Applications of nonlinear polymer viscoelasticity in rubber industry

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Even if the early developments of rheology were carried out by Mooney (and many others) with special focus on rubber polymer melts, namely Natural Rubber, later on, the rheological community devoted much more attention to polymer melts for plastics industry. In this presentation, the focus is on the use of transient shear and extensional flow startups of rubber polymers of industrial interest, such as Styrene Butadiene Rubber (SBR), Nitrile Butadiene Rubber (NBR), high cis polybutadiene (cis-BR), and thermoplastic rubbers (TPR), to assess their processing and performance.

Using the variable speed "Mooney viscometer", multiple overshoots were observed in shear flow startups on polydisperse branched polymers (Bacchelli, 2008; Marrucci et al., 2008). Testing different polymer structures, it was also possible to highlight specific rheological fingerprints of different branching patterns. Systematic recoil experiments after nonlinear shear flow were subsequently performed in our labs on polydisperse branched polymers (Coppola et al., 2014). These experiments displayed an unusual recovery route on the way back to the original stress response. A discussion is made on such complex recovery route, also with the help of calculations based on a tube model similar to pom-pom. It is also discussed how these results are relevant to interpret the change of rheological properties during storage, a phenomenon frequently observed with branched rubber polymers.

The Payne effect is the measure of dynamic moduli and hysteresis strain dependency. It is often observed with filled polymeric systems in a wide range of shear or tensile strain (Payne, 1962). This effect is typically measured with single frequency strain sweeps, and it is very often used to assess the hysteresis of rubber compounds for tyre application. Here, a revisited version of the Payne effect is presented, that allows a better elucidation of the polymeric systems rheological response after application of shear strain out of the linear region. Basically, the uncured filled polymer is characterized with low strain frequency sweep, before and after a large strain stressing test. In most cases, the stressing test has the effect of reducing the agglomeration state of the filled systems. Another "picture" is taken with low strain frequency sweep after a subsequent ageing phase, to evaluate possible filler re-agglomeration effects. Differently from the standard Payne effect measurements, it is therefore possible to get a fingerprint of the relaxation spectrum before and after a stressing test as well as after the re-agglomeration phase.

Extensional flow is well-known to be important for the mixing operation of polymers with fillers. The stress transmittable to the filler agglomerates as well as the maximum polymer deformability govern the result of such compounding operation. Polymer strain hardening and its elongation at rupture are clearly expected to be crucial. It is shown here how a careful extensional characterization was useful to elucidate the rheological effect of different branching patterns, also comparing experimental results with Molecular Stress Function predictions. Furthermore, using a sensible approach proposed long ago by Tokita and Pliskin (1973), the qualitative behavior during mixing was also predicted from the extensional characterization. A further example is briefly shown about the use of extensional rheology for TPR in model compounds with plastics.

References

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