DETERMINING THE AGEING OF POLYPROPYLENE NANOCOMPOSITES USING RHEOLOGICAL MEASUREMENTS

STEPHAN LASKE[1]*, ANDREAS WITSCHNIGG[1], HANNELORE MATTAUSCH[1], MILAN KRACALIK[1], GERALD PINTER[2], MICHAEL FEUCHTER[2], GUENTHER MAIER[3], CLEMENS HOLZER[1]

[1] Polymer Processing, Montanuniversitaet Leoben, Otto Gloeckel-Strasse 2, 8700 Leoben, Austria
[2] Materials Science and Testing of Plastics, Montanuniversitaet Leoben, Otto Gloeckel-Strasse 2, 8700 Leoben, Austria
[3] Materials Center Leoben Forschung GmbH, Roseggerstrasse 12, Leoben 8700, Austria

* Corresponding author: stephan.laske@unileoben.ac.at
Fax: x43.3842.4023502

Received: 20.9.2011, Final version: 27.1.2012

ABSTRACT:

The principle of silicate layer reinforcement in a polymer matrix is known as the formation of a 3D network of single layers. Nevertheless there is still a lack of knowledge about the physical ageing of nanocomposites respectively the stability of this network over time. As most of the nanocomposite applications have a more or less long-term shelf life respectively storage time, the investigation of the storage-time dependent behavior of the layered 3D structure in a polymer matrix is of major interest. In this study, the rheological (shear and elongational) properties of different polypropylene nanocomposites were measured using a cone-plate rheometer and a Rheotens apparatus. To evaluate the structural stability over time, the samples were measured immediately after processing and after defined periods (18 and 36 months) stored under constant conditions. Furthermore the network structure was determined using XRD and TEM measurements. The results show, that, depending on the clay rate and especially the degree of exfoliation, the rheological properties are changing significantly. Thereby chain-splitting caused by photo-oxidative degradation, leading to a loss in molecular weight, as well as a weakened 3D network by reverse diffusion of the polymer chains out of the clay gallery and/or reagglomeration of the nanoparticles are the two main factors.

ZUSAMMENFASSUNG:

Das Prinzip der Aufbereitung von Polymeren mit Schichtsilikaten wird generell durch die Bildung eines 3D Netzwerkes der einzelnen Schichten erklärt. Diesbezüglich gibt es noch immer wenig Wissen über das physikalische Altern von Nanocomposites beziehungsweise über die Stabilität dieses Netzwerkes in Abhängigkeit von der Zeit. Da die meisten Nanocomposite-Anwendungen eine mehr oder minder lange Lebensdauer bzw. Lagerungszeit haben, ist das zeitabhängige Verhalten dieser 3D Schichtstruktur von großem Interesse. In dieser Studie wurden die (scher- und dehn-) rheologischen Eigenschaften von unterschiedlichen Polypropylen-Nanocomposites unter Verwendung eines Kegel-Platte-Rheometers und einer Rheotensapparatur gemessen. Um die Strukturstabilität in Abhänghigkeit von der Zeit zu bestimmen, wurden Probekörper unmittelbar nach der Herstellung und nach definierten Zeiträumen (18 beziehungsweise 36 Monate unter definierten Bedingungen) untersucht. Des Weiteren wurde die Struktur mittels XRD und TEM untersucht. Die Ergebnisse zeigen, dass abhängig von der Menge an Schichtsilikat und im Speziellen des Exfolierungsgrades die rheologischen Eigenschaften sich stark unterscheiden. Dabei sind sowohl Kettenspaltung durch photo-oxidativen Abbau, der zu einer Reduktion der Molmasse führt, als auch ein durch umgekehrte Diffusion der Ketten aus den Zwischenschichten beziehungsweise Reagglomeration geschwächtes 3D-Netzwerk die beiden wesentlichen Faktoren.

RÉSUMÉ:

Le principe du renforcement d'une matrice polymère par de la silice est connu comme la formation d'un réseau tridimensionnel de couches simples de silice. Néanmoins, il n'existe pas d'explication pour le vieillissement physique des nanocomposites, c-à-d pour la stabilité dans le temps du réseau. Comme la plupart des applications des nanocomposites contemple des durées de vie plus ou moins longues, l'étude du comportement de la structure tridimensionnelle au cours du temps de stockage est d'un intérêt majeur. Dans cette étude, les propriétés rhéologiques (en cisaillement et en élongation) de différents nanocomposites de polypropylène ont été mesurées en utilisant un rhéomètre cône-plan et un appareil Rheotens. Afin d'évaluer la stabilité structurelle au cours du temps, les échantillons ont été mesurés immédiatement après la mise en œuvre et après des périodes de stockage définies (18 et 38 mois) dans des conditions constantes. De plus, la structure du réseau a été déterminée à l'aide de la diffraction de RX et des mesures de TEM. Les résultats montrent que, en fonction de la vitesse et spécialement le degré d'exfoliation de l'argile, les propriétés rhéologiques changent de manière significative. Ainsi, la scission de chaîne causée par la dégradation photo-oxydative, qui conduit à une perte de la masse

© Appl. Rheol. 22 (2012) 24590 DOI: 10.3933/ApplRheol-22-24590

Figure 11 and table 6 show the results of the elongation tests right after and 18 and 36 month after production. The results of the elongation measurements reflect the same trend as the results from the rotational rheometer. Depending on the degree of exfoliation and the clay content the drawing force is decreasing more or less. The most exfoliated structures (e.g. 300 rpm or 15 wt% compatibilizer or geometry 2) show the highest level of 3D physical network and after storage the largest decrease in drawing force. The same can be seen with the clay content, as the sample with 20 wt% clay has a larger loss in drawing force, than that with 5 wt%. Generally spoken, the more the 3D network is established, the more sensitive it reacts on ageing respectively the easier it is damaged.

4 CONCLUSIONS

In this work the rheological (shear as well as elongational) properties of different nanocomposites (varying formulation and process conditions) where measured right after respectively 18 and 36 months after production. The results show clearly, that the long-term stability is massively influenced by the size of the reactive filler surface (interface) monitored by the clay content and the degree of exfoliation. With increasing clay content as well as a higher degree of exfoliation the possible interface to the polymer matrix is increasing, leading to a faster and higher material degradation. Additionally, the results of the rheological experiments show clearly the two factor degradation mechanism. Firstly, the chain splitting caused by photo-oxidative degradation leading to a loss in molecular weight shown by the decreased zero shear viscosity (Newtonian plateau). This well known chemical factor is mainly influenced by the interface between polymer and the particles. When using nanofillers, this effect is multiplicated because of the nano-scale particles and the resulting massively increased interface.

The second factor is the weakened 3D network displayed in the range of higher angular frequencies by a decrease of the complex viscosity (shear thinning range) as well as a higher loss in drawing force respectively melt strength. This physical factor can be explained by the reverse diffusion of the polymer chains out of the clay gallery and/or reagglomeration of the nanoparticles, when the distance between the layers is too small to overcome the interparticular forces. This can happen in intercalated as well as high-filled systems. The grafted compatibilizer with very low graft grades has only minor influence itself but is a major factor to achieve a high exfoliated nanocomposite. The degradation incidents are occurring very fast, as no difference could be seen in the 18 months respectively 36 months samples. Therefore also a short-term storage or shelf-life is affected.

REFERENCES

[1] Gilman JW, Kashiwagi T, Lichtenhan JD: Nanocomposites: A revolutionary new flame retardant approach, Sampe J. 33 (1997) 40.

[2] Ray SS, Okamoto M: Polymer/layered silicate nanocomposites: a review from preparation to processing, Progr. Polym. Sci. 28 (2003) 1539.

[3] Witschnigg A, Laske S, Kracalik M, Feuchter M, Pinter G, Maier G, Märzinger W, Haberkorn M, Langecker GR, Holzer C: In-line characterization of polypropylene nanocomposites using FT-NIR, J. Appl. Polym. Sci., 117 (2010) 3047.

[4] Laske S, Kracalik M, Feuchter M, Pinter G, Maier G, Märzinger W, Haberkorn M, Langecker GR: FT-NIR as a determination method for reinforcement of polymer nanocomposites, J. Appl. Polym. Sci. 114 (2009) 2488.

[5] Ray SS, Yamada K, Okamoto M, Ueda K: New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology, Polymer 44 (2003) 857.

[6] Krishnamoorti R, Giannelis EP: Rheology of End-Tethered Polymer Layered Silicate Nanocomposites, Macromolecules 30 (1997) 4097.

[7] Wagener R, Reisinger TJG: A rheological method to compare the degree of exfoliation of nano-composites, Polymer 44 (2003) 7513.

[8] Laske S, Kracalik M, Gschweitl M, Langecker GR: Abhängigkeit des Exfolierungsgrades von Silikatschichten in einer Polymermatrix vom Compatibilizer – Nanoclay Mischungsverhältnisses, Proceedings, International Conference Polymermischungen, Bad Lauchstaedt, Germany (2007).

[9] Laske S: Verbesserung der rheologischen Eigenschaften von unverzweigtem Polypropylen mit Nanofüllstoffen im Hinblick auf das Extrusionsschäumen, M.Sc. Thesis, University of Leoben (2005).

[10] Cabedo L, Plackett D, Gimenez E, Lagaron J M: Studying the degradation of polyhydroxybutyrate-co-valerate during processing with clay-based nanofillers, J. Appl. Polym. Sci. 112 (2009) 3669

[11] Pfaendner R: Additives to Enhance Manufacturing and Long-term Performance of Nanocomposites, Proceedings NanoEurope 2009.

[12] Lewicki JP, Liggat JJ, Pethrick RA, Patel M, Rhoney I: Investigating the ageing behavior of polysiloxane nanocomposites by degradative thermal analysis, Polym. Degr. Stab. 93 (2008) 158.

[13] Li J, Yang R, Yu J, Liu Y: Natural photo-aging degradation of polypropylene nanocomposites, Polym. Degr. Stab. 93 (2008) 84.

[14] Vlasveld DPN, Bersee HEN, Picken SJ: Creep and physical aging behaviour of PA6 nanocomposites, Polymer 46 (2005) 12539.

[15] Fordiani F, Aubry T, Grohens Y: Structural changes evidenced by rheology in PPgMA nanocomposites during oxidative ageing, J. Appl. Polym. Sci. 114 (2009) 4011.

[16] Ren J, Silva SS, Krishnamoorti R: Linear Viscoelasticity of Disordered Polystyrene–Polyisoprene Block Copolymer Based Layered-Silicate Nanocomposites, Macromolecules 33 (2000) 3739.

[17] Solomon MJ, Almusallam AS, Seefeldt KF, Somwangthanaroj A, Varadan P: Rheology of Polypropylene/Clay Hybrid Materials, Macromolecules 34 (2001) 1864.

[18] Vermant J, Ceccia S, Dolgovskij MK, Maffettone PL, Macosko CW: Quantifying dispersion of layered nanocomposites via melt rheology, J. Rheol. 51 (2007) 429.

[19] Galindo-Rosales FJ, Moldenaers P, Vermant J: Assessment of the Dispersion Quality in Polymer Nanocomposites by Rheological Methods, Macromol. Mater. Eng. 296 (2011) 331.

[20] Bachelli F: A Rheotens-based setup for the constant strain rate uniaxial extension of uncured elastomers, Rheol. Acta, 46 (2007) 1223.

[21] Burghelea TI, Griess HJ, Münstedt H: Comparative investigations of surface instabilities (“sharkskin”) of a linear and a long-chain branched polyethylene, J. Non-Newtonian Fluid Mech. 165 (2010) 1093.

[22] White JL, Yamane H: A collaborative study of the stability of extrusion, melt spinning and tubular film extrusion of some high-, low- and linear-low density polyethylene samples, Pure App. Chem. 59 (1987) 193.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org