TG which can be due to variation of level or type of added processing oil.

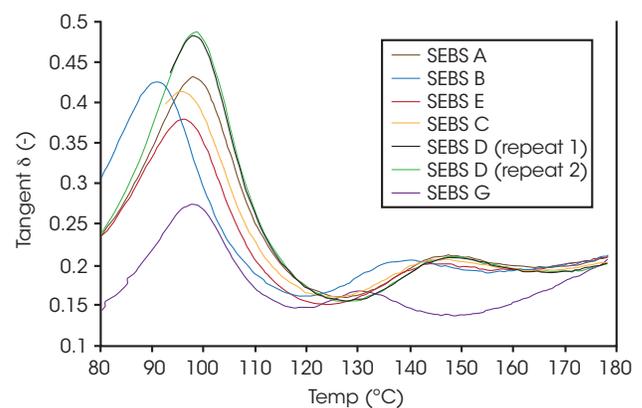


Figure 2

In addition, a small but significant secondary transition was observed between 120° C and 150° C. The meaning of this transition is not yet fully understood but is mainly variable on polymer source. This can be another valuable characteristic for material discrimination or screening.

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The graph of G^* versus temperature with G^* axis being logarithmic, enables the prediction of G^* and therefore hardness on TPR solid state. The graph of G^* versus temperature is illustrated on Fig. 3.

Conclusion

To perform this analysis, the closed cell oscillatory rheometer needs to be programmed as follow:

1. Load SEBS as granules or powder onto the bottom die. Close instrument at TPR processing temperature (ex: 200° C). Close the instrument in standby mode. Wait one minute. Open the instrument and add some more material on the bottom die and close the instrument again in standby mode. Repeat this operation until the sample is clear, indicating a homogeneous sample and the presence of a small material flash in the spew channel. Place this excess material on the sample and start the test.

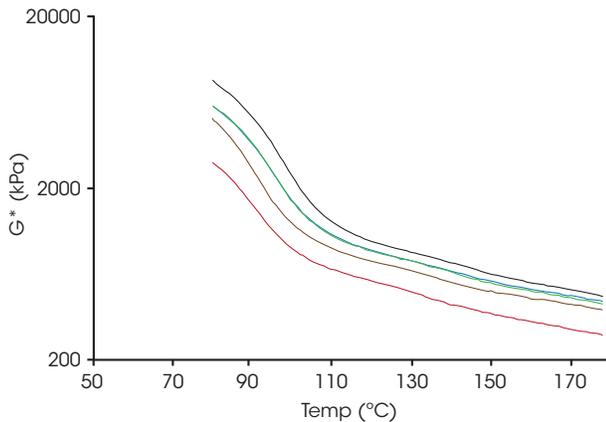


Figure 3

2. Oscillate at very low strain and moderate frequency to stabilize material behavior (ex: 0.5% and 2 Hz for 5 to 10 minutes). Record S' and S'' to verify that stationary conditions are reached (constant or quasi constant S' and S'').
3. Perform a variable temperature test with typically a moderate frequency, small strain (2 Hz, 2% strain) from 200° C till 80° C ideally at temperature rate of 1° C/min. Higher temperature rate may reduce transition amplitude.
4. Plot G^* versus temperature on logarithmic scale for G^* only. G^* tentative plateau shall be proportional to hardness at the same temperature
5. Plot tangent δ versus temperature, both on linear scale.