

Crystalline and Amorphous Natures of Polymers

The nature of crystalline and amorphous polymer states is often misconstrued and misused. The term amorphous means to have no defined shape, or an easily altered shape, like a liquid or a rubber. Crystalline, on the other hand, insinuates that there is a regular, defined pattern to the molecular aggregates --- crystallized carbon forms a substance we call “diamond”. These terms are used to define two separate “solid” states that exist particularly in polymers. The confusing part is that they coexist in many polymers --- the so-called semi-crystalline polymers.

The amorphous nature of polymers is analogous to a plateful of spaghetti --- loose and randomly coiled. While the crystalline state is more like the uncooked spaghetti in the box --- the chains are all tightly bundled and ordered in the same direction.

In a polymer, these two states coexist, with adjacent sections of polymers packing into tight crystalline bundles held together by secondary attraction forces, while other sections of the same molecules are unable to physically move into the crystalline lattice and remain amorphous. For the most part, the probability of a particular polymer segment being crystalline or amorphous is purely a random event controlled by the dynamics of the crystallization process --- in effect, the portion of the segment that is in the amorphous state is no different from that part of the polymer which got “trapped” in the crystallized state.

Oftentimes someone will discuss extracting the “amorphous” material out of the polymer. To some extent, this can be performed particularly where the amorphous state is composed of polymer fractions that are not acceptable into the polymer lattice, i.e., highly branched species, or very low molecular weight polymer fractions. This procedure was once used to extract atactic polypropylene from a polymerization to enhance its crystalline content. In reality, this is merely a procedure for removing a contaminant, non-crystallizable atactic polypropylene, from the crystallizable isotactic polymer form. For most polymers, however, one cannot extract the amorphous material from the crystalline sections.

In general, polymers which can crystallize, do so until they can no longer get into a conformation or position to “pack” with other chains because of some physical restraint. The only difference between amorphous polymer and crystalline polymer is that the amorphous material physically could not enter the crystalline lattice at the time it was formed. The amorphous state, therefore, consists of loose chain ends, “loops” of polymer segments that exit and then reenter the same crystalline domain, as well as polymer

segments which crystallize in two adjacent lattices --- tie molecules. Tie molecules are amorphous polymer segments which hold the crystalline segments together --- they form the mortar between the bricks which enhances the properties of semi-crystalline polymers. Without these intercrystalline links, there would be nothing holding the polymer together except weak secondary attractive forces.

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