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Temperature-dependence of dynamic rheological properties for high-density polyethylene filled with graphite

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The addition of inorganic filler has been one of the important methods for the modification of polymeric materials. Recently, increasing attention has been devoted to developing polymer/graphite (GP) composites for some important applied cases in which electrical or/and thermal conductivity is required [1–3]. It is evident that the rheological and mechanical properties of the particle filled polymer composites are much different from those of virgin polymers [3–6]. Many researchers have paid their interests to the viscoelasticity of the particle filled polymer composites over the past several decades [4–6]. It is also accepted that dynamic rheological measurement is a preferred method for characterizing the morphology of materials because the structure/morphology can be kept under the condition of the small strain amplitudes [6]. In this article, we report the results of a brief study of the dynamic storage modulus G' and its dependence on filler concentration Φ (vol%) and temperature T for high-density polyethylene (HDPE)/graphite (GP) composites.

Disk-shaped GP (HuaDong Graphite Processing Factory, China) with density of 2250 kg/m^3 and mean diameter of 130 μm was used as fillers, HDPE (H005239 0430A, Samsung General Chemicals Co., Ltd., Korea) with density of 970 kg/m^3 as the matrix. After GP was pre-treated by the silicane-coupling agent (SCA, SCA/GP = 3 wt%) and antioxidant 1010 (with 0.2 wt% of HDPE) was added to HDPE, composite of HDPE/GP was kneaded using a Hakke Rheomix at 175 °C for 10 min. For rheological tests, specimens with 25 mm in diameter and 2 mm in thickness were prepared through identical molding conditions. The rheological measurements were performed on an Advanced Rheometric Expansion System (ARES) with a parallel-plate model at reference temperature of 140–180 °C and small strain amplitude of 2%.

Fig. 1 gives the frequency ω dependence of G' for HDPE filled with GP of various Φ at 160 °C. It is indicated that G' increases with increasing ω and Φ, implying that the deviation of GP-filled composites from the viscoelasticity of matrix increases with increasing Φ. The increase of G' with Φ in low ω region (<0.1 rad/s) is much more significant than that in high ω region (>10 rad/s), meaning that the viscoelasticity of GP-filled composites in low ω region are much more sensitive to GP particles than that in high ω region. It is also apparent that, for the composites containing GP above 22 vol%, plateaus of G' at low ω's expectantly occur, and G' appears ω-independent. Such phenomenon is referred to "*pseudo solid-like*" behavior [7, 8]. Some results which have been reported for the last decades have attributed this phenomenon to the restraint in the long-range molecular motions of polymer melt induced by the formation of particle network [4, 5, 7–9].

The relationship of log G' vs. log ω for virgin HDPE and HDPE/GP composites over 140–180 °C range is presented in Fig. 2A and B. Accordingly, some significant facts can be noted. First, for virgin HDPE system, the increase rates of log G' with the decreasing T at the whole observed ω range are nearly the same. On the other hand, in high ω region ($\omega > 10$ rad/s), the increase rates of logG' with the decreasing T for HDPE/GP composites containing $\Phi = 5$ and 30 vol% GP are nearly the same as that of matrix, meaning that the effect of GP on the thermo-sensitivity of G' is negligible in this ω region. Furthermore, in low ω region ($\omega < 0.1$ rad/s), a small amount of GP added to the matrix ($\Phi = 5$ vol%) magnifies the thermo-sensitivity of G'. On the contrary, for the composites containing high level of GP ($\Phi = 30$ vol%), filler addition minifies the thermo-sensitivity of G', and the data of log G' at $\omega = 0.01$ rad/s are hardly T-dependent.

In order to obtain a better understanding of the thermo-sensitivity of G', Fig. 3 presents the comparison of G' at arbitrary temperature T and G' at reference temperature $T_r = 180$ °C, (G'_T/G'_{T_r}), measured at $\omega = 100$ and 0.016 rad/s for both GP filled HDPE and virgin one. It is evident that $G'_T/G'_{T_r} \sim \boldsymbol{T}$ curves at $\omega = 100$ rad/s for three systems are very close to each other, suggesting that the thermo-sensitivity of G' at high ω's are mainly governed by the matrix, and the effect of GP particles can be neglected. However, $G'_T/G'_{T_r} \sim \boldsymbol{T}$ curves at $\omega = 0.016$ rad/s for these systems is very different from each other. The curve for the composite containing 5 vol% GP is the steepest while the curve for 30 vol% system is the most level, meaning

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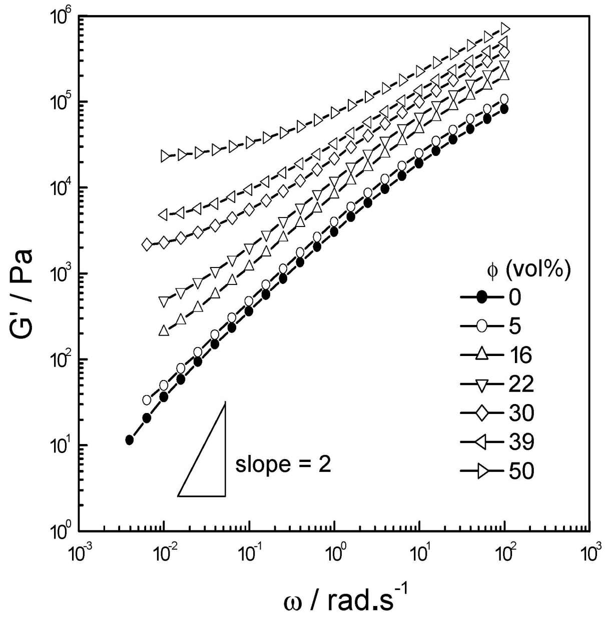

Figure 1 Frequency ω dependence of dynamic storage modulus G' for HDPE filled with GP of various concentration Φ (vol%) at 160 °C.

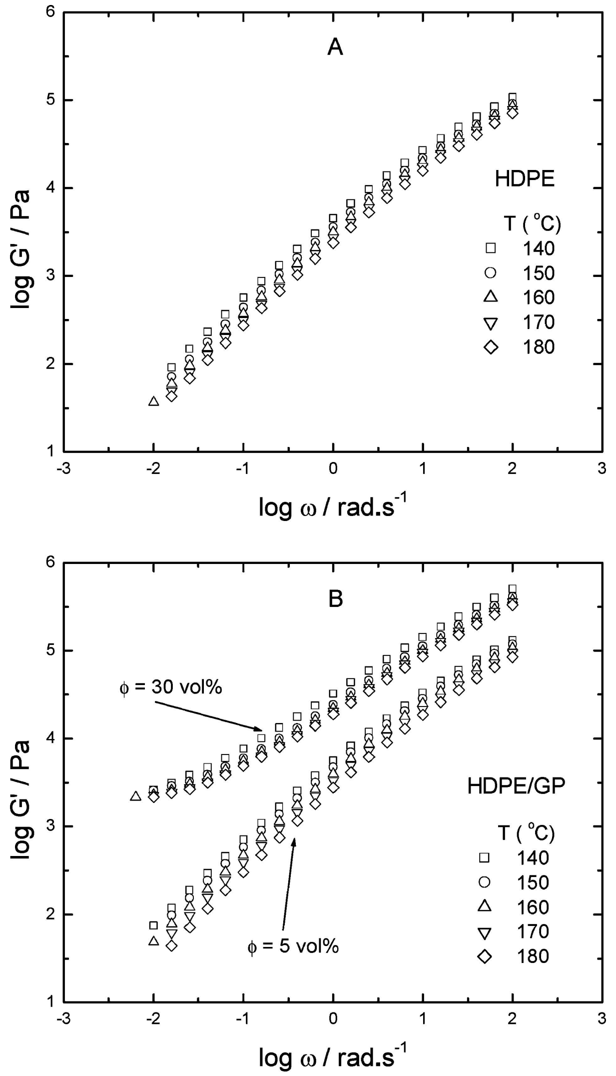

Figure 2 Log G' vs. log ω relationship for virgin HDPE (A) and HDPE/GP composites (B) over the T range of 140–180 °C.

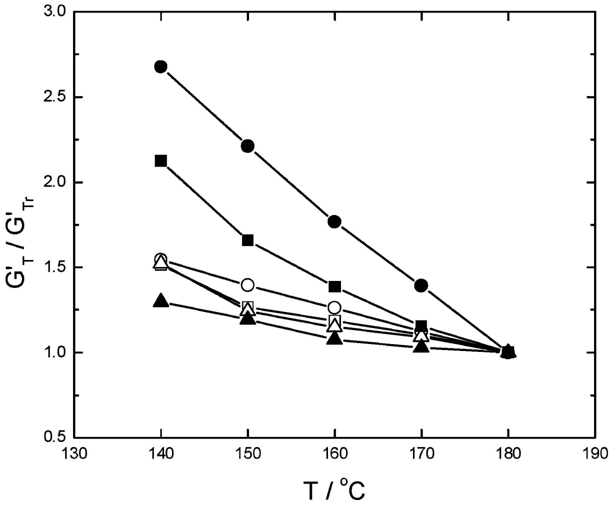

Figure 3 Comparison of the temperature-dependence of G'_T/G'_{T_r} for HDPE filled with GP of various Φ (vol%) at $\omega = 100$ (open) and 0.016 rad/s (solid). $\Phi = 0$ (square), 5 (circle), 30 (triangle).

that the thermo-sensitivity of matrix can be amplified by addition of a small amount of GP particles, but excessive GP amount results in the opposite effect.

The contrary effect of different GP concentration on the thermo-sensitivity of G' in low ω region can be qualitatively explained by the combination of thermal expand and percolation theory [3, 4]. For the low-loaded composites, the distance between the adjacent filler particles is considerably large and restraint of filler on the long-range molecular motions is subtle. Hence, matrix is the main factor monitoring the long-range rheological behavior. On the other hand, the change of T alters Φ due to the considerable thermal expansion of matrix volume without appreciably affecting the inert and relatively incompressible filler. As results of the thermo-sensitivity of matrix and the change of Φ, composites with a small amount of filler appear more thermo-sensitive than matrix. However, when Φ is high enough (e.g., $\Phi = 30$ vol%), particles are easy to contact with each other and form particle network structure. Such percolated structure remarkably limits the long-range molecular motions and minifies the thermal expansion of matrix, leading to the T-independence of G' in low ω region.

It is well-accepted that the rheological behavior at high ω's reflects the motions of short molecular chains [9] and is rarely affected by the fillers, which can explain why the thermo-sensitivity of rheological properties at high ω's is hardly changed by the addition of filler.

From the above research, some conclusion can be drawn. Within high ω region, the addition of GP hardly modifies the thermo-sensitivity of G'. However, within low ω region, GP particles can largely change the temperature-dependence of G'. Furthermore, the GP concentration plays a key role in the thermo-sensitivity of G' within low ω region. The thermo-sensitivity of G' within low ω region can be magnified by the addition of a small amount of GP particles; but, is largely weakened in the cause of excessive filler amount.

Acknowledgments

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