

RHEOLOGY INNOVATION IN THE STUDY OF MIXING CONDITIONS OF POLYMER BLENDS DURING CHEMICAL REACTION

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Received: 7.1.2005, Final version: 13.7.2005

ABSTRACT:

Polymer melts can be mixed with many monomers, plasticizers, antistatics or foaming additives. Properties of such mixtures can change during blending because of chemical reactions like polymerization or crosslinking. The process may be carried out either in stirred tanks, extruders or in motionless mixers. In this paper we focused on the mixing time and the diffusion time of reagent, plasticizer and polymer thanks to rheological tools, and on the way how rheological properties can be studied during chemical reaction in polymer blending. The concept of rheoreactor and Couette analogy were introduced since we have a reactor on our disposal that can mix solution and measure rheological properties without taking sample. This apparatus appears to be an appreciable tool in complement of internal mixers that are specific to polymer blending. For example, we show the importance of the competition between mixing time and reaction time for reactive systems.

ZUSAMMENFASSUNG:

Polymerschmelzen können mit vielen Monomeren, Weichmachern und antistatischen und schäumenden Additiven gemischt werden. Die Eigenschaften solcher Mischungen können sich während des Blendens aufgrund chemischer Reaktionen wie Polymerisation oder Vernetzung ändern. Die Verarbeitung kann entweder in Rührmischern, Extrudern oder statischen Mischern durchgeführt werden. Die Zielsetzung dieser Arbeit war die Untersuchung der Mischzeit und der Diffusionszeit des Reagens, des Weichmachers und des Polymeren mittels rheologischer Methoden sowie die Möglichkeit, wie rheologische Eigenschaften während der chemischen Reaktion beim Blenden der Polymere untersucht werden können. Das Konzept des Rheoreaktors und der Couette-Analogie werden eingeführt, da uns ein Reaktor zur Verfügung steht, der Lösungen mischen kann und ohne Probenentnahme die rheologischen Eigenschaften messen kann. Dieses Messgerät scheint ein wertvolles Instrument zu sein in Ergänzung zu internen Mischern, die zum Blenden von Polymeren konstruiert worden sind. Beispielsweise zeigen wir die Bedeutung der Konkurrenz zwischen Misch- und Reaktionszeit für die reaktiven Systeme.

RÉSUMÉ:

French Abstract: Les polymères fondus peuvent être mélangés à différents monomères, plastifiants, aditifs anti-statiques ou de moussage. Les propriétés de tels mélanges peuvent évoluer pendant l'opération de mélangeage si des réactions chimiques comme des polymérisations ou réticulations ont lieu. Ce procédé peut être mené dans des réacteurs agités, des extrudeuses ou des mélangeurs statiques. Dans cet article, nous avons étudié de près le temps de mélange, le temps de diffusion des réactifs, des plastifiants, des polymères grâce à des outils rhéologiques et la manière dont nous pouvions suivre les propriétés rhéologiques lors d'une réaction chimique dans un mélange polymère. Nous avons alors introduit le concept de rhéoréacteur et d'analogie Couette. Il s'agit d'un réacteur sous forme de cuve agitée qui peut donc mélanger des solution et mesurer des propriétés rhéologiques en s'affranchissant du prélèvement d'échantillon. Cet appareil est un outil fort appréciable et permet un bon complément d'informations au mélangeur interne traditionnel qui est plus spécifique au mélange de polymères. Par exemple, nous montrons l'importance de la compétition entre le temps de mélange et le temps de réaction pour les systèmes réactifs.

KEY WORDS: Polymer blend, rheoreactor, mixing conditions, crosslinking, diffusion

© Appl. Rheol. 15 (2005) 314–325

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Applied Rheology
Volume 15 · Issue 5
<http://www.appliedrheology.org>

that of literature data for networks based on low molecular weight precursor ($n \approx 0.7 - 0.8$ [25]), whereas EVA33-400 can be assimilated to an intermediate molecular weight precursor ($n \approx 0.4 - 0.7$). In a previous work [26] we have reported a value of $n = 0.5$ for a high molecular weight precursor.

5 CONCLUSION

On the one hand, a comparison between rheological data from classical parallel plate geometry and those from a rheoreactor permitted to justify the use of the rheoreactor with melt polymer. On the other hand, the complementary uses of a rheoreactor, a classical rheometer and an internal mixer allowed to establish a mixing law for the incorporation of small quantities of low viscous liquid into highly viscous polymer melt. The more in-depth study of diffusion in polymer helped us to understand the relationships between macromixing and diffusion and the effect of the striation thickness on the diffusion rate.

Besides these results, the rheoreactor allowed us to point out mixing phenomena and reagent dispersion during a polymer crosslinking. Without considering viscous dissipation, the kinetics of EVA crosslinking is all the more fast that shear rate is high when crosslinking reagent are not premixed. Moreover, when the reagents are premixed at low temperature in order to melt EVA, we should distinguish two cases depending on the shear rate range. At very low shear rates, EVA crosslinks faster when shear rate decreases, and a more usual tendency is observed for higher shear rates, that is to say the kinetics increases with shear rate. This was possibly due to a competition between frequency meeting and contact time between active functions. In addition, this phenomenon shows the importance of the competition between mixing time and reaction time. Finally, a very interesting advantage of the rheoreactor concerns the measurement of the viscoelastic properties of a material during mixing. For example, the gel point can be accurately determined in situ.

On the other hand, we have focused in this paper on the diffusion and mixing time in an EVA matrix. Indeed, as the material experiences a shear rate action during mixing, a relation between mixing time and diffusion time was established.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Multibase Company for making this work possible. Discussion with Daniel Milesi, the research and development manager of Multibase, was especially fruitful.

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