SUSTAINABLE POLYMERS

Alternative plastics

Plastics have posed substantial environmental and human health risks, therefore their design, manufacturing and disposal should incorporate sustainability considerations. Now a study reports success in developing hydroplastics from renewable cellulosic biomass that can be shaped in water.

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More than 9 billion metric tons of petroleum-derived plastics have been produced since the early 1950s, penetrating almost every aspect of daily life[1]. However, growing awareness of the severity and urgency of the plastic crisis is driving the scientific communities to create new alternatives towards sustainable polymer solutions[2]. As the focus of ongoing research is largely on the synthesis of degradable polymers and the development of renewable feedstocks and recycling strategies[3], sustainable processing of polymers has received little attention[4].

The manufacturing of plastic products — mainly injection moulding, extrusion and blow moulding — is energy intensive, for example with about 272 trillion British thermal units of energy consumed in the United States alone in 2010[5]. During these processes, polymers are heated well above their glass transition temperature (T_g) or melting temperature (T_m)[6]. In the molten state, polymer chains become much more mobile and can be moulded or extruded into desired shapes, then solidified upon cooling below T_g or T_m (Fig. 1a). The processing temperature is typically above 200 °C; for instance, it is in the range of 270–320 °C, 250–270 °C and 280–320 °C for poly(ethylene terephthalate), polypropylene and polycarbonate, respectively. However, these high temperatures are associated with side effects, such as destabilizing thermally vulnerable functional groups, in addition to high energy consumption.

Writing in *Nature Sustainability*, Zhang and co-workers[7] have reported a class of bio-based hydroplastic polymers with shape processability in an aqueous system (hydrosetting). In the absence of thermal processing, hydroplastics can be moulded into various shapes in water. A drying process then fixes their shapes with the concomitant loss of water. Notably, the starting material is cellulose, the most abundant natural polymer on Earth, with high biodegradability, crystallinity and hydrophilicity. Molecular engineering enables the hydrophobicity and thermal processability of cellulose for the fabrication of bio-based plastics[8], which are typically processed at over 200 °C. In this work, a sweet spot of the hydrophilicity and hydrophobicity for cellulose enables unique hydrosetting behaviour. Specifically, cinnamic acid, a derivative of natural cinnamon oil, holds the key. The installed hydrophobic cinnamoyl moieties endow cellulose with essential properties required for the preparation of hydroplastics: (1) they are hydrophobic, in favour of the solubility of cellulose and forming an initial shape assisted by organic solvents; (2) the hydrophobicity of cellulose can be finely tuned by the degree of cinnamoyl modification to reach a favourable state for hydrosetting; and (3) the molecular interactions between the cinnamoyl groups

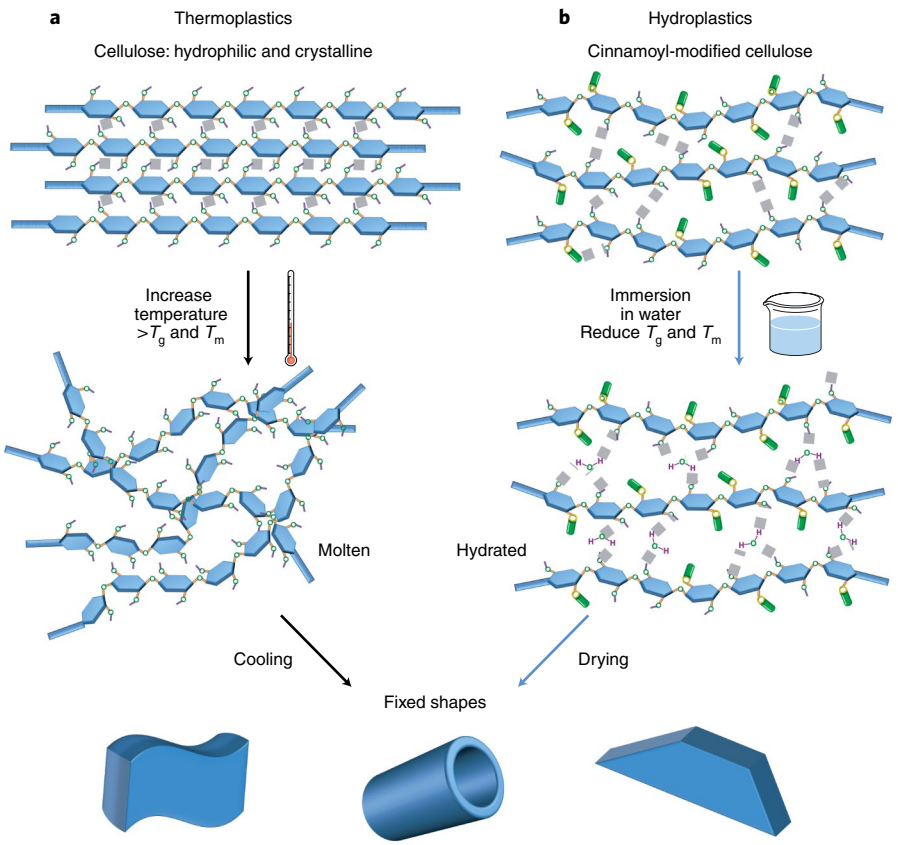

Fig. 1 | A comparison of processing between thermoplastics and hydroplastics. a, Using microcrystalline cellulose reported by Zhang and co-workers[7] as an example. For thermoplastics such as virgin cellulose, thermo-moulding at a temperature notably higher than T_g or T_m is required to promote mobility of polymer chains under the molten state for moulding into different shapes, followed by shape locking upon cooling. **b**, For hydroplastics, cinnamoyl-modified cellulose can be shape-programmable in water with the aid of multilayer water sorption. A drying process fixes the shapes.

could improve the mechanical strength of the cellulose-based hydroplastics, facilitating shape programmability in water.

Understanding the role of cinnamoyl-modified cellulose at the molecular level affords insights into shape programmability under hydrosetting. As shown in Fig. 1b, the installation of bulky cinnamoyl groups disrupts the chain packing of microcrystalline cellulose via the reduction of intermolecular hydrogen bonding, creating more free molecular spaces. The modification also facilitates the solvent processing of cellulose into membranes. In addition, cellulose is hydrophilic. Once the membranes are immersed in water, water molecules can migrate into the inter-chain spaces and form new hydrogen bonding. These supramolecular interactions provide further chain mobility to reshape the membranes, a process similar to thermal moulding above T_g or T_m of thermoplastics. The water molecules must also transport quickly into the inter-chain spaces to allow for not only efficient shape-programming but also rapid drying that can lock the permanent shapes. Again, this drying process resembles the cooling stage of the moulding or extrusion in the thermal treatment of thermoplastics. The quick sorption/desorption of water facilitates precise shape-programming and rapid shape-fixing. Thus, this class of hydroplastic polymer can be shaped into diverse two- and three-dimensional forms with excellent mechanical properties and recyclability.

The work by Zhang and colleagues[7] highlights the possibility to replace thermoplastics with a sustainable bio-based alternative. Featuring excellent shape programmability and reduced energy inputs, the demonstrated hydroplastics provide useful principles for the future design of a broader spectrum of polymers. This success also suggests that a polymer must be intrinsically hydrophilic, while the commodity polymers are normally hydrophobic. As a result, a possible strategy would be to install hydrophilic groups onto hydrophobic polymers and reach a desirable balance between hydrophilicity and hydrophobicity for a hydrosetting property. On the other hand, the hydroplastics are initially processed in an organic solvent, which is not ideal from a sustainability point of view. Another challenge is how to maintain the lifetime of hydroplastics under varying humidity levels. Categorically, this contribution will inspire further research in the development of hydrosetting materials and energy-efficient manufacturing routes to supplement or even replace thermal processing. ❐

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Competing interests

The authors declare no competing interests.