Editorial corner – a personal view

Physically Networked Polymers: Materials that change with their environment

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Polymer networks have continuity of molecular and intermolecular links throughout their structure. These links can be established by covalent, polar or dispersive forces. The choice of link depends on whether a permanent or a reversible structure is required. The continuous network and matrix phase may be different, either chemically or physically, if there is identifiably separate phases. When network formation is through a filler a percolation threshold concentration must be exceeded. Agglomeration of the filler will produce a non-linear strain response. When the matrix phase is of distinct chemistry and physically it can be a gas (aerogel), liquid (gel) or solid (dispersed or co-continuous). The emphasis of this discussion is on reversible networks. They require a reversing stimulus, typically heat, shear, pH, electrical or magnetic. The magnitude of the reversing force is important for application.

Thermoplastic rubbers require reversal of physical cross-links during processing, for all other circumstances they must have a permanent network structure. Reological additives exhibit network reversal on shear and the gelling forces should be weak and potentially rapidly reversible. Dispersive forces, called hydrophobic forces when a polar medium is the matrix, meet networking criteria. Ionic or dipolar forces can be enhanced by molecular orientation formed by shear or an electrical field thus causing an increase in structure formation with a rheopectic or shear thickening effect. In solids such additives modify the viscoelastic properties. The distinction

between a liquid and a solid is uncertain for amorphous materials.

A feature of more recent research is the formation of self-assembling network systems, often using functionalized polymers with interacting groups having high specificity and facile reversibility. Reversibility is either self-controlled in response to changes in the environment or activated by external stimuli, such as those mentioned above. Materials with these responsive changes to their structure have been called smart materials. A reverse situation may apply where changes in the structure of the material lead to changes in the stimulus field. Changing chemical, mechanical or shear conditions may lead to a change in conductivity or light transmission, so the material can become a sensor. Nematic liquid crystalline ordering of side-chain mesogens can be controlled by electro-optical stimuli. Thermo-reversible networks are much studied, but network formation can be activated by electrical or magnetic fields. Many new materials are based upon the principles that have been discussed with the similarity that they include reversible supramolecular structures.

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