Microwave Enhancement of Elasticity in Poly(propylene)–Carbon Nanotube Composites

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(Received November 28, 2005; CL-051475; E-mail: mass@yz.yamagata-u.ac.jp)

Irradiating weak microwave to a poly(propylene) composite containing a small amount of single-walled carbon nanotubes (SWCNTs) enhances the storage modulus but has no effect on the loss modulus. We postulate that local melting and recrystallization of the polymer in the close vicinity of the SWCNT surface lead to better wetting and larger contact areas for the improved elastic response.

Large mechanical moduli and electric conductivity of single-walled carbon nanotubes (SWCNTs) have attracted many researchers to develop high-performance polymer composites. In particular, poly(propylene) (PP) has been studied intensively for its wide applications.[1–5] Yet, one of the largest problems facing the development is poor wettability of SWCNT surfaces. It results in poor dispersibility and easy aggregation of SWCNTs in a polymer matrix. Even when they are forced to disperse, the SWCNT surface is not fully covered by the polymer. Since the friction coefficient between SWCNTs is extremely small, a part of SWCNTs slides off easily when an external force is applied to their aggregates. Both effects lead to poor load transfer, resulting in the composites with the mechanical properties below what's expected from the intrinsic values of SWCNTs.

It is known that many carbon compounds have huge dielectric losses at high frequencies. This means that SWCNTs are heated efficiently by microwave radiation. For instance, our previous study shows that irradiating only 100 W of microwave for 30 s is enough to raise the average temperature of a few mg of SWCNTs to over 200 °C.[6] Microwave heating also has a characteristic property that only SWCNTs are heated even though they are imbedded within the polymer matrix. The present study was initiated by an idea that, by locally melting the polymer in the vicinity of SWCNTs without affecting other parts of the matrix, the interfacial modification alone may improve mechanical properties of the composite. In order to elucidate the interfacial contribution rather than the bulk effect, both the amount of SWCNTs and the microwave irradiance were restricted to small values.

Purified SWCNTs (HiPco) was sonicated in a 3:1 mixture of H_2SO_4/HNO_3. The filtered SWCNTs were re-dispersed in water and both large aggregates and small tubes were removed by retaining the sediment after centrifuging at 40,000 *g* and the supernatant at 1700 *g*. The resulting tubes consist mostly of SWCNT bundles with the average length of 1 μm. Approximately 0.01 wt % of dried SWCNTs were mixed in isotactic PP (iPP) melts at 200 °C by mechanical stirring. The composite was pressed (10 MPa, 200 °C) to obtain a thin plate (0.5-mm thick). Many identically shaped strips were cut from this plate and annealed at 120 °C before applying microwave irradiation at 2455 MHz. The rheological properties were measured by FT-rheospectrometer (DVE-V4, Rheology Co.) at room temperature.

Figure 1 shows the storage modulus (G′) of the composites,

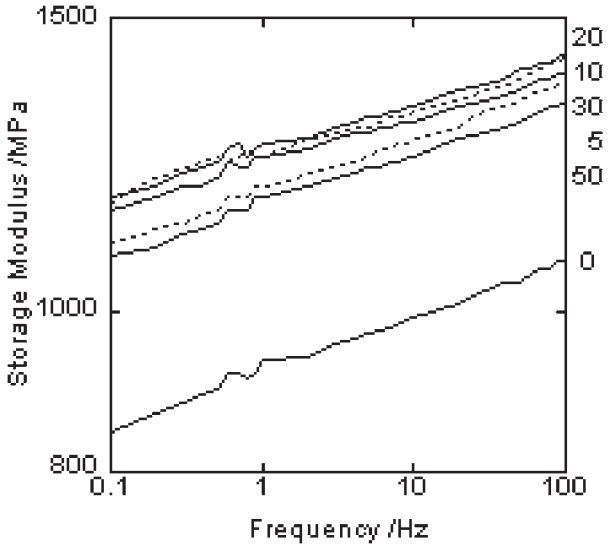

Figure 1. Logarithmic plots of storage modulus against frequency. The numbers on the right axis indicate the irradiation period in s.

for various irradiation times at the power of 80 W. Before irradiation, the composite gave nearly the same curve as a pure iPP sample (not shown). Upon irradiation, G′ increases without changing the shape. As seen more clearly in Figure 2, where G′ at 1 Hz is plotted against the irradiation time, G′ increases rapidly within the first several seconds, then levels off at near maximum for longer times. The similar situation was also found at different microwave powers. G′ at longer irradiations increas-

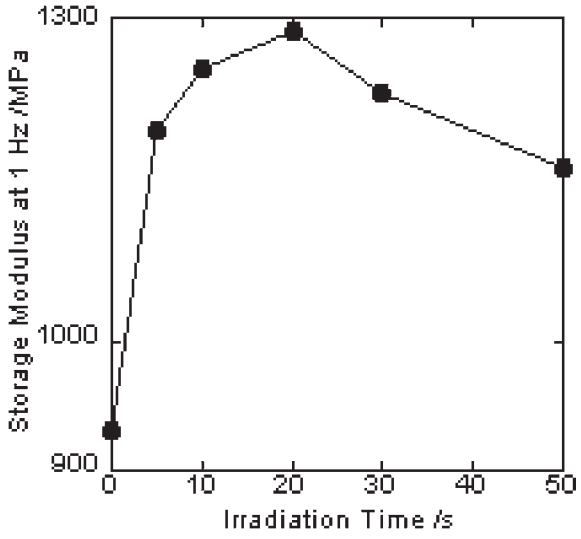

Figure 2. Semi-logarithmic plot of storage modulus at 1 Hz against microwave irradiation time.

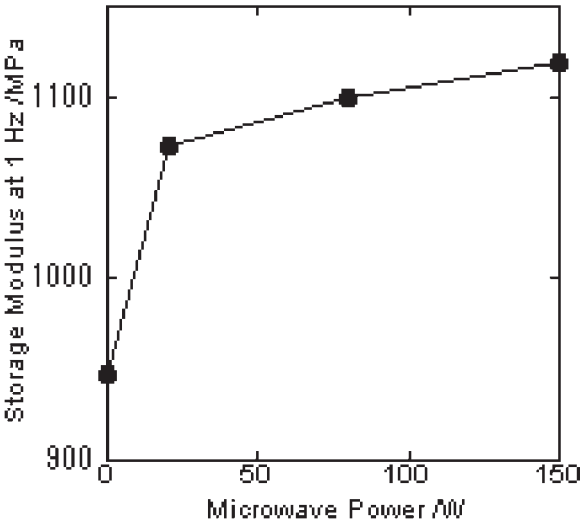

Figure 3. A plot of storage modulus at the "level-off" point against microwave power.

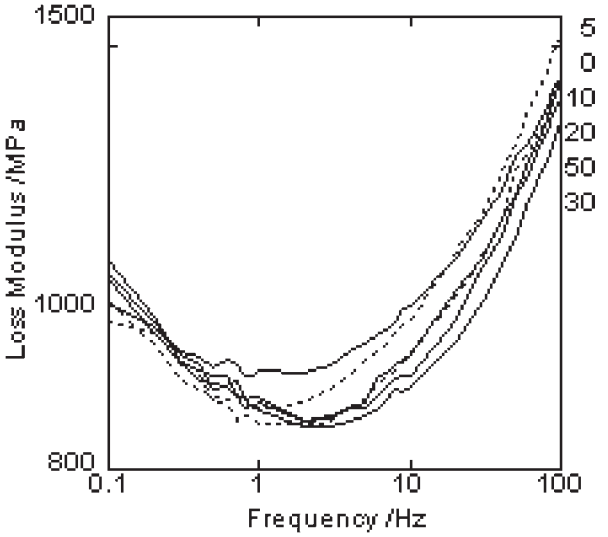

Figure 4. Logarithmic plots of loss modulus against frequency. The numbers on the right axis indicate the irradiation time in s.

es rapidly at small powers, but remain nearly the same above 20 W (Figure 3). Contrarily, the loss modulus hardly changes during the same irradiation (Figure 4). Thus, the microwave irradiation enhances the elastic response.

The differential scanning calorimetory of the composite gave the melting point of 164 °C and the crystallization temperature of 107 °C. The glass-transition temperature was difficult to discern and estimated to be around −10 °C. During the microwave irradiation as shown in Figure 1, the average temperature of the solid composite increased from 25 to 35 °C. In particular, the average temperature for the first several seconds stayed nearly at room temperature. Because this level of temperature raise has been detected in the iPP sample without SWCNTs, 0.01 wt % SWCNTs hardly contributes to the increase in the average temperature.

Our previous study indicates that the temperatures of SWCNTs at the irradiance similar to the long time irradiations in Figures 1 and 3 exceed well above the melting temperature of iPP.[6] Considering a small thermal conductivity of the polymer, it is reasonable to assume that the SWCNTs in the iPP matrix are also heated to the similar temperatures. Then, iPP in the immediate vicinity of SWCNTs should have melted and recrystallized. When we monitored the sample under a polarized optical microscope, we could not detect any visual change by the irradiation. Thus, at the optical microscopy level, the polymer away from SWCNTs has remained unchanged, implying that the melt–recrystallization process has stayed only at the surface.

Based on these results, we propose a following mechanism. SWCNTs are known to be an excellent nucleating agent for PP crystallization.[7–13] It is likely that the SWCNTs in the composites are surrounded by many iPP crystallites. Yet, poor wettability of SWCNTs suggests that iPP crystallites are not in good contact with the SWCNT surface, leaving many nano-sized voids. When only the iPP chains near the SWCNTs surface have melted, they could not spread away from the SWCNTs since they were surrounded by other un-melted crystallites. Then, entropy drives the melted chains to spread along the SWCNT surface, filling the voids. The recrystallized iPP now has better contact with the SWCNT surface. The larger contact area improves the load transfer and results in the enhanced elastic response due to intrinsically high elasticity of SWCNTs. Because the rest of iPP in the matrix remains intact, the loss modulus is not affected. The level-off seen in G' can be explained as spreading of the melted region away from the SWCNT surface due to longer heating, which has allowed the recrystallized iPP to dewet the surface again. The present results indicate that the microwave treatment is a useful technique to improve mechanical properties of polymer–SWCNT composites.

References

1 J. C. Kearns, R. L. Shambaugh, *J. Appl. Polym. Sci.* **2002**, *86*, 2079.
2 M. K. Seo, S. J. Park, *Chem. Phys. Lett.* **2004**, *395*, 44.
3 T. E. Chang, L. R. Jensen, A. Kisliuk, R. B. Pipes, R. Pyrz, A. P. Sokolov, *Polymer* **2005**, *46*, 439.
4 M. A. L. Manchado, L. Valentini, J. Biagiotti, J. M. Kenny, *Carbon* **2005**, *43*, 1499.
5 X. F. Shi, J. L. Hudson, P. P. Spicer, J. M. Tour, R. Krishnamoorti, A. G. Mikos, *Nanotechnology* **2005**, *16*, S531.
6 K. Kubota, M. Sano, T. Masuko, *Jpn. J. Appl. Phys.* **2005**, *44*, 465.
7 B. P. Grady, F. Pompeo, R. L. Shambaugh, D. E. Resasco, *J. Phys. Chem. B* **2002**, *106*, 5852.
8 L. Valentini, J. Biagiotti, J. M. Kenny, S. Santucci, *J. Appl. Polym. Sci.* **2003**, *87*, 708.
9 E. Assouline, A. Lustiger, A. H. Barber, C. A. Cooper, E. Klein, E. Wachtel, H. D. Wagner, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 520.
10 A. R. Bhattacharyya, T. V. Sreekumar, T. Liu, S. Kumar, L. M. Ericson, R. H. Hauge, R. E. Smalley, *Polymer* **2003**, *44*, 2373.
11 M. Sarno, G. Gorrasi, D. Sannino, A. Sorrentino, P. Ciambelli, V. Vittoria, *Macromol. Rapid. Commun.* **2004**, *25*, 1963.
12 K. Wiemann, W. Kaminsky, F. H. Goiny, K. Schulte, *Macromol. Chem. Phys.* **2005**, *206*, 1472.
13 W. Leelapornpisit, M. T. Ton-That, F. Perrin-Sarazin, K. C. Cole, J. Denault, B. Simard, *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 2445.

Published on the web (Advance View) January 28, 2006; DOI 10.1246/cl.2006.262