Application of Creep Test to Obtain the Linear Viscoelastic Properties at Low Frequency Range for Polyethylene Melts

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Abstract:
We applied the creep test that allows obtaining rheological information in the long-time domain (low-frequency range) that is not reachable by the use of the dynamic frequency sweep test to characterize the linear viscoelastic properties of polyethylene melts for industrial research and development. We considered the time scale for the creep test and what this imposes as limitations on the ability to make such measurements on a large group of samples. For the long- time creep test in the molten state at high temperatures, polyethylene demands very good stabilization with anti-oxidation packages to allow one to obtain useful data. The time for the sample relaxation from mounting and trimming in the parallel plate geometry of the controlled-stress rheometer prior to initiation of a creep test was also considered. The issue of what stress level to use in the linear viscoelastic region was addressed as was the issue of signal to noise. The creep test was performed within 4 hours for practical use, and the frequency range was extended down 10^{-4} rad/s. We tested several polyethylene samples as examples taking account of above variables and showed that the data obtained by the creep method overlapped well with low frequency end of the dynamic frequency sweep data. By testing several high molecular weight resins having broad molecular weight distribution and/or long chain branching, we demonstrated the utility of this methodology.

Zusammenfassung:
Wir führten den Kriechversuch durch, um rheologische Informationen über das linear-viskoelastische Verhalten von Polyethylenschmelzen im Langzeitbereich (Bereich niedriger Frequenzen) für die industrielle Forschung und Entwicklung zu erhalten, die durch dynamische Frequenztests nicht gewonnen werden können. Die Zeitskala des Kriechversuchs und ihr Zusammenhang mit der Durchführbarkeit der Experimente wurde für eine große Gruppe von Proben untersucht. Für diese Langzeitkriechversuche in der Schmelze bei hohen Temperaturen ist für Polyethylen eine Stabilisierung durch Antioxidantien erforderlich. Die Zeit für die Relaxation der Probe und das sogenannte Trimmen in der parallelen Platte-Geometrie im spannungskontrollierten Rheometer vor dem Kriechversuch wurden ebenfalls betrachtet. Des Weiteren wurde der Wert der Spannung und das Signal zu Rausch-Verhältnis in Betracht gezogen. Der Kriechversuch wurde innerhalb von 4 Stunden für die praktische Anwendung durchgeführt, und der Frequenzbereich wurde bis 10^{-4} rad/s erweitert. Wir führten Tests an verschiedenen Polyethylen-Proben durch und zeigten, dass die Daten der Kriechversuche mit denen der Frequenztests im Überlappbereich übereinstimmten. An Tests mit Proben mit unterschiedlichen (relativ breiten) Molekulargewichtsverteilungen und/oder Langkettenverzweigung belegen wir die Nützlichkeit des Kriechversuchs.

Résumé:
Dans le but de caractériser les propriétés viscoélastiques de polyéthylènes fondus industriels dans le cadre d'études de recherche industrielle et de développement, nous avons appliqué le test de fluage qui permet d'obtenir des données rhéologiques dans le domaine des temps longs (domaine de basses fréquences), qui ne peut être atteint au moyen de tests dynamiques de balayage en fréquence. Nous avons considéré l'échelle de temps pour le test de fluage et ce que cela impose comme limitations sur la possibilité d'effectuer de telles mesures pour un large groupe d'échantillons. Pour le long test de fluage à l'état fondu à haute température, le polyéthylène requiert une très bonne stabilisation, qui est obtenue au moyen de méthodes antioxydantes, afin d'obtenir des données utiles. Le temps nécessaire à la relaxation de l'échantillon après l'insertion dans la géométrie plateau-plateau du rhéométre à contrainte imposée, avant de commencer le test de fluage, a aussi été considéré. La question de savoir quel niveau de contrainte à imposer pour obtenir le régime linéaire a aussi été étudiée, ainsi que le problème du ratio signal sur bruit. Pour des raisons pratiques, la durée du test de fluage a été limitée à quatre heures, et le domaine de fréquence a pu être étendu jusqu'à 10^{-4} rad/s. A titre d'exemple, nous avons testé plusieurs échantillons de polyéthylène en tenant compte des variables mentionnées ci-dessus. Nous montrons que les données obtenues avec le test de fluage se super-

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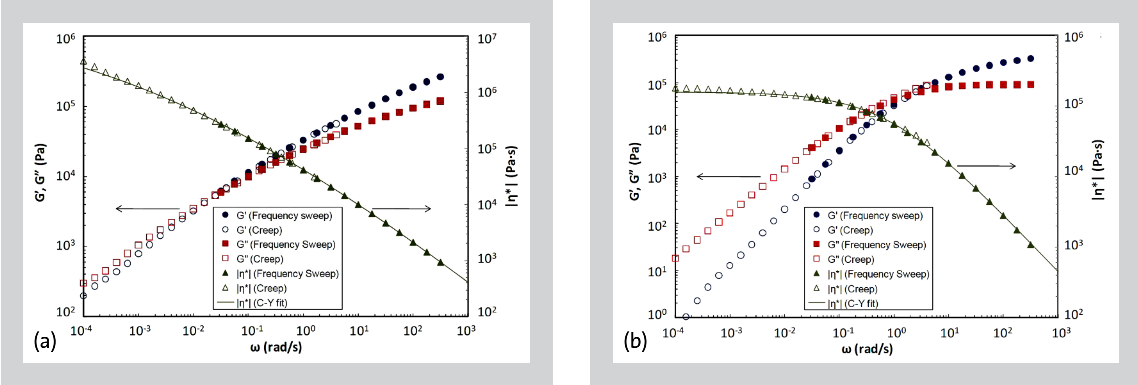

Figure 4 (above): Storage and loss moduli and complex viscosities as functions of frequency obtained by the dynamic frequency sweep (solid symbols) and converted from the creep test (open symbols) for (a) C4 and (b) D1 resins. Solid line is the C-Y fit to the frequency sweep data.

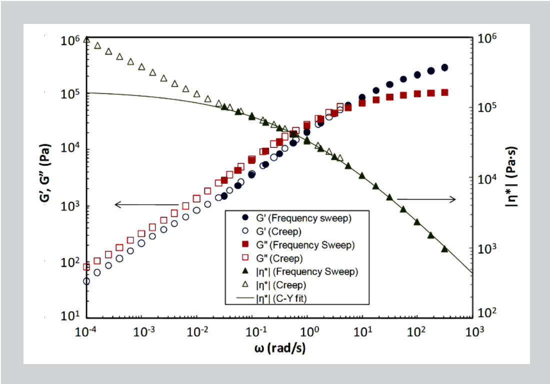

Figure 5 (left below): Storage and loss moduli and complex viscosities as functions of frequency obtained by the dynamic frequency sweep (solid symbols) and converted from the creep test (open symbols) for D3 resin. Solid line is the C-Y fit to the frequency sweep data.

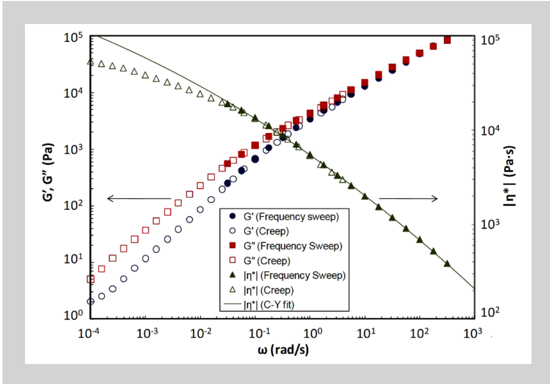

Figure 6 (right below): Storage and loss moduli and complex viscosities as functions of frequency obtained by the dynamic frequency sweep (solid symbols) and converted from the creep test (open symbols) for E1 sample. Solid line is the C-Y fit to the frequency sweep data.

the complex viscosities from the dynamic test is extrapolated to low frequencies to compare with the viscosities obtained from the creep test. These two sets of data from the creep and dynamic tests show very good agreement in the range of frequencies in which they overlap and demonstrate the accuracy of two different tests. The C-Y fits to the dynamic frequency sweep data give reasonable results for extrapolations in comparison to the low frequency data from the creep tests for these two samples.

Figure 5 shows the storage and loss moduli and complex viscosities obtained from the creep test and dynamic frequency tests for the D3 developmental resin which was developed to improve melt strength by increasing the high molecular weight component and long-chain branching. The dynamic frequency sweep data and the C-Y fits to these data are not able to capture the long-time characteristics of this sample. When the frequency window is extended to lower frequencies by using the creep measurement and analysis, the high viscosity features at the low frequencies can be revealed and provide correct and complete rheological information. Such behavior clearly suggests another "rise" to a lower Newtonian plateau region relating to this longer relaxation time component, something that was expected based on the molecular feature. Another example is shown in Figure 6 for the experimental resin E1. The viscosity curve obtained from the dynamic frequency sweep test appears to have a slight down-turn at low frequencies relative to the C-Y fitting curve. The extended viscosities from the creep measurement and analyses indeed show lower values than the extrapolated C-Y fitted curve. This demonstrates that the creep test provides more reliable rheological information at the low-frequency/long-time domain.

5 CONCLUSIONS

The creep test method is applied to obtain lower frequency viscosities for polyethylene resins in a shorter time than would be required to simply perform a frequency sweep down to the lower frequencies. In order to reliably perform the creep test on the polyethylene resins, which are very sensitive to thermal oxidation, it is critical to make sure that the resins contain enough stabilizers, approximately more than 0.4 weight % of anti-oxidants. The creep test needs to be conducted after 2000 seconds of waiting time after sample loading to relax the residual stress from sample trimming. In order to measure a wide range of samples without the need for an extensive search for the right stresses for each sample, the applied creep stress is empirically chosen to be the complex modulus $|G^*|$ at frequency of 0.01 rad/s multiplied by 0.04 based on multiple creep tests at different stresses on several polyethylene resins. The creep tests are performed for 10200 s, and the time-dependent creep compliances are converted to frequency-dependent dynamic data by calculating the retardation time spectra. By combining the dynamic and creep data, the frequency window is extended to 10^{-4} rad/s. The creep tests were performed on sever-

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al polyethylene resins where the standard frequency sweep test doesn't get close to reaching the plateau region and successfully demonstrated the utility of this methodology for practical use in industrial research and development.

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