

NANOSCOPIC STRAINING MECHANISMS IN INJECTION-MOULDED TPU MATERIALS AS REVEALED BY SAXS

Norbert Stribeck^a, Xuke Li^a, Ahmad Zeinolebadi^b, Frauke Harpen^a, Gerrit Luinstra^a, Berend Eling^c, Stephan Botta^d

^aUniversity of Hamburg, Dept. Chemistry, 20146 Hamburg, Germany. [e-mail: norbert@stribeck.de](mailto:norbert@stribeck.de)

^bPolymer Consult, 22397 Hamburg, Germany

^cBASF Polyurethanes, 49448 Lemförde, Germany

^dHASYLAB at DESY, 22603 Hamburg, Germany

ABSTRACT

Composites of thermoplastic polyurethane (TPU) (Elastollan[®] 685A by BASF) and 0 to 0.5 wt-% 3-aminopropyltriethoxysilane functionalized silica spheres (diameter 14 nm) are strained and subjected to slow load-cycling¹. The mechanical tests are monitored by small-angle X-ray scattering (SAXS). The fiber patterns from the injection-molded test bars are converted into chord distribution functions² (CDF) in real space for analysis of the nanostructure. It is found that the arrangement of the hard domains in the soft phase is poor. As the result, the scattering entities are very simple: There is only correlation between two hard-domains and the soft domain in between (“sandwich”). SAXS shows that the rubber-elastic extensibility of the soft phase is very limited. Macroscopic strain is accomplished by localized failure of single “springs” that relieve majority of the sandwiches. The nanostructure dissociates into broken and unbroken scattering entities. A broken entity is an elongated soft domain sandwiched between two fragments of hard domains. The nanoscopic strain of the sacrificed sandwich equals the macroscopic strain at the time of rupture. Initially with increasing strain the failure process propagates from regions with poorly arranged entities (PAE) regions that are invisible in the SAXS into the well-ordered ensembles (WAE) of hard domains. The more nanospheres are in the material, the earlier the dissociation arrives in the well-ordered fraction. Outbursts of local failure happen at strains of 100% and 200%. They relieve the global nanostructure considerably and the long period decreases. Very slow load-cycling of the pure TPU at low strain does not yet induce the failure mechanism. The material is elastic. In the nanocomposites (NC) the failure-induced dissociation starts already in the first cycle and increases during the application of cyclic load. Consequently, in the NCs the oscillation of the nanostructure decays from cycle to cycle whereas it stays constant with the pure TPU. The fraction of material that is not subjected to the decay is a function of the nanosphere content. Linear extrapolation yields a fraction of 1.25 wt.-% nanospheres at which the complete material would become homogeneous. Such a material would stop showing nanostructure oscillations after ca. 70 cycles. The relevance of these and other parameters for the prediction of mechanical properties in computer simulation is discussed. The SAXS patterns of relaxed samples are little different from that of the virgin materials, but the typical signature of the sandwich ensembles is much clearer their CDFs. The advantage of a CDF analysis with respect to a direct analysis is demonstrated and discussed.

Acknowledgement: The authors thank the Hamburg Synchrotron Radiation Laboratory (HASYLAB) for beam time granted in the frame of project I-2011-0087.

References

¹ Stribeck, N.; Zeinolebadi, A.; Harpen, F.; Luinstra, G. A.; Eling, B.; Botta, S. *Macromolecules* **2013**, *46*, 4041.

² Stribeck, N. *J. Appl. Cryst.* **2001**, *34*, 496.