Molecular origin of physical ageing and rejuvenation in glassy polystyrene

The term "polymer" is derived from the Greek word πολύ (polu, meaning "many, much") and μερές (meres, meaning "part"), and refers to a molecule which is composed of numerous repeating units. We chose to use a polymer named polystyrene because it is used in a great quantity in industry and academia. Below a characteristic temperature, called the glass transition, these polymers are in the glassy state: they are disorder solids. Above the glass transition the polymer chains are in the liquid state.

In the glassy state the polymers are out of equilibrium: they are not in a crystal structure and are therefore in a higher energy state. Physical ageing is when their molecular rearrangement shifts towards an equilibrium state. Physical ageing limits the applications of polymers by causing embrittlement of the material, which ultimately leads to failure. Physical ageing can be erased by heating (above the glass transition), i.e. thermal rejuvenation, or deforming the material, i.e. mechanical rejuvenation.

In this study we investigate the molecular origin of physical ageing and the molecular similarities and or differences between thermal and mechanical rejuvenation. Thermal and mechanical rejuvenation are macroscopically considered to be the same, however, we show that on a molecular level these two types of rejuvenation are dramatically different. Moreover, we reveal that physical ageing is connected to large-scale and small-scale motions of the polymer chain.

Furthermore, we investigated the effect of tacticity on the ageing kinetics of polystyrene. Tacticity is the arrangement of the units in the main chain of a polymer. When the arrangement is at the same side of the main chain the polymer is called isotactic; when the arrangement is at alternate positions of the main chain the polymer syndiotactic. In atactic polymers the arrangement of the units random. We show that the ageing kinetics are dependent on the tacticity of the polymer, with the isotactic polystyrene ageing the fastest, syndiotactic the slowest, and atactic being between these two extremes. In other words, tacticity can be translated into chain flexibility. Syndiotactic polymers are known to be stiff, while isotactic flexible. A schematic representation of the connection between tacticity, chain flexibility and ageing kinetics is shown below.

Consequently, when designing a material, its molecular architecture should be taken into account, since it plays a role in the physical ageing kinetics.

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