1. INTRODUCTION

1.1 GENERAL FEATURES OF POLYMER ALLOYS

At different times in the history of polymer science and engineering, specific subjects have come to "center stage" for intense investigation because they represented new and important intellectual challenges as well as technological opportunities. Dilute solution behavior, chain statistics, rubber elasticity, tacticity, single crystal formation, and viscoelastic behavior have all had their day of peak interest and then taken their place for continuing investigation by the community of polymer scientists. These periods of concentrated effort have served to carve out major new areas of macromolecular science to add to and build on the efforts of previous workers.

Polymer alloys (blends) have now come to the fore as such a major endeavor[1-3]. Their current and potential importance especially in technological field is remarkable, since sophisticated applications that demand combinations of properties not attainable with simple homopolymers are being developed. Shen and Kawai[4] were the first who defined polymer alloys as the multicomponent polymer system. In Fig. 1.1, a classification of polymer based materials is shown.

There are essentially two general approaches for forming polymer alloys. The first and simplest approach is that of physically blending two homopolymers. The second general approach is 'chemical' blending, i.e. the formation of copolymers.

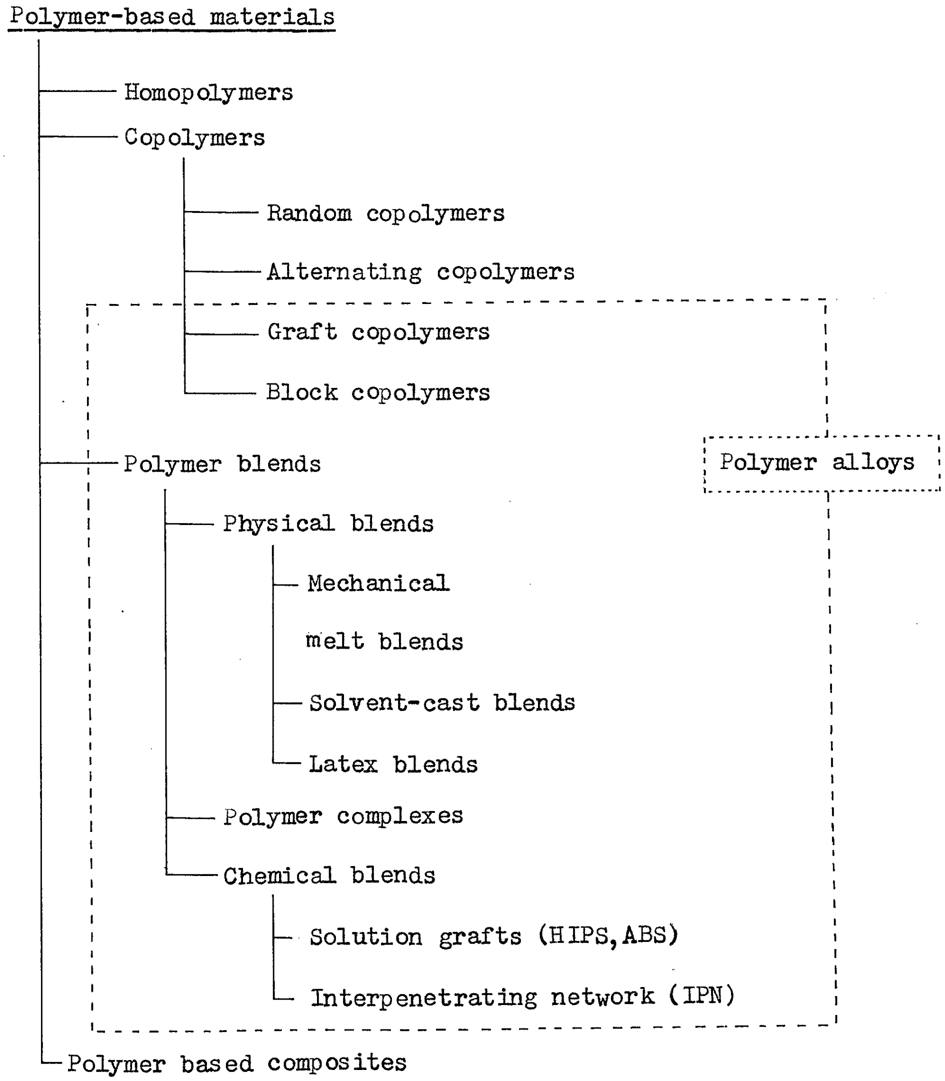


Fig.1.1 A classification of polymer based materials

1.2 GENERAL INTRODUCTION TO COPOLYMERS

Now-a-days, scientific and industrial interest in the field of macromolecules is shifting increasingly from polymers to copolymers, from polymerization to copolymerization. It is widely recognized that the simultaneous polymerization of two monomers in a mixture leads to products that are quite different from the mixtures obtained by polymerizing the two monomers separately and then mixing the two polymers. The copolymerization of the monomers thus must lead to mixed units of two monomers in a single polymer chain. The general term copolymer includes all polymeric products in which two or more monomer units are chemically joined and form part of the same chain. This is a feature which distinguishes a copolymer from a mixture of two homopolymers. Thus polyvinyl chloride does not give fibres with adequate suppleness, and polyvinyl acetate gives fibres having a low softening point and poor mechanical properties. On the other hand, the copolymer of vinyl acetate (12%) and vinyl chloride (88%) is a material well suited for fibre manufacture (vinyon). The introduction of a certain amount of vinyl acetate also has the advantage of making the polymer soluble in acetone, a cheap solvent suitable for dry spinning. In fact, hard polymers like polyvinyl chloride (PVC) are made softer by copolymerization with monomers which form soft homopolymers, such as vinyl acetate. On the other hand, soft polymers, like polyisoprene are made harder by copolymerization with monomers which form hard homopolymers such as styrene or acrylonitrile. Thus, copolymerization with a few percent of a second monomer can produce profound changes in the properties of a polymer which can not be obtained by using mechanical mixtures of homogeneous polymers. The importance of copolymers and the copolymerization as a method of modifying the properties of polymers is reflected in the thousands of copolymers described in scientific and patent literature[5-13].

The properties of copolymers depend not only on the chemical nature of the co-monomers but also on their relative proportions in as well as on the sequence of their distribution in the macrochain of the product. In condensation copolymerizations where the monomers or homopolymers are heated together until equilibrium is reached, the copolymer composition will be directly determined by that of the starting mixture. In addition polymerization, the reactivities of the monomers to the free radical chain ends which are propagating the reaction are in general different, which in turn control the composition of the copolymer.

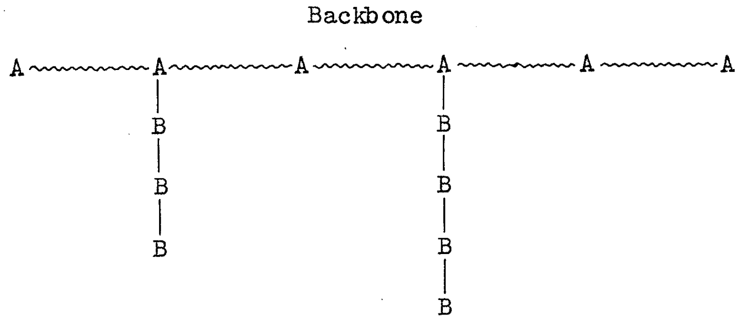
1.3 TYPE OF COPOLYMERS

As shown in Fig. 1.1, copolymers can be divided into four general groups based on the arrangement of monomer units in the chain.

Random copolymers are characterized by a statistical placement of the comonomer repeat units along the backbone of the chain i.e. ~AABABBA~ , where A and B are two different monomers. They are most versatile, economical and easily synthesized type of copolymer. A wide variety of free radical and ionic addition and ring opening polymerization techniques, as well as many step growth reactions, are suitable for their preparation.

Alternating copolymers are characterized by the alternate, rather than statistical, placement of the comonomer repeat units along the chain i.e. ∼ABABAB∼ . This type of copolymer is relatively rare due to the requirements for (a) pairs of monomers with highly specific copolymerization reactivity ratios and/or (b) special reaction conditions.

Graft copolymers are characterized by the chain of same monomeric units attached pendant to the back bone chain of different monomer units i.e.



There is considerable latitude as to the chemical nature of the backbone and the grafted segments and the techniques for joining them. This class of polymer alloys provides the basis for a number of commercially important polymeric materials, such as impact polystyrene, ABS, and methacrylate-butadiene-styrene (MBS) copolymer.