

effect of the diluting solvent molecules, the polymer chains of a fully swollen network are in their rubbery state and capable of undergoing large conformational changes in response to external stress or pressure. The effect of diluting molecules on the glass transition temperature,  $T_g$ , of a polymer chain has been described with several equations such as the Fox equation:

$$1/T_g = w_s/T_{g,s} + w_p/T_{g,p} \quad 1$$

where  $T_{g,s}$  and  $T_{g,p}$  are the glass transition temperatures of the solvent and dry polymer respectively and  $w_s$  and  $w_p$  are their respective weight fractions. Table 1 lists common hydrophilic polymers often used to make hydrogels along with their  $T_g$  and the amount of water calculated from Equation 1 that is required in their network to reduce the overall  $T_g$  to below the freezing point of water. Because water has a very low  $T_g$  ( $-137^\circ\text{C}$ ), even small amounts of water can decrease the hydrogel  $T_g$  to well below room temperature, causing the polymer chains to enter their rubbery state. Hence, the mechanical performance of a swollen hydrogel closely resembles that of an elastic network diluted with small solvent molecules. To understand the mechanical behaviour of swollen hydrogels and the impact of network parameters on their mechanical properties, it is best to begin with the mechanics of rubber networks.

The mechanical evaluation of a rubber network has been the subject of an extensive body of literature. Conceptually, there are two different approaches to treat mechanical properties of polymeric networks: the *phenomenological approach* and the *molecular approach*. In the latter case, statistical thermodynamics is used to establish a correlation between mechanical properties of a network and network parameters. In the former case, a purely mathematical method is employed to describe the mechanical properties of the network. Here, unlike the molecular approach, the focus is not to explain and interpret the network behaviour, but to develop an accurate mathematical model that can capture the overall mechanical behaviour of the network. Both approaches began and evolved separately, although it is possible to establish some correlation between parameters from different models.

The first comprehensive method to describe the phenomenological behaviour of an elastic structure was developed by Mooney in 1940. Mooney began with the assumptions of rubber incompressibility and Hooke's law to develop a purely mathematical explanation for the strain energy density function of an isotropic elastic network,  $W$  (Mooney 1940). The strain energy density function is used to describe the mechanical contribution of network deformation to the overall free energy. Based on

**Table 1.** List of some of the most commonly used hydrophilic polymers used to make hydrogels, along with their average  $T_g$  and the minimum amount of water that is required to shift the  $T_g$  of the swollen network to below the freezing point of water.

Commonly used hydrogels	$T_g$ ( $^\circ\text{C}$ ) of dry polymer	Required water content (%) to form a rubbery network
Poly(acrylamide)	165	28
Poly(acrylic acid)	105	22
Poly(2-hydroxyethyl methacrylate)	57	15
Poly(vinyl alcohol)	85	19
Poly(N-isopropylacrylamide)	85–130	19–25