

Tie Molecules

Crystalline polymers, such as polyethylene and polypropylene, exist as composites of regularly-ordered, closely-packed, hard, crystalline segments in a matrix of unordered, rubbery, amorphous polymer. Chemically, the two phases of polymer are indistinguishable from each other, yet they form separate discrete phases. Not unlike other heterophasic structures, the strength of the composite is largely a function of the cohesiveness of the two phases.

While there is considerable secondary bonding in the crystalline phase, the amorphous phase has too little order and too much free volume to permit any significant amount of secondary bonding to occur between the two phases for any appreciable time. Short molecular ends (cilia) in the amorphous phase do not have enough length to develop a significant amount of entanglement, and therefore, provide little resistance to separation under the slightest stress. It is possible for entangled “loose loops” to occur --- looped segments of the same molecule which initiate and terminate within the same crystalline entity, with the central portion forming a loop in the amorphous matrix. These structures, however, have a low probability of occurrence and would very likely be relatively weak.

It is the molecular segment which initiates in one crystalline domain, crosses the amorphous region and, yet, has enough length to become securely locked in an adjacent crystalline phase, the so-called “**tie molecule**”, which provides the strength to keep the crystalline and amorphous phases from separating under even the slightest load. It is the proverbial “**mortar between the bricks**” which provides strength to the “composite”, semi-crystalline structure.

These tie molecules are believed to be responsible for high elongation, exceptional toughness and impact resistance, and good resistance to slow-crack growth, as well as environmental stress cracking. It is thought that polymers with a higher average molecular weight have a higher likelihood of these intercrystalline linkages occurring -- therein the concept of “tie-molecule density”.

This same concept can be applied to the so-called “amorphous” polymers which don't have the clear-cut phase differences that the crystalline polymers exhibit. In the amorphous polymers, short chains readily slip past each other and can be easily separated from the polymer mass. Such a polymer would exhibit a low elongation with a characteristically low toughness and impact strength. In high molecular weight amorphous polymers, however, the extreme length of the chain causes it to get so entwined that it is difficult to pull it out of the entanglement. Thus, these long-chain

molecules behave similarly to the tie molecules in crystalline polymers and provide comparable improvements in mechanical behavior.

While seemingly hypothetical and scientific, the notion of tie molecules is a basic concept that needs to be understood in order to fully appreciate how polymers behave in actual use.

Rich Geoffroy
POLYMER SERVICES GROUP