Elongational Viscosities of Polymethylmethacrylate / Nano-Clay Composites

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Abstract:
The elongational flow of polymethylmethacrylate / nano-clay composites was studied during stressing and creep experiments using a Münstedt tensile rheometer (MTR). The dispersion of the nano-clay was controlled by means of transmission electron microscopy (TEM) and the layer distance was measured with X-ray diffraction (XRD). With growing volume fraction of the filler an increase of the viscosity is observed under constant strain rate and constant stress conditions. The results for the elongational viscosities for both modes are consistent with each other. Furthermore, a strain softening behavior can be measured, which is the more pronounced the higher the nano-clay content is. As the Trouton rule is not valid, deviations from the linear behaviour are related to an envolope curve for the elongational viscosities instead of the threefold zero shear viscosity.

Zusammenfassung:
Die dehnrheologischen Eigenschaften von Polymethylmethacrylat/Schichtsilikat Nanokompositen wurden in Spann- und Kriechversuchen mit einem Dehnrheometer nach Münstedt (MTR) untersucht. Die Verteilung des Füllstoffs wurde mittels Rasterelektronenmikroskopie überprüft und der Schichtabstand der Silikatplättchen mittels Röntgendiffraktometrie (XRD) gemessen. Mit steigendem Füllstoffgehalt wird bei konstanter Dehnung bzw. konstanter Spannung ein Anstieg der Viskosität beobachtet. Die Ergebnisse der Dehnviskositäten aus Spann- und Kriechversuchen sind dabei auch quantitativ konsistent. Desweiteren führt die Füllstoffzugabe zu einem dehnentfestigenden Verhalten der Komposite, welches umso ausgeprägter ist, je höher der Schichtsilikatgehalt wird. Da die Trouton Regel nicht angewendet werden kann, werden Abweichungen vom linearen Verhalten nicht auf das Dreifache der Schernullviskosität, sondern auf die Einhüllende der Dehnviskositätskurven bezogen.

Résumé:
Le comportement mécanique sous écoulement élongationnel de nanocomposites de polyméthacrylate de méthyle / silicates lamellaires a été étudié en mode écoulement et en mode fluage au moyen d'un rhéomètre élongationnel de type Münstedt (MTR). La dispersion des nanoparticules de silicates a été contrôlée par microscopie électronique à transmission (TEM) et la distance entre les lamelles a été mesurée par diffraction de rayons X (XRD). Lorsque la fraction volumique des nanoparticules augmente, une augmentation de la viscosité peut être observée, aussi bien à déformation constante qu'à contrainte constante. Les résultats de la viscosité élongationnelle sont ainsi quantitativement consistants entre les deux modes. De plus l'ajout de silicates fait apparaître un comportement d'adoucissement mécanique du composite, d'autant plus prononcé que la fraction volumique des nanoparticules augmente. Comme la règle de Trouton n'est pas applicable, les déviations par rapport au comportement linéaire sont à relier à la courbe enveloppant les viscosités élongationnelles et non pas au triple de la viscosité à gradient nul.

Key words: nano-clay, polymethylmethacrylate, uniaxial elongation, elongational viscosity, stressing experiment, creep experiment

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The elongational and shear measurements were repeated several times with different measuring modes to eliminate any possibility of measuring artefacts. As the viscosity of PMMA is very sensitive to temperature changes, the temperature of 180°C was checked with an external temperature sensor for the MTR and the ARES. To exclude any temperature deviations PS 158K, as well a polymer with a viscosity very sensitive to changes in temperature, was measured with the same apparatuses at the same conditions. Here the Trouton-rule is valid as can be seen in Figure 10. The envelope of the transient elongational viscosity $\eta_e^+(t)$ and the three-fold transient shear viscosity $\eta_o^+(t)$ fit to each other. Linster and Meissner found similar results for PS 158K [17]. Therefore, temperature mistakes can be excluded when looking for the reasons for the deviation from the Trouton rule.

It is furthermore conceivable that the silicone oil in the oil bath of the elongational rheometer diffuses into the polymer sample. Here the oil molecules could act as plasticizer. However, this would cause a decrease of the elongational viscosity and therefore a factor for the Trouton-rule below 3 and not above.

As the incompressibility of a material is a requirement for the Trouton-rule it was checked via pvT-measurements if this is fulfilled for PMMA. Within the experimental errors no compressibility was found for a pressure range comparable to the stresses applied in the elongational experiments. Therefore, it cannot be clarified why there is a deviation for the Trouton rule for the unfilled PMMA. In Figure 11 and 12 the transient elongational viscosities and the transient shear viscosities are plotted for highly filled polymer / nano-clay composites. For the PMMA / nano-clay composites and the PS / nano-clay composites the Trouton-rule is not valid. For the PMMA / nano-clay composite with a volume fraction of 8.9 % clay the transient enveloping elongational viscosity $\eta_e^+(t)$ is 10 times higher than $\eta_o^+(t)$, for the PS / nano-clay composites with a volume fraction of 4.8 % of clay it is 3.5 times the transient shear viscosity $\eta_o^+(t)$.

A deviation from the Trouton-rule for filled systems is described in literature several times. Takahashi et al. [8] observed a deviation from the Trouton-rule for LDPE filled with anisotropic glass fibres and explained it by the different orientation of glass fibres in elongational and shear samples. The deviation from the Trouton-rule for polymer / nano-clay composites could similarly be attributed to the different orientation of clays in elongational and shear samples as described in Figure 1. There is an alignment of clay in extrusion direction in elongational samples whereas the distribution in the shear samples is random.

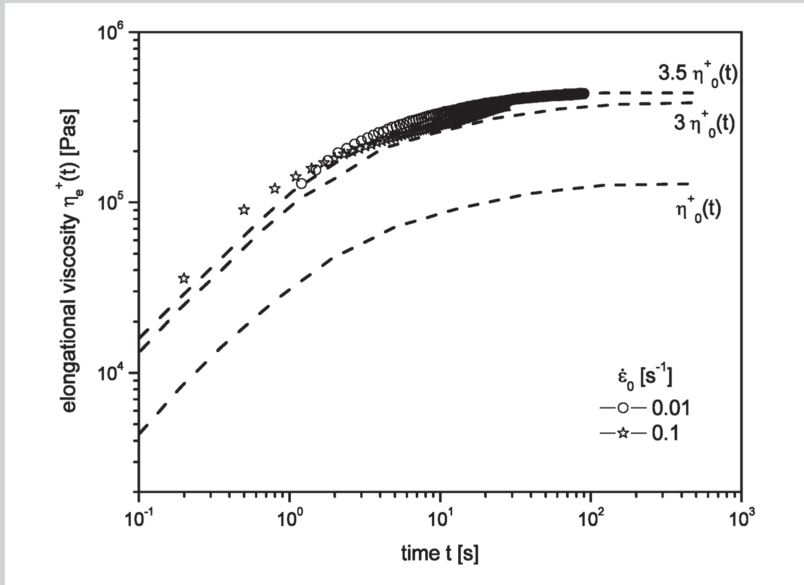

Figure 12: Transient elongational and shear viscosity of PS / 4.8 vol% nano-clay at 180°C.

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REFERENCES

[1] Okamoto M, Nam PH, Maiti P, Kotaka T, Hasegawa N, Usuki A: A House of Cards Structure in Polypropylenclay Nanocomposites under Elongational Flow, Nano Letters 1 (2001) 295-298.

[2] Dong GS, Tae JK, Jae RY: Rheological characterization of polymer-based nanocomposites with different nanoscale dispersions, e-Polymers (2005) 1-14.

[3] Kotsilkova R: Rheology-Structure Relationship of Polymer/Layered Silikate Hybrids, Mechanics of Time-Dependent Materials 6 (2002) 283-300.

[4] Kotaka T, Kojima A, Okamoto M: Elongational flow optorheometer-(EFOR), Rheol. Acta 36 (1997) 646-656.

[5] Gupta RK, Pasanovic-Zujo V, Bhattacharya SN: Shear and extensional rheology of EVA/layered silicate-nanocomposites, J. Non-Newt. Fluid Mech. 128 (2005) 116-125.

[6] Park JU, Kim JL, Kim DH, Ahn KH, Lee SJ: Rheological behavior of polymer / layered silicate nanocomposites under uniaxial extensional flow, Macromol. Res. 14 (2006) 318-323.

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[7] Münstedt H, Kurzbeck S, Egersdörfer L: Influence of molecular structure on rheological properties of polyethylenes II. Elongational behaviour, Rheol. Acta 37 (1998) 21-29.
[8] Takahashi T, Takimoto JI, Koyama K: Uniaxial elongational viscosity of various molten polymer composites, Polymer Composites 20 (1999) 357-366.
[9] Kojima Y, Usuki A, Kawasumi M: Novel prefered orientation in injection-molded nylon 6-clay hybrid, Journal of Polymer Science, Part B: Polymer Physics 33 (1995) 1039-1045.
[10] Feng M, Gong F, Zhao C, Chen G, Zhang S, Yang M: Effect of clay on the morphology of blends of poly(propylene) and polyamide 6/clay nanocomposites, Polymer Inter. 53 (2004) 1529-1537.
[11] Kobayashi M, Takahashi T, Takimoto J, Koyama K: Influence of glass beads on the elongational viscosity of polyethylene with anomalous strain rate dependence of the strain hardening, Polymer 37 (1996) 3745-3747.
[12] Schmidt M: Scher- und dehnrheologische Untersuchungen an Suspensionen auf der Basis sphärischer Füllstoffe., Ph.D. Thesis, Shaker Verlag, Aachen (2000).
[13] Takahashi T, Wu W, Toda H, Takimoto JI, Akatsuka T, Koyama K: Elongational viscosity of ABS polymer melts with soft or hard butadiene particles, J. Non-Newt. Fluid Mech. 68 (1997) 259-269.
[14] Takahashi T, Nakajima H, Mascubuchi Y, Takimoto JI, Koyama K: Strain-hardening property and internal deformation of polymer composite melts under uniaxial elongation, Sen-Igkkaishi 54 (1998) 538-543.
[15] Batchelor GK: The stress generated in a non dilute suspension of elongated particles by pure straining motion, J Fluid Mech 46 (1971) 813-829.
[16] Goddard GD: The stress field of slender particles oriented by a non newtonion extensional flow, J Fluid Mech 78 (1976) 177-206.
[17] Linster JJ, Meissner J: Melt elongation of a commercial poly(methyl methacrylate) product and a commercial polystyrene, Makromol. Chem. 190 (1989) 599-611.

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