RHEOLOGICAL MASTER CURVES OF CRYSTALLIZING POLYMER MIXTURES

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ABSTRACT:
We present a simple methodology for extending linear viscoelastic measurements of crystallizing polymers to the high-frequency regime, where usually crystallization kinetics represents an obstacle. The idea is to perform rapid quenches, below the melting temperature (which corresponds to the high-frequency region), account for the thermal equilibration and the very slow early stages of crystallization, and perform the measurements before really crystallization sets in, in the "quasi-equilibrium" state. Albeit tedious, when properly done, this method works remarkably well, as demonstrated for a particular polybutadiene mixture, and opens the route for obtaining rheological master curves in a wide variety of crystallizing polymers.

ZUSAMMENFASSUNG:
Wir stellen eine einfache Methode vor, um linear-viskoelastische Messungen von kristallisierenden Polymeren auf den hochfrequenten Bereich auszudehnen, in dem die Kristallisationskinetik üblicherweise ein Hindernis darstellt. Die Idee ist, schnell unterhalb der Schmelztemperatur (die dem hochfrequenten Bereich entspricht) abzukühlen, das thermische Gleichgewicht und die sehr langsamen, frühen Stadien der Kristallisation nachzuweisen und die Messungen in dem „quasi Gleichgewichtszustand" durchzuführen, bevor die Kristallisation wirklich einsetzt. Obgleich die Methode etwas aufwendig ist, wenn man sie korrekt durchführt, wie am Beispiel einer besonderen Polybutadien-Mischung gezeigt wird, funktioniert sie bemerkenswert gut und erschließt einen Weg, um rheologische Masterkurven für eine Vielzahl kristallisierender Polymere zu erhalten.

RÉSUMÉ:
Nous présentons une méthodologie simple pour étendre les mesures de viscoélasticité linéaire des polymères cristallisants au régime de hautes fréquences, où habituellement la cinétique de cristallisation représente un obstacle. L'idée est d'appliquer des refroidissements rapides en dessous de la température de fusion (qui correspond au régime de hautes fréquences), de tenir compte de l'équilibre thermique à obtenir et de la très lente cristallisation initiale, et de faire les mesures dans un état de «quasi-équilibre» avant que la cristallisation réelle ne prenne place. Malgré son caractère fastidieux, lorsqu'elle est appliquée correctement, cette méthode fonctionne remarquablement bien, comme le montre une étude faite avec un mélange particulier de polybutadiène. Cette méthode présente une perspective pour obtenir des courbes maîtresses rhéologiques d'une grande variété de polymères cristallisants.

KEY WORDS: Time-temperature superposition, polybutadiene, crystallizing polymer, crystallization, master curve

1 INTRODUCTION

The anionic synthesis of polybutadiene with alkyl lithium, which is used for controlling the polymerization process, yields a mixture of two microstructures, the 1,4-addition (that contains roughly equal amounts of cis and trans units) and smaller amounts of 1,2-addition (typically amounting to 5 - 12 %, as measured by NMR) [1 - 3]. The two microstructures possess clearly different glass transition temperatures (typically, from - 101 to - 91°C for 1,4- and from - 12 to 0.5°C for 1,2-addition, depending on molecular weight) [4 - 8].

As reported by Colby et al. [9], low-molecular weight polybutadiene samples exhibiting significant amounts of 1,2-microstructure crystallize below - 26°C, and the respective rheological measurements are restricted to the terminal region. Consequently, the full viscoelastic spectrum of polybutadiene blends containing significant amounts of low-molecular weight linear polybutadienes (in the amorphous phase, extending to high frequencies or low temperatures below the melting point) is not readily obtainable.

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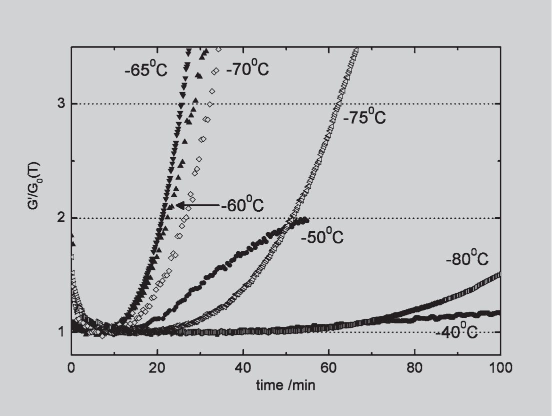

Figure 3: Storage modulus for mixture containing 3% 165k-PBd at frequency 10 rad/s and at various temperatures: (■ - 40°C, ● - 50°C, ▲ - 60°C, ▼ - 65°C, ◇ - 70°C, ◁ - 75°C, ▷ - 80°C).

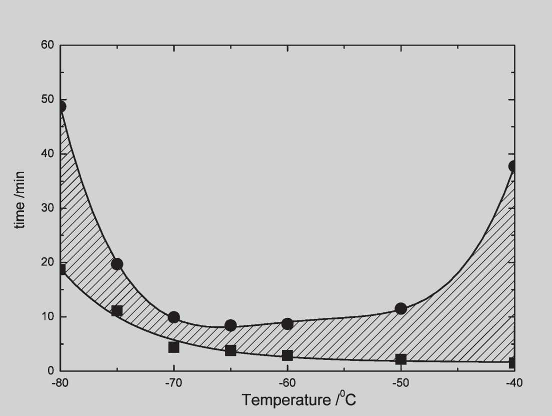

Figure 4: The thermal equilibration time (■) and the time at which crystallization kinetics becomes important (●) are shown for a mixture of 4k-PBd containing 3 % 165k-PBd.

dependent viscoelastic moduli. After the initial temperature equilibration stage of the moduli (corresponding to their early decrease in Figs. 1 – 4), we observed a quasi-equilibrium region (indicated by a constant modulus G_o, in Fig. 1) before they increased monotonically until they reached a final steady state at long times (indicated as G_∞ in Fig. 1). As the rheological data reflected the crystallinity (concentration, size, shape and orientation of crystallites), they were analogous to the DSC curves; this is demonstrated in Fig. 1.

Apart for the shear effects, the crystallization kinetics depend on the molecular weight, the microstructure and the percentage of the crystallizing chains in the mixture [12 - 14]. As shown in Fig. 2, the crystallization process (as evidenced by the enhancement of the storage modulus G') was clearly delayed (i.e. longer steady state time regime) by the presence of even a tiny fraction (3 %) of long non-crystallisable polybutadiene chains; however, it was not eliminated. In addition to the rheological evidence, the quenched samples became progressively opaque after long times, signifying the creation of large-scale heterogeneities.

Therefore, it appears possible to perform reliable rheological measurements at temperatures below T_m during the short time interval after the initial temperature equilibration and before crystallization kinetics sets in; during this period, the samples are under quasi-equilibrium conditions. The exact duration of this period for any given sample can be determined by careful rheological measurements, as illustrated here, and depends largely on the quenching temperature. The overall procedure can be tedious, as it is required for each sample, and some additional experimental support (e.g. DSC) is necessary. However, the acquired linear viscoelastic data (in the virtually amorphous metastable state) are quite accurate. A crucial task in this process is choosing the most convenient test temperatures to conduct the experiments. To do so, one needs accurate information on the evolution of the viscoelastic moduli.

The time-dependent rheological measurements reveal the kinetics of crystallization. Indeed, Fig. 3 depicts the initial stages of time scans, for a 3 % wt 165k-PBd mixture, at different chosen quench temperatures. It can be observed that there is a maximum rate of crystallization at intermediate temperatures; at low temperatures crystallization is hindered by the reduced chain mobility (diffusion controlled process), whereas at high temperatures it is limited by the nucleation and growth process. The allowable time and temperature window for quasi-equilibrium (steady state) rheological measurements can be determined from the dynamic time sweeps at different frequencies and at the specific temperature, as described above. The analysis of these data yields a working 'process diagram' indicating the accessible time window for quasi-equilibrium experiments, shown in Fig. 4. It is obvious from this figure, that close to the glass (lower end) or crystallization (higher end) temperatures, the quasi-equilibrium time interval is much longer. Also, the operating window becomes larger as the fraction of high-molecular weight polymer increases.

It should be noted that this method is similar in spirit to the inverse quenching technique [15], recently proposed for the rheological studies of the early stages of crystallization. In that case, the viscoelastic properties of semi-crystalline polymers, were measured at temperatures below but close to T_m, after a prolonged deep quench to a much lower temperature, followed by heating to the test temperature; this resulted in a frozen degree of crystallinity, whose effects on the rheology were subsequently explored.

The feasibility and accuracy of this procedure are confirmed by the successful application of the time-Temperature Superposition principle in these crystallizing samples. Indeed, Fig. 5 depicts the master curves and shift factors (T_{ref} = - 30°C) of mixtures spanning the full concentration range (i.e. different crystallization tempera-

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tures). The same method has been successfully applied in mixtures with branched polybutadiene molecules [16].

4 CONCLUSIONS

We proposed a method to measure reliably the linear rheology of crystallizing samples, in the amorphous metastable state, below their crystallization temperature. It is based on the determination of the time window for accurate 'quasi-equilibrium' rheological measurements. Using this methodology, we successfully applied the time-Temperature Superposition principle in order to obtain the complete frequency spectrum of various polybutadiene polymers dissolved in low molecular weight crystallisable polybutadienes.

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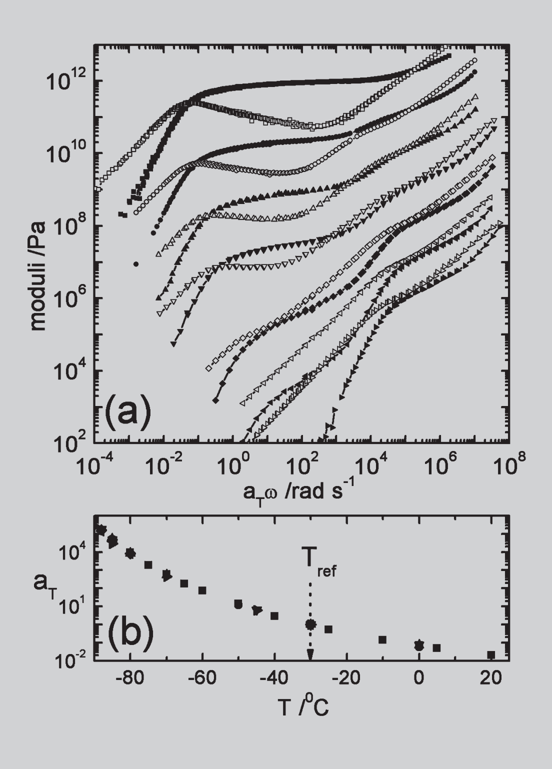

Figure 5: (a) The master curves and (b) the horizontal shift factors for several mixtures of 165-PBd and 4k-PBd. The symbols are for 165k-PBd volume fractions: (■, □ 1.0; ●, ○ 0.5; ▲, △ 0.3; ▼, ▽ 0.2; ◆, ◇ 0.1; ◄, ◁ 0.03; ►, ▷ 0.0). The curves have been multiplied by 10^6, 10^5, 10^4, 10^3, 100, 10 and 1 respectively. All data refer to a reference temperature of - 30°C.

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