TPV Flow Properties Determination by Dynamic (Oscillatory) Rheology

TPE materials or Thermo-Plastic Elastomers, in the past 10 to 20 years, have gained considerable interest. They offer interesting properties such as rubber like final properties and aspect and easy plastic processing. They do not require curing and therefore reduce energy and processing costs. TPE is actually a family of different products such as TPR (Thermo-Plastic Rubber), TPV (Thermo-Plastic Vulcanisate), TPU (Thermo-Plastic Urethane) and more.

This paper is focused on TPV, as this kind of material is one of the most prevalent for replacement of cured rubber parts, having a world consumption well over 1 M tons a year.

Since TPV can be processed like plastics, characterization of their flow behavior is essential. Actually, most TPV producers offer not only variable hardness grades but as well materials with tailor-made processing behavior such as injection molding, blow molding or extrusion grades.

Like common polymeric materials, TPV are non-Newtonian materials. This implies that their viscosity varies considerably with shear rate. This property is indeed very important to measure for accurate flow prediction. The simplest viscosity model currently in use is the "power law" model. It predicts a logarithmic decrease of viscosity against shear rate. This simple model can be expressed as $\eta = k \cdot \dot{\gamma}^{(n-1)}$ where n is the pseudo-plasticity index or the expression of shear thinning effect. This parameter can be measured by capillary rheometers or oscillatory rheometers. Oscillatory rheometers have the advantage over capillary rheometers to measure viscosity at much lower shear rate and, at all shear rates, without wall slip. Capillary rheometers are capable of measuring at high to very high shear rate but in most cases suffer of catastrophic wall slip preventing meaningful viscosity measurements. TPE viscosity characteristic test on an oscillatory rheometer is based on a frequency sweep in the melt and is illustrated in Fig. 1. This test provides the respective level of viscosity for 4 different products but provides as well their respective viscosity shear rate dependency.
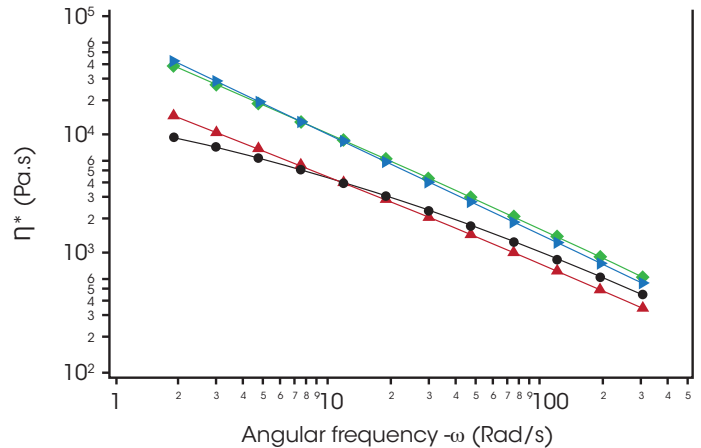

Figure 1

But TPV are complex materials. They are hetero-phasic with a discontinuous cured rubber phase finely dispersed in a continuous poly-olefin phase. The ratio of cured rubber phase over poly-olefin phase is essentially used to adjust hardness. Hard material is poly-olefin rich while soft material is rubber rich. This nature is close to polymer/rubber compounds where the dispersed rubber phase can be considered as filler fraction. Therefore, the simple power law model is not sufficient for accurate prediction. By extension of the shear rate range to lower values, one can easily observe a clear separation of one sample over the others. These results are illustrated in Fig. 2.
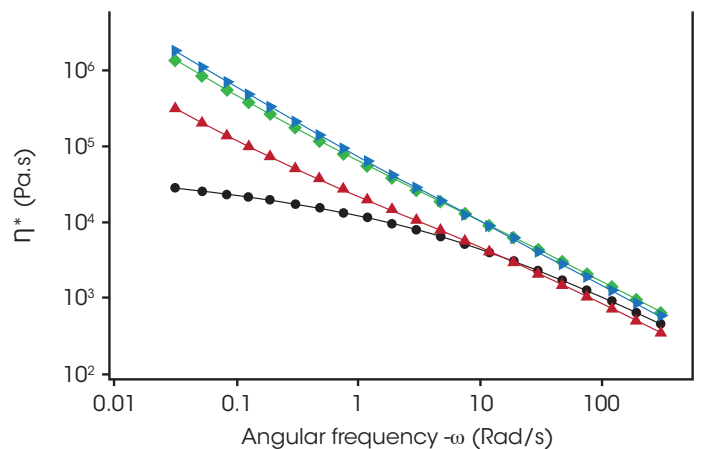

Figure 2

The black curve sample behaves as a pure polymer showing

a clear pseudo-plastic nature with a viscosity Newtonian plateau (η^*_0). This material has a hardness value of 50 Shore D indicating a poly-olefin rich material, so low level of dispersed rubber particles. All other materials have hardness values from 50 to 75 Shore A and are rubber rich materials. Therefore, hard TPV can be considered as low "filler" fraction while soft TPV as high "filler" fraction. Consequently, rather than using the lower law model for all material, it is recommended to apply a different model for high hardness material than for low hardness. The best respective models for these materials are the "Carreau-Yasuda" – and the "Hershel-Bulkley"

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda \cdot \dot{\gamma})^a]^{\frac{(n-1)}{a}}$$

$$\sigma = \sigma_c + K(\dot{\gamma})^n$$

This last model is specifically used for compounded materials such as rubber and plastic compounds containing fillers (CB or Silica) above percolation level. It highlights a critical stress (σ_c) at which viscosity is infinite and therefore under which the material does not flow. This information is particularly important for injection mold and extruder die design. The critical stress for rubber rich TPV is perfectly illustrated in Fig. 3. This graph also proves that poly-olefin rich materials (Black curve) do not exhibit a critical stress.
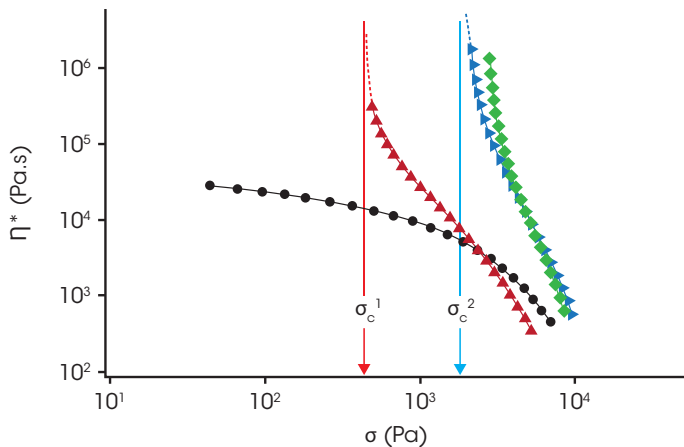

Figure 3

Conclusion

To perform this analysis, the oscillatory rheometer should be programmed as follows:

1. Close instrument at TPV processing temperature (ex: 180° C). Preferably use a pre-molded disc to test a perfectly homogeneous sample. TPV granules tend to "sinter" thus giving poor homogeneity.
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 frequency sweep at low strains not exceeding 1 to 2% over two to three decades of frequency (ex: 0.3 to 300 Rad/s). It is essential to keep strain constant over the full frequency range. All compounded materials exhibit a strong to very strong non-linear behavior against strain.
4. Plot η^* versus S* or better σ^* on a double logarithmic scale. In closed test chamber DMA's, complex torque is linearly proportional to stress.
5. Plot σ^* versus shear rate. Perform a non-linear regression using the Hershel-Bulkley equation as per Fig. 4 here below.
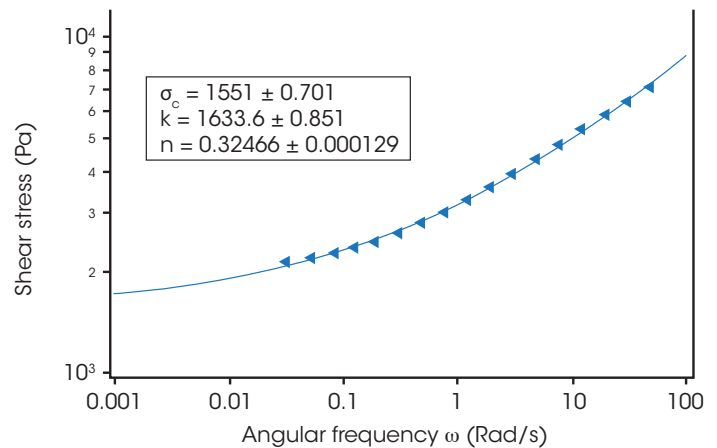

Figure 4

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.