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Editorial corner – a personal view
Strengthening of crosslinked polymer by solid-state drawing

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Solid-state drawing is an effective measure to improve strength of semi-crystalline polymers by introducing orientation above T_g. Consequently, the fraction of the macromolecules having extended conformations is increased, which in turn enhances load bearing capability of the polymers. Nevertheless, the method is not suitable for crosslinked polymers because macromolecules elongation is greatly hindered by the crosslinking networks. In some specific cases, thermoplastics are firstly stretched at rubbery-like state, and then crosslinked to fix the structure. So far, there has not been any report concerning directly bringing in orientation in crosslinked polymers.

It is interesting that researches on dynamic covalent chemistry in correlation to polymer processing reveal the possibility of solving the problem. By using dynamic disconnection and reconnection behavior of the C–C bonds in aromatic pinacol units above the homolysis temperature, a crosslinked polyurethane carrying the pinacol unit proved to be able to be strengthened by solid-state drawing under the reversible circumstances https://doi.org/10.1002/adfm.201706050. The main mechanism lies in the fact that when the crosslinked polyurethane was drawn after the C–C bonds in the pinacol unit started to participate in dynamic reversible reaction, equilibrium of the dynamic reversible reaction of C–C bonds was gradually re-built up throughout the material. Accordingly, upon the restriction on any macromolecules imposed by the reversible crosslinks is released due to fission of C–C bonds, the relevant chains became stretched.

The results showed that the strength parallel to the drawing direction increased with a rise in the drawing ratio at 80 °C (the onset homolysis temperature of the pinacol units) and approaches to 115.2 MPa at drawing ratio of 19. Meanwhile, the strength in the direction vertical to drawing remained nearly unchanged because the crosslinks in this direction were simultaneously re-established. The phenomenon differs from the case of thermoplastics, in which solid-state drawn used to result in significant reduction in strength perpendicular to the stretching direction. On the other hand, the elongation to break along the drawing direction was found to decrease with drawing ratio as usual, but the value in the vertical direction was also nearly independent on drawing ratio. Such an anisotropy of strength and failure strain has not been reported before.

Basically, the technique is not limited to reversible C–C bonds and vitrimers but applicable to the systems having other reversible bonds according to dynamic covalent chemistry https://doi.org/10.1016/j.progpolymsci.2018.03.002. The boundary between traditional thermosets and thermoplastic polymers can thus be broken.

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