Effect of Absorbed Water on Dynamic Modulus for Short Fiber–CR Composites

MICHIO ASHIDA and TORU NOGUCHI, *Department of Industrial Chemistry, Faculty of Engineering, Kobe University, Nada, Kobe 657, Japan,* and SATOSHI MASHIMO, *Mitsuboshi Belting Ltd., Nagata, Kobe 653, Japan*

Synopsis

Short fiber–elastomer composites with 10 vol % fiber, nylon 6–CR and PET–CR composites, absorbed water either in the moisture atmosphere or in water. The effect of absorbed water on the viscoelastic properties for these composites was investigated. The temperature dependence of tan δ for the nylon–CR composite showed that the α-dispersion peak of nylon shifted to lower temperatures with increasing absorbed water content and that after displacement of the α-dispersion peak the additional small hump appeared at about 90°C. For the PET composite, the α-dispersion peak of PET shifted slightly to lower temperatures and the small shoulder at 90°C diminished with increasing absorbed water. The additional dispersion probably was caused by the interface between fiber and CR matrix and was independent of fiber orientation. The results suggested that nylon fiber absorbed a larger amount of water than CR matrix, while the water absorption for PET fiber was considerably less than for nylon fiber. The absorbed water in nylon fiber bonded stronger than that in CR matrix and was only slightly diminished by heat treatment under 100°C.

INTRODUCTION

The short fiber–elastomer composites have two advantages: flexibility of elastomer and stiffness of fiber. The authors[1-3] have studied the mechanical properties of short fiber–CR composites in relation to adhesion and orientation of fibers and the viscoelastic properties of these composites. The temperature dependence of tan δ showed that nylon–CR composites had two dispersions ascribed to nylon 6 fiber and CR matrix, respectively. Dynamic modulus for PET–CR composites consisted of three components: Two of them were ascribed to PET fiber and CR matrix and the third component formed at the interface between fiber and elastomer.[1]

Water absorbed by hydrophilic fibers such as nylon and rayon has a profound effect on the mechanical properties of these fibers. The effect of absorbed water on the dynamic mechanical properties of various polyamides has been studied.[4,5] Physical properties of hydrophobic polyesters were considerably affected by absorption of a small amount of water.[6,7] Willett[8] reported the effect of temperature, humidity, and geometric structure on the viscoelastic properties of tire cords such as rayon, nylon 66, and PET. Thus, the dynamic mechanical properties of short fiber–elastomer composites may be considerably affected by absorbed water content.

In the present paper, the effect of absorbed water on the viscoelastic properties for short fiber–elastomer composites was investigated using two different kinds of fibers.

EXPERIMENTAL

Materials. The elastomer used was CR (Denka Co. Ltd.) and short fibers used were nylon 6 (Toray Co., Ltd.) and PET (Teijin Co., Ltd.) filaments, whose length was 6 mm. Diameters of nylon 6 and PET were 27 and 21 μm, respectively. The adhesion treatment on filaments was as follows: Nylon filaments were dipped in RFL bonding agent, and PET filaments were dipped in isocyanate solution and then treated with RFL bonding agent. The dry add-on of adhesive was approximately 9%. The unidirectional fiber–CR composites, which contained 10 vol % of respective fibers, were prepared by mixing and vulcanization as described in the previous article[1] and formed into a sheet 2 mm thick. The specimens of the composites were cut in a 70 × 10 × 2 mm strip.

Absorption of Water. The dry specimens of the composites were prepared by drying in a desiccator containing phosphoric pentoxide. The wet specimens were prepared either by being placed in a closed vessel, which was maintained at relative humidities of 20, 56, and 76% or by dipping in distilled water.

Measurement of Viscoelastic Properties. The dynamic complex modulus E^* and tan δ of the composites were measured by a direct reading dynamic viscoelastometer Rheovibron Model DDV-III, (Toyo Baldwin Co., Ltd.). The temperature range to determine the properties was −100–150°C at a heating rate of 1.0°C/min, at a frequency of 11 Hz with a strain amplitude of 0.06%.

RESULTS AND DISCUSSION

Figure 1 shows the change in absorbed water content in the short fiber–CR composites against treating time in three kinds of relative humidities (RH) at 20°C. Nylon composites absorbed a little more water than PET composites in a given time. The absorbed water content in these composites was higher than those in the CR compound without fiber as shown in the case of 76% RH. The results suggest that water is absorbed in nylon and PET fibers more readily than in CR matrix. The absorbed water content
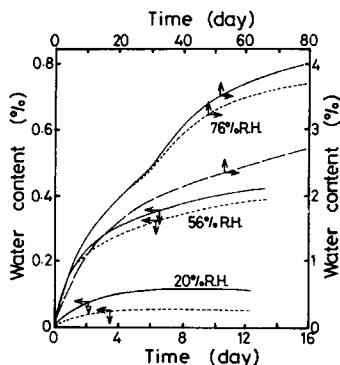

Fig. 1. Absorbed water content of fiber–CR composites and CR compound against treating time in three kinds of relative humidity: (———) nylon–CR composite; (· · ·) PET–CR composite; (— — —) CR compound in 76% RH.

contained in these composites reached equilibrium values of 0.13, 0.42, and 4.26 wt % in 20%, 56%, and 76% RH, respectively.

Figures 2 and 3 show the temperature dependence of the dynamic storage modulus E' and loss modulus E'' in the longitudinal direction of fiber for the nylon–CR composites which absorbed water in the moist atmosphere. The storage modulus for the composites decreased by two steps with rising temperature. The first drop, appearing at about −40°C, coincided with the glass transition of CR matrix and the β-dispersion of nylon fiber and occured in the same temperature range independent of the absorbed water content. The second drop, appearing at about 60°C, shifted to a lower temperature with increasing absorbed water content, and, finally, this step disappeared when the composite absorbed 4.26% water. The loss modulus (Fig. 3) for the composites have two maximum dispersions: one dispersion peak at −35°C is caused by the glass transition of CR matrix and the β-dispersion of nylon fiber and the other dispersion at 82°C is consistant with the α-dispersion of nylon fiber. As the absorbed water content increased, the former high peak did not change its height and position, but the latter medium peak shifted to lower temperatures while maintaining its height.

As mentioned earlier, it took a very long time to obtain the composites containing absorbed water over 1% in the moist atmosphere. In contrast, when the composites were dipped in water, the absorbed water content increased progressively with time and reached 3% after 10 days. In order to observe more closely the effect of absorbed water on the α-dispersion, tan δ as a function of temperature was obtained in the range 0°C to 120°C. In this case, water was absorbed into the composites by the dipping method. Figure 4 shows the effect of absorbed water content on the temperature dependence of tan δ for the nylon–CR composite. The peak of tan δ shifted downward to lower temperatures similar to that of the loss modulus with increasing absorbed water. Becker and Oberst[4] reported that the maximum of tan δ for polyamide with 8% water content shifted to about 0°C. According to Woodward et al.,[5] the α-dispersion appearing at about 100°C for
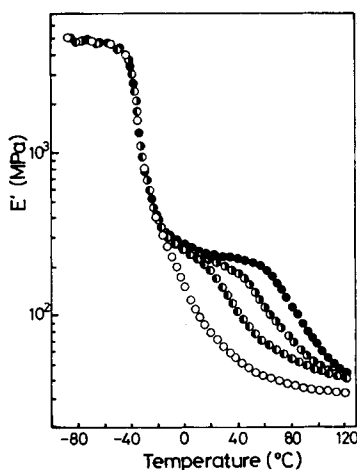

Fig. 2.   Effect of absorbed water on the dynamic storage modulus as a function of temperature for nylon–CR composites: (●) 0% H_2O; (◖) 0.13% H_2O; (◑) 0.42% H_2O; (○) 4.26% H_2O.
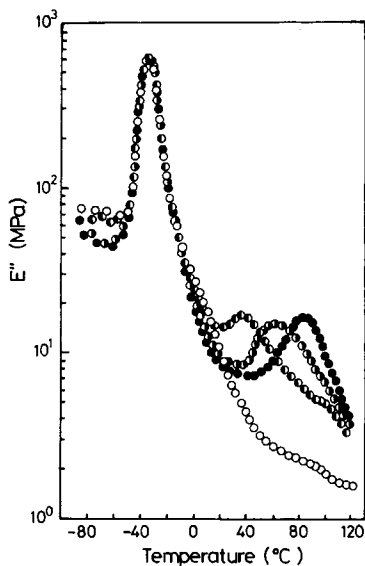
Fig. 3. Effect of absorbed water on the dynamic loss modulus as a function of temperature for nylon–CR composites: (●) 0% H_2O; (◑) 0.13% H_2O; (◐) 0.42% H_2O; (○) 4.26% H_2O.

nylon fiber shifted to lower temperatures with increasing water content and the peak reached 0°C for the 6.4% water specimen. The change has been attributed to segmental motion in the amorphous regions as a consequence of the breaking up of hydrogen bonds between chains.[7] Therefore, the α-dispersion of nylon fiber in the composite takes the same behavior as that of fiber alone with increasing absorbed water. A small hump appeared at 90°C after displacement of the α-dispersion peak to lower temperatures (Fig. 4). The small hump in the dry composite is shielded by overlapping the α-dispersion peak of nylon fiber. The additional dispersion may be caused by the third component in the composite because the hump appears only in the composite. Figure 5 shows the temperature dependence of tan δ for the PET–CR composite containing absorbed water. The maximum peak at 135°C, corresponding to the α-dispersion of PET fiber, shifted slightly to lower temperatures with increasing absorbed water content. A small shoulder appearing at about 90°C diminished as absorbed water increased and disappeared for the composite containing 3.4% water. This
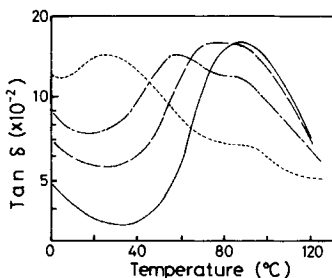

Fig. 4. Effect of absorbed water on tan δ as a function of temperature for nylon–CR composites: (———) 0% H_2O; (– – –) 0.35% H_2O; (– · – ·) 1.3% H_2O; (- - -) 2.4% H_2O.
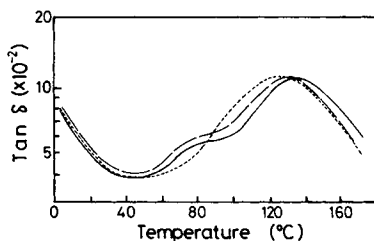
Fig. 5. Effect of absorbed water on tan δ as a function of temperature for PET–CR composites: (———) 0% H_2O; (– – –) 2.8% H_2O; (- - -) 3.43% H_2O.

dispersion corresponds to the additional disperson of nylon composite mentioned above.

The change in peak temperatures of the α and additional dispersions against absorbed water is shown (Fig. 6) for the nylon composite. The α-dispersion peak shifted to lower temperatures linearly with increasing absorbed water content, while the additional dispersion peak stayed at the original temperature over a range of water contents. In contrast, the maximum value of the α-dispersion remained at nearly the same height, whereas the additional dispersion peak diminished to lower values with increasing absorbed water content. The tan δ peak for the nylon composite shifted at the approximate rate of 25°C/% water. The rate is faster than those for nylon reported by Howard and Williams[9] and Willett.[8] On the other hand, the temperature shift of the PET composite was too small to determine the rate. These results indicate that nylon fiber absorbs much more water than the CR matrix, while the water absorption for PET fiber is considerably less than for nylon fiber.

The results described above were obtained from the longitudinal direction of fiber. Figure 7 shows the effect of absorbed water on the temperature dependence of tan δ in the transverse direction. In the case of the nylon composite, the small peak of α-dispersion overlapped with the additional dispersion and gave rise to one broad peak. When the composite absorbed water, the α-dispersion shifted to lower temperatures and the additional dispersion peak decreased the height at the constant temperature of 90°C. On the other hand, for the dry PET composite the additional dispersion

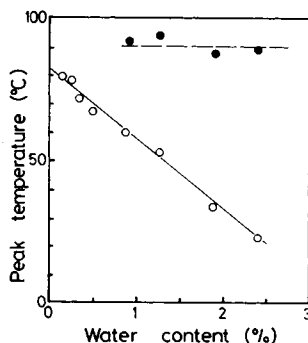Fig. 6. Change of dispersion peak of tan δ against absorbed water content for nylon–CR composite: (○) α-dispersion of nylon; (●) additional dispersion.
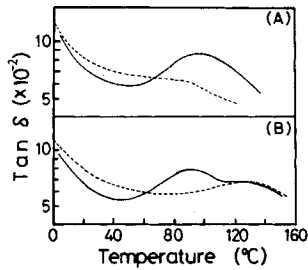
Fig. 7. Effect of absorbed water on tan δ as a function of temperature in the transverse direction of fiber for nylon–CR(A) and PET–CR(B) composites: (———) dry sample; (- - -) wet sample.

peak was higher than the α-dispersion peak. The former peak diminished with increasing absorbed water content while the latter one was slightly affected by absorbed water. Because the dynamic properties in the transverse direction are scarcely affected by fiber in the composites, the intensity of α-dispersion takes the lowest value in this direction.[1] Consequently, although the α-dispersion peaks for nylon and PET took the lowest value in the transverse direction, the additional dispersion was independent of fiber orientation and diminished with increased absorbed water.

Figure 8 shows the effect of absorption and desorption of water on the dynamic storage modulus for nylon–CR composites at 20°C. The composites containing absorbed water under 0.2% kept the same value of E'. The values of E' decreased linearly as the absorbed water increased from 0.3% to 2.5%. The composites containing absorbed water over 2.5% took the same low value of E'. When the absorbed water was removed from the composites by heating at about 100°C, the values of E' decreased along the hysteresis curve (Fig. 8), that is, E' kept nearly the same value until the absorbed water content decreased to 1.8% and then increased sharply to the original value. This finding suggests that water is absorbed more strongly in nylon fiber than in CR matrix and the absorbed water in CR matrix is removed by heat treatment.

The effect of heat treatment on tan δ for the nylon–CR composite containing 1.0% absorbed water is shown (Fig. 9). As described earlier, the α-dispersion peak of nylon shifted from 90°C to 45°C as the composite absorbed
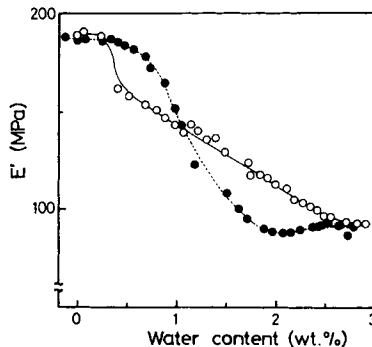

Fig. 8. Effect of absorption and desorption of water on the dynamic storage modulus at 20°C for nylon–CR composite: (—○—) absorption curve; (—●—) desorption curve.
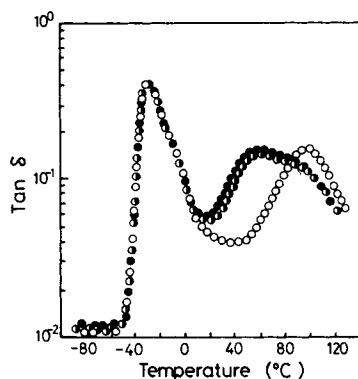
Fig. 9. Effect of heat treatment on tan δ as a function of temperature for the nylon–CR composite containing 1.0% absorbed water: (●) wet sample; (◑) treated at 100°C for 1 h; (○) treated at 120°C for 1 h.

1.0 % water. When the wet sample was heated for 1 h at 100°C, the α-dispersion peak remained at 45°C in spite of the fact that the absorbed water content decreased to 0.7%. After treating the wet sample for 1 h with heat at 120°C, the α-dispersion peak returned to 90°C, the temperature of the original dry sample. The result again reveals that the absorbed water in nylon fiber bonds stronger than that in CR matrix and is scarcely removed by heat treatment under 100°C.

Therefore, the α-dispersion of fibers behaved reversibly according to the absorbed water in the composites. However, the additional dispersion for the composites diminished by absorption of water, but did not reappear by desorption of water. Intensive study on the additional dispersion is in progress and will be reported shortly.

CONCLUSION

The viscoelastic properties for short fiber–CR composites were affected by absorbed water. The temperature dependence of tan δ for the nylon–CR composite showed that the α-dispersion peak of nylon shifted to lower temperatures with increasing absorbed water content, and with displacement of the dispersion peak the additional small hump appeared at about 90°C. For the PET composite, the α-dispersion peak of PET shifted slightly to lower temperatures and the small shoulder at 90°C diminished with increasing absorbed water. The additional dispersion was probably caused by the interface between fiber and CR matrix. The additional dispersion was independent of fiber orientation and diminished with increasing absorbed water.

Nylon fiber absorbs much more water than the CR matrix, while the water absorption for PET fiber is considerably less than for nylon fiber. The absorbed water in nylon fiber bonds stronger than that in CR matrix and is only slightly removed by heat treatment under 100°C.

References

1. M. Ashida, T. Noguchi, and S. Mashimo, *J. Appl. Polym. Sci.*, **29**, 661 (1984).
2. T. Noguchi, M. Ashida, and S. Mashimo, *Nippon Gomu Kyokai Shi*, **56**, 768 (1983).

3. T. Noguchi, M. Ashida, and S. Mashimo, *Nippon Gomu Kyokai Shi*, **57**, 171 (1984).
4. G. W. Becker and H. Oberst, *Kolloid Z.*, **152**, 1 (1957).
5. A. E. Woodward, J. M. Crissman, and J. A. Sauer, *J. Polym. Sci.*, **59**, 23 (1960).
6. E. Ito and Y. Kobayashi, *J. Appl. Polym. Sci.*, **22**, 1143 (1978).
7. E. Ito and Y. Kobayashi, *J. Appl. Polym. Sci.*, **25**, 2145 (1980).
8. P. R. Willett, *J. Appl. Polym. Sci.*, **19**, 2005 (1975).
9. W. H. Howard and M. L. Williams, *Text Res. J.*, **36**, 691 (1966).