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Comment on ‘Absorption of CO_2 and subsequent viscosity reduction of an acrylonitrile copolymer’ by Michael J. Bortner and Donald G. Baird

In the paper (Polymer, 2004, 45, 3399–3412) [1] by Bortner and Baird, they reported the capability of CO_2 to plasticize an acrylonitrile (AN) copolymer. They performed the ex situ measurements of the amount of CO_2 absorbed in the copolymer, viscosity, and glass transition temperature (T_g) using thermogravimetric analysis (TGA), pressurized capillary rheometry, and differential scanning calorimetry (DSC), respectively. The Williams–Landel–Ferry (WLF) equation was used to estimate the viscosity reduction based on the T_g reduction. The predicted viscosity reduction using the universal constant for WLF equation was, however, 34–85% higher than the measured values.

In the paper they reported that significant CO_2 loss was not observed between sample decompression and ex situ measurements. However, it would be easily supposed that a certain amount of CO_2 was diffused and lost from the sample via depressurizing before the ex situ measurements were conducted. Additionally, the CO_2 loss amount will vary depending on the interval of elapsed time during depressurization, and may not be negligible for some measurements.

Fig. 1 shows the correlation between the viscosity reduction and the amount of absorbed CO_2. The solid line denotes a linear fit of the compiled data obtained by Bortner and Baird. The linear fit of the data is represented in Eq. (1)

$$\Delta\eta = 13.25\,W - 29.275 \tag{1}$$

where $\Delta\eta$ is the viscosity reduction and W is the weight percent uptake of CO_2. As shown in Fig. 1, the solid line does not pass through the origin. This suggests that the correlation is not consistent with the phenomenon, and that CO_2 may have been lost before the viscosity measurement starting in their paper. In other words, the amount of CO_2 determined through TGA might be larger than that in the rheometry because of the significant CO_2 loss before viscosity measurement. Here, it might be possible for us to make a new assumption that the CO_2 amount in sample polymers may be different for various measurements. Along this assumption, we can propose a dashed line, which passes through the origin by shifting the solid one, namely changing the CO_2 amount, W.

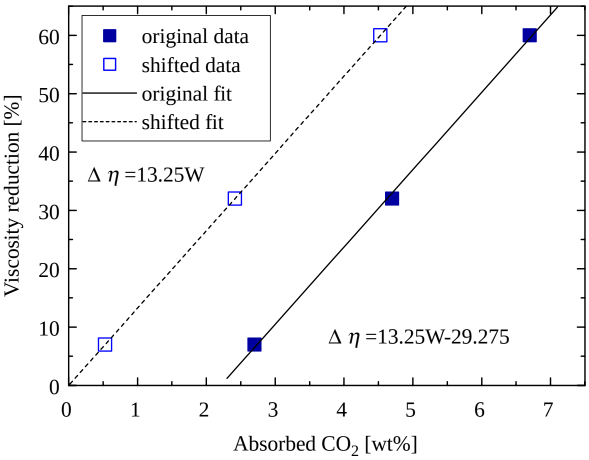

Fig. 1. Correlation between the viscosity reduction and the amount of absorbed CO_2.

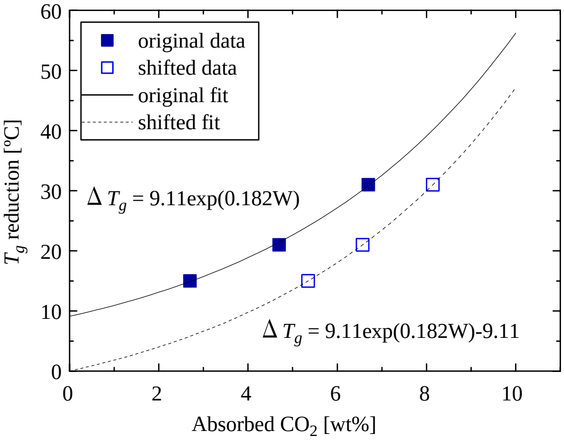

Fig. 2. Correlation between the T_g reduction and the amount of absorbed CO_2.

Fig. 2 shows the correlation between the T_g reduction and the amount of absorbed CO_2. The solid line denotes an exponential fit of the compiled data obtained by Bortner and Baird. The exponential fit of the data is represented in Eq. (2)

$$\Delta T_g = 9.11\,\exp(0.182\,W) \tag{2}$$

where ΔT_g is the T_g reduction and W is the weight percent uptake of CO_2. As shown in Fig. 2, the solid line does not pass through the origin. This suggests that it is possible that much more CO_2 may have been lost for TGA measurement than the authors had expected. In other words, the lost CO_2 amount between sample decompression and DSC measurement may

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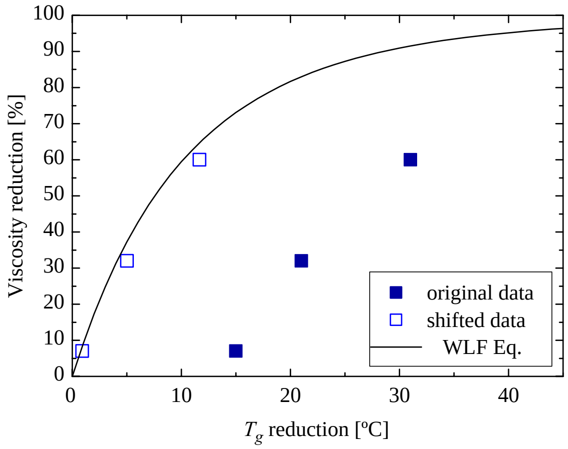

Fig. 3. Correlation between the viscosity reduction and the T_g reduction.

possibly be less than that of TGA. Along this assumption we can get the solid line, which passes through the origin by shifting the solid one.

Fig. 3 shows the correlation between the viscosity reduction and the T_g reduction. The solid line is the WLF analysis. By shifting the fits in Figs. 1 and 2, the error between the WLF analysis and the experimentally measured values diminishes as seen in Fig. 3.

They did not refer to the shape/size of samples, although it affects the amount of CO_2 loss between sample decompression and each ex situ measurement. Furthermore, there is not enough information to infer the differences in the required minutes to perform each separate measurement after sample saturation. This lack of information makes it difficult to confirm our assumption at this moment. Anyway, it would be noted that ex situ measurement possibly involves CO_2 loss of which consideration can improve the accuracies of proposed correlations.

References

[1] Bortner MJ, Baird DG. Polymer 2004;45:3399–412.

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