Effect of Spherical Iron Silicon (FeSi) Microparticles on the Viscosity Behaviour of Polypropylene Melt

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Abstract:
In this study the steady flow viscosity, complex viscosity and relative viscosity of PP/FeSi composite melts with filler contents up to x =0.7 (70 vol.%) of spherical Iron Silicon (FeSi) microparticles (in 10 vol.% steps) with diameter of d < 106 μm have been investigated. Plate-plate and capillary rheometry at different shear rate and angular frequency in the range from 0.12 to 16000 s^{-1} (rad/s) were used. The results show an inflection point at high filler contents $x \geq 0.4$ (40 vol.%) and low shear rates (< 1 s^{-1}) caused by particle/particle interactions. With increasing shear rate and angular frequency the typical shear thinning flow behaviour of polymer melts was found for all investigated filler contents. The viscosity increases with increasing filler content at constant shear rate and angular frequency. Time-temperature-superposition (TTS) and Cox-Merz relation were fulfilled at filler contents up to x =0.3 (30 vol.%). The results of complex viscosity were normalized to a superimposed master curve. The three parameter of the new modified Carreau model were calculated for PP melt and shifted by two factors depending on the filler content. Based on these modifications, the complex viscosity was calculated for each filler content up to x = 0.3. The complex viscosity graphs were reduced to a general master curve of the investigated PP/FeSi composites up to x = 0.3. Finally, the relative viscosity of the examined composites shows the best fit to the Quemada model.

Zusammenfassung:
Die vorliegenden Ergebnisse beschreiben den Einfluss von sphärischen Eisensilizium (FeSi) Mikropartikeln auf die stationäre, komplexe und relative Viskosität in PP/FeSi-Kompositen mit Füllgraden bis zu 70 Vol.% (in 10 Vol.% Schritten), ermittelt in Platte/Platte und Hochdruckkapillar-Rheometrie. Der Scherraten- und Winkelfrequenzbereich wurde von 0.12 bis 16000 s^{-1} (rad/s) variiert. Für kleine Scherraten (< 1 s^{-1}) und mittlere bis hohe Füllgrade $x \geq 0.4$ konnte ein Fließgrenze gezeigt werden, die aus den Partikel/Partikel-Wechselwirkungen resultiert. Mit steigender Scherrate und Winkelfrequenz konnte das scherverdünnende Viskositätsverhalten von Polymerschmelzen bei allen untersuchten Füllgraden dargestellt werden. Dabei wurde die Viskositätskurve mit steigendem Füllgrad zu höheren Viskositätswerten verschoben. Die Zeit-Temperaturabhängigkeit (TTS) konnte für Füllgrade bis zu x = 0.3 (30 Vol.%) gezeigt werden, wodurch die Ergebnisse der komplexen Viskosität bis zu einem Füllgrad von x = 0.3 mittels der Cox-Merz-Beziehung zu einer Masterkurve überlagert wurden. Die Parameter des neu modifizierten Carreau-Modells wurden für PP-Schmelze ermittelt und durch zwei füllgradabhängige Verschiebefaktoren bei Füllgraden bis zu x = 0.3 beschrieben. Daraus resultierend wurde eine Masterkurve für PP/FeSi-Komposite bei Füllgraden bis zu x = 0.3 generiert. Die relative Viskosität kann anhand des Modells nach Quemada im betrachteten Füllgradbereich hinreichend genau beschrieben werden.

Résumé:
Dans cette étude la viscosité d'écoulement stationnaire, la viscosité complexe et la viscosité relative des fontes de PP/FeSi avec des teneurs en charge jusqu'à x = 0.7 (70 vol.%) de microparticules sphériques de (FeSi) (de 10 vol.% d'étapes) avec des diamètres de d<106 µm ont été étudiés. Plate/plate et rhéométrie capillaire à différents taux de cisaillement et de fréquence angulaire de l'ordre de 0.12 à 16000 s^{-1} (rad/s) ont été utilisés. Les résultats montrent un point d'inflexion aux teneurs élevées $x \geq 0.4$ (40 vol.% en fines) et à bas taux de cisaillement (< 1 s^{-1}) provoqués par la particule/particule-interactions. Avec l'augmentation du taux de cisaillement et de fréquence angulaire le comportement typique d'éclaircissement d'écoulement des fontes de polymère a été trouvé pour toutes les teneurs en charge étudiées. La viscosité augmente avec l'augmentation de la teneur en charge au taux constant de cisaillement et de fréquence angulaire. la Temps-température-superposition (TTS) et la relation de Cox-Merz ont été accomplies aux teneurs en charge jusqu'à x = 0.3 (30 vol.%). Les résultats de la viscosité complexe ont été normalisés à une courbe principale superposée. Les trois paramètres du nouveau modèle modifié de Carreau ont été calculés pour les fontes de PP et décalés de deux facteurs en fonction de la teneur en charge. Sur la base de ces modifications, la viscosité complexe a été calculée pour chaque teneur en charge jusqu'à x = 0.3. Les courbes de viscosité complexe ont été réduites à une courbe principale générale des composés étudiés de PP/FeSi jusqu'à x = 0.3. Enfin, la viscosité relative des composites examinés montre le meilleur ajustement au modèle de Quemada.

Key words: viscosity, composites, Cox-Merz rule, Carreau model, magnetic particles

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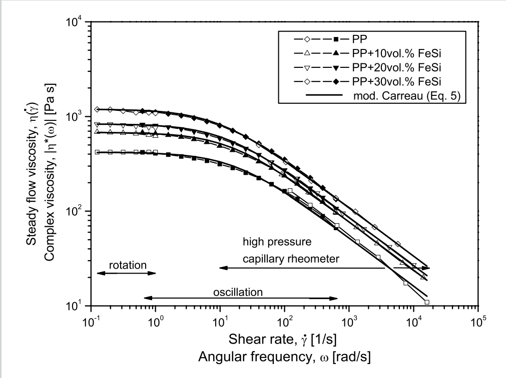

Figure 11 (left above): Comparison and extrapolation of modified Carreau model calculation (Equation 5) and experimental results for PP/FeSi composites with filler contents up to x = 0.3.

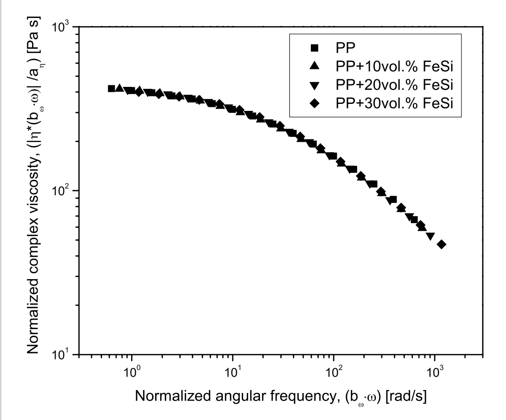

Figure 12 (left below): Master curve of normalized complex viscosity of PP/FeSi composites with filler contents up to x = 0.3.

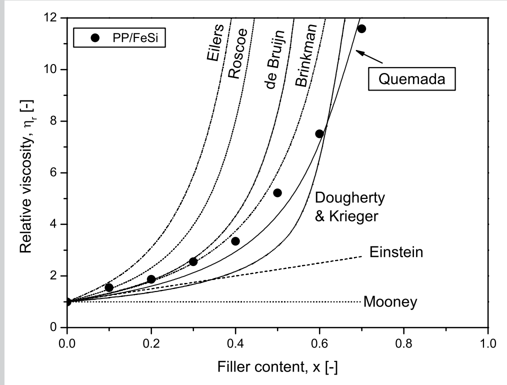

Figure 13 (right): Comparison of relative viscosity measured for PP/FeSi composites at constant shear rate (1 s^{-1}) and calculated by theoretical models (Table 1 at $k_o = [\eta] = 2.5$, $x_{max} = 0.74$ and $S = 1.35$).

low shear rates the experimental results fit to the models according to Roscoe ($x \leq 0.1$), de Bruijn ($x \leq 0.3$) as well as Brinkman ($x \leq 0.4$). The experimental results coincide approximately with the Quemada model at filler contents up to $x = 0.7$. In literature, suspensions in polymer melt with particles ($d = 0.7\ \mu$m) were described at filler content up to $x = 0.3$ with maximum packing density of $x_{max} = 0.68$ by the model obtained by Dougherty-Krieger [38]. For other particle sizes (up to $d = 2.7\ \mu$m) an increase of relative viscosity, equal to the results in Figure 13, was predicted. The approach has to be limited to a shear limit, large enough to prevent inflection points caused by particle/particle interactions, but small enough to avoid any unstable effects or turbulence in the flow and/or damage of the particles. Furthermore, shear force has to overcome sedimentation effects and Brownian motion.

5 CONCLUSIONS

Rheological experiments using rotational as well as capillary rheometer were carried out to determine the effect of spherical FeSi microparticles on the flow behaviour of polypropylene (PP) melt at filler content up to $x = 0.7$ (70 vol.%). In general an increase of steady flow and complex viscosity was found with increasing filler content. At high filler content ($x > 0.3$) particle/particle interactions were observed by means of an inflection point at low shear rates (< 1 s^{-1}). In regard to the Cox-Merz relation, the experimental results were superimposed at filler content $x \leq 0.3$ in a wide measuring range to resulting viscosity graphs. The three-parameter Carreau model was applied to the complex viscosity and the Carreau parameters were calculated for PP melt. The addition of FeSi microparticles results in a shift of the viscosity graph to higher viscosity and lower angular frequency (shear rate). This displacement was described by two shift factors, a_η and b_ω. The vertical shift factor a_η increases almost linear and the horizontal shift factor b_ω decreases linear with filler content until $x = 0.3$. The modified Carreau model is not able to describe the inflection point at low shear rates (< 1 s^{-1}) and high filler content ($x > 0.4$), but fits to the results at filler content up to $x = 0.3$. The new shift factors a_η and b_ω can be applied to reduce the complex viscosity graphs to a master curve for $x \leq 0.3$. Furthermore, relative viscosity of PP/FeSi composites approximately correlate to the results of Quemada model at all examined filler contents. The viscosity of PP/FeSi composite melts is significantly increased by adding filler materials, which significantly influence the process ability of these composite materials for example in extrusion and injection moulding process. Transfer to other polymer/particle compositions will be done in future work.

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