4.1. POLYSTYRENE/POLYSTYRENE IPNs

Most areas of modern research contain two concurrent factors: a basic aspect, which somehow aims at an improvement in scientific understanding, and an applied aspect, which is directed toward a practical goal such as a new or improved material or process. While one or the other factor frequently predominates in a given piece of work, sometimes the two are inextricable.

This chapter emphasizes the role of IPNs as model polymer compositions. It is concerned with aspects of rubber elasticity, physical and chemical crosslinks, and swelling behavior. While much of Chapters 7 and 8 to follow are much more practically oriented, a study of the molecular structure of IPNs will make more apparent the need for fundamental understanding in arriving at the best possible practical materials.

In recent years, important advances in the theory of rubber elasticity have been made. These include the introduction of the so-called phantom networks by Flory(1) and a two-network model for crosslinks and trapped entanglements by Ferry and co-workers, (2,3) The latter builds on work by Flory(3) and others on networks crosslinked twice, once in the relaxed state, and then again in the strained state. In other studies, Kramer(5) and Graessley(6) distinguished among the three kinds of physical entanglements as crosslink sites: the Bueche–Mullins trap, the Ferry trap, and the Langley trap.

These several papers discuss the contribution, or lack of contribution, of physical crosslinks to retractive stresses in the theory of rubber elasticity. (7) In most sequential IPNs described in this monograph, a crosslinked polymer I is swollen with monomer II, plus crosslinking and activating agents, and monomer II is polymerized in situ. (8–13) Chapter 5 is devoted to a review of synthetic detail. If the two polymers are identical, the product will be designated as a homo-IPN. These homo-IPNs, because of reduced (or absent) domain formation, provide model networks suitable for the study of the presence or absence of physical crosslinks, as well as other factors, such as the suggested domination of one network over the other.
When both polymer networks are chemically identical, the naive viewpoint suggests that a mutual solution will result with few ways to distinguish network I from network II. As will be shown below, this is emphatically not the case.

There have been four major research reports using IPNs where both networks are identical\(^{(14-17)}\) as well as other studies and applications.\(^{(18-20)}\) All four major studies, the basis for the analysis in this chapter, interestingly enough used networks of polystyrene (PS) crosslinked with divinyl benzene (DVB). The first publication on PS/PS-type IPNs was a study of swelling by Millar which appeared in 1960.\(^{(15)}\) IPNs having both networks identical in chemical composition have sometimes been called Millar IPNs, after his pioneering work\(^{(14)}\). Shibayama and Suzuki published a paper in 1966\(^{(16)}\) on the modulus and swelling properties of PS/PS IPNs, followed by Siegfried, Manson, and Sperling,\(^{(14)}\) who also examined viscoelastic behavior and morphology. Most recently, Thiele and Cohen\(^{(17)}\) studied swelling and modulus behavior, and derived a key equation with which to study the swelling behavior of IPNs.

In important aspects, this chapter will describe a reexamination of the homo-IPN data by Siegfried \textit{et al.}\(^{(21,22)}\) The results will be scrutinized in the light of the new theoretical developments.\(^{(1-6)}\) For clarity, all PS/PS IPNs will be denoted by two pairs of numbers: vol\% DVB in network I/vol\% DVB in network II, \% network I/% network II.

While all four investigators employed PS/PS IPNs crosslinked with DVB, each differed in important details. Table 4.1 summarizes the principal synthetic variations.\(^{(14-17)}\) The extent of swelling and polymerization conditions probably influences the final results.

\* A word must be interjected about these other homo-IPNs. Lipatov \textit{et al.}\(^{(20)}\) studied epoxy/epoxy homo-IPNs, and found that the \(T_g\) of the product declined steadily through four successive swelling and polymerization steps. One might speculate if this was due to an increased number of gauche states in the stretched chains. Siegfried \textit{et al.}\(^{(14)}\) found greater relaxation effects than expected, but interpreted the data in terms of the low crosslinking level in polymer I.

Clark\(^{(18)}\) employed poly(dimethyl siloxane) (PDMS) homo-IPNs to make improved adhesives. Three separate linear PDMS chains were mixed, each with reactive groups. Polymers I and II reacted to form a network, yielding a semi-IPN. The remaining linear polymer provided the adhesive properties. After adhering the two required surfaces together, raising the temperature initiated a self-crosslinking of polymer III to form the IPN.

Years earlier, Staudinger and Hutchinson\(^{(20)}\) employed a homo-IPN of acrylic composition to make optically smooth surfaces. As amplified in Chapter 1, network I was swollen with more monomer of the same type to smooth out surface wrinkles by the stretching incurred on swelling. Polymerization of the new monomer yielded a homo-IPN.