COPOLYMERS, ALLOYS, AND BLENDS — THEY ARE EVERYWHERE YOU LOOK

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What are copolymers, alloys, and blends?

The answer is given most easily in terms of thermoplastics, but the concepts are very important for thermosets, including polyesters, as will be seen later in this article. Definitions of the three terms — copolymers, alloys, and blends — are not universally accepted by all experts, but here are some definitions that seem to work and are gaining support:

- Copolymer: Made by mixing at least one more monomer type than is needed to create a polymer and then polymerizing to create a polymer that is composed of all the monomers present. This rather cumbersome definition is needed because some polymers are made with just one monomer type and some are made from two polymer types. In either case, if an additional monomer type is added, a copolymer is produced. Invariably, the combining of monomers to make a copolymer results in a single phase material that is a new polymer. The new polymer has some properties expected from all the monomer types, based upon their physical and chemical interactions.
- Alloy: Made by mixing traditional polymers which have already been formed. In this case, the mixing results in a single-phase material because the polymers have some interaction that combines them together. The properties of the alloy depend upon the physical interactions of the polymers.

- Blend: Made by mixing traditional polymers which have already been formed but, in this case, the mixing results in a multi-phase system. Physical interactions between the polymers are responsible for the properties of the blend.

Some experts do not make a distinction between the terms alloys and blends but simply identify whether the material is single or multi-phased. We will, however, use the definition listed above in which alloys and blends are different material types.

Some important copolymers were created early in the days of plastics. For instance, common household glue products (similar to Elmer's) can be made by copolymerizing ethylene and vinyl acetate monomers, to create the copolymer which is called EVA. Likewise, the combination of ethylene and acrylic acid monomers yields the class of polymers called EAA. When EAA is mixed with a metallic salt, the class of copolymers called ionomers is formed. Ionomers are used for, among many other things, golf ball covers, and are much tougher than either pure polyethylene or pure polyacrylic acid.

Perhaps the most important of all the copolymers is made by the combination of styrene, butadiene, and acrylonitrile monomers to make the common thermoplastic resin ABS. Various combinations of the monomers in ABS will produce widely different materials, as is represented in Figure 1. The three pure polymers (made when only one monomer is polymerized) are represented by the three corners of the triangle and the combination of all three monomers to make ABS is shown in the middle of the triangle. Increasing the concentration of one of the monomers relative to the others will result in a polymer that has properties dominated by the high concentration material and is represented by moving in the direction of the polymer made from that pure monomer. For instance, pure styrene is a hard, clear and brittle material that is called crystal PS (polystyrene). If a small amount of butadiene monomer is added during the polymerization, the resulting polymer becomes tougher and is called HIPS (high impact polystyrene). If a new polymer is made with even more butadiene, that polymer would be quite elastomeric and would be called SBR (styrene butadiene rubber). Likewise, mixtures of styrene and acrylonitrile result in properties that are intermediate between those of pure polystyrene and pure acrylonitrile. This chart, while specific to ABS, represents the basic principle underlying all copolymers. That is, combinations of monomers result in new polymers which have properties intermediate between those of the polymers made from the pure monomers.

Copolymer repeating patterns

The above discussion of copolymers has largely ignored an important factor in making copolymers. By carefully choosing the conditions under which the copolymerization takes place, the pattern of monomer units can be altered. Four basic patterns are known and are pictured in Figure 2. The patterns for regular (alternating), random, and block copolymers are largely determined by the reaction rate differences for the competing reactions which would form the polymers. These have been studied extensively in the polymer literature, but are beyond the scope of this paper.

Most of the copolymers are random or regular with little effort to choose between them as the properties do not change very much from one to the other. Block copolymers, however, can have significantly different properties from random or regular. An excellent example of this is the styrene-butadiene-styrene block copolymer made by Shell and called Kraton®. At room temperatures these block copolymers are elastomeric and act as though they were crosslinked, like vulcanized rubber, exhibiting high resilience and low creep. However, they flow like a true thermoplastic when heated above 200 °F. The reason is that the large polystyrene blocks form glassy crystalline aggregates that function as crosslinks at low temperatures, then flow at higher temperatures. The results can be quite astounding, as seen in Table 1.

The use of graft copolymers has been very rewarding in recent years. The properties of the graft copolymer are generally those of the backbone polymer, with minor changes made by the grafted side chains. One of the most important applications of this technique is the modification of natural polymers, such as wool, with synthetic polymers, like nylon. When short grafts of nylon (as little as 1% total weight) are placed onto wool fibers, the wool can be machine-washed and tumble-dried without danger of shrinkage. Over 30 similar grafts have been made to silk, cotton, wool, rayon, wood, bamboo, and other synthetic fibers to decrease water absorption, reduce shrinkage, and enhance dyeability.

Copolymers in thermoset polyesters

We rarely think of copolymers in connection with crosslinkable (unsaturated) polyesters, but almost all commercial crosslinkable polyesters today are copolymers and we can understand the nature of these materials better if we think of them as copolymers. To establish the foundation for consideration of the copolymer nature of polyesters, let’s first consider the simplest polyester polymer and then we can understand why copolymers have become so important.

Polyesters are made by combining two monomers — a di-acid and a diol. These are shown in Figure 3 and their resulting product, the polyester is also shown. The polyester is shown in its general form, that is, the repeating unit (shown in the parentheses) which implies that many diols and di-acids have reacted to form the polymer. (The small n after the molecular repeating unit signifies that many of the units are linked together.) For the polyester to be crosslinkable, either the di-acid or the diol must contain a carbon-carbon double bond, which is also called an unsaturation point. Most often, it is the acid that has the double bond, and that is shown in Figure 3.

Notice that when the two monomers are mixed as shown in Figure 3, every repeat unit contains an unsaturation. Although this is the type of unsaturated polymer that was first made, experience in using this polymer quickly showed that too many crosslinks were formed when the polymer cured, and the resulting cured polymer was far too brittle to be useful. Therefore, the resin manufacturers reasoned that if some of the repeat units did not contain the unsaturation, the amount of crosslinking (crosslink density) would be less and the polymer would be less brittle. Hence, another di-acid was added, this time, one that did not contain a carbon-carbon double bond. That new di-acid would compete with the original di-acid and, depending on the relative concentrations of the di-acids, the resulting polymer would have varying degrees of repeat units with unsaturation. The variation in the number of each of the di-acid types is represented by the n and the m in Figure 4, where this new reaction is shown. The measure of the amount of units with unsaturation has been called the acid number and is an indication of the amount of crosslinking that can occur.

The case shown in Figure 4 shows one of the di-acids to be an iso type. This is, of course, a common type of polyester resin. The iso monomer does not participate in the crosslinking but adds other desirable properties to the polymer (such as toughness, durability, and light stability). Other di-acids which could be used include ortho-types and DCPD-types.

In another example, the resin manufacturer may want to have some bromine in the polymer to improve the non-flammability of the polymer. That can be done by adding yet another di-acid polymer which would contain bromine or, if preferred, adding a second diol polymer which contains bromine. In either case, the bromine-containing monomer would be included in the final polymer along with the unsaturation and the iso groups.

The power of the copolymer system in making unsaturated polyesters can be seen from these examples. If the resin manufacturer wants to increase the toughness of a polymer, more of the monomer which gives toughness is added, or if more crosslinking is desired, then that monomer concentration is increased, or if more flame retardance, then the bromine-containing monomer is added. This situation is similar to the ABS case for thermoplastics shown in Figure 1 where increasing the concentration of the monomer is represented by moving within the triangle.

Polyester systems have yet one more place where copolymers can be utilized. That is in the crosslinking reaction itself. Normally, crosslinking occurs when styrene forms a bridge between two polymer chains by connecting them at the unsaturation points. However, styrene is just another monomer which enters the reaction during a special phase of the process (cure). What if a second monomer were added with the styrene? That monomer would compete with the styrene and, therefore, some of the crosslinks would be formed by the new monomer. This is exactly what is happening in the formulations in which MMA (acrylic) monomer is added to the polymer/styrene system. The acrylic gives certain desirable properties to the finished product, such as lower smoke generation, and therefore forms a valuable copolymer with the polyester and styrene.

Alloys and blends employing unsaturated polyesters

Alloys and blends are made by mixing fully formed polymers rather than monomers. In the case of unsaturated polyesters, this could be done in the molding shop by simply mixing resins of two different types. In other words, the molder can vary the properties of the final polymer product by mixing together two polymers. Because these two polymers are usually dissolved in styrene, the mixing operation is done by simply stirring the resins together. The results are not, however, easy to predict. Figure 5 represents the three types of polymer products that can result. If the polymers are compatible, the properties can be synergistic, that is, the combined properties can actually be better than either of the two pure polymers. (For instance, if the property being examined is toughness, the combined polymer product could have better toughness than either of the two separate polymers.) Sadly, this case is rare.

If the polymers are non-compatible, the resulting mixture could be worse than properties of either of the two polymers separately. It is also possible that the mixture of the polymers would be a simple linear average of properties of the two pure polymers. These cases are also shown in Figure 5.

The chances of getting a synergistic mixture are enhanced if the resins are compatible. Sometimes that compatibility can be increased by adding another material that is separately compatible with two otherwise incompatible resins. In unsaturated polyesters, the styrene may serve as a compatibilizer which becomes effective after curing has occurred.

Thermoplastic alloys and blends

Making thermoplastic polymers and copolymers is an expensive process requiring large reactors and lots of specialized equipment. However, making blends and alloys is a much simpler process, usually requiring only an extruder to melt and mix the polymers. Hence, the field of polymer blends and alloys is growing rapidly as molders are experimenting on their own by making new blends and alloys. Some of those which have proven to be successful are sold by the major resin manufacturers and others are sold by compounders and are less widely known.

Examples of typical work involves the blends formed by combining ionomers with polypropylene and then with polyamide (nylon). In the first case, the blends are strongly incompatible whereas in the second, the blends are so compatible that the multi phase nature of the blend is only detected at extremely high magnification. This is presumably because the ionomer, which is a polar molecule, has poor interactions with the polypropylene (which is non-polar) but good interactions with the polyamide (which is polar).

As already discussed, when two polymers are incompatible, as with ionomer and polypropylene, a compatibilizing agent can be added. These agents often have one end of the molecule that is like one polymer and the other end like the other polymer. In this way, the polymers are linked together and compatibility is improved. This same technique is used to combine oil and water in washing your hands where the compatibilizing agent is soap. The technique is also used to improve the compatibility of fiberglass and resin by using a fiberglass coupling agent.

Just a small sampling of the commercially available blends and alloys include: polycarbonate/ABS, ABS/PVC, ABS/polyamide, polycarbonate/PET, polyphenylene oxide/high impact polystyrene, ABS/polycarbonate, and polyamide/polyolefin. More of these blends and alloys are coming and you could even experiment yourself.

Table 1. Comparison of a block copolymer (Kraton®) with Typical Natural and Synthetic Vulcanized Rubbers

	Tensile strength (lb/in^2)	Elongation (%)	Cycles to Failure
Triblock thermoplastic rubber (Kraton® 101)	40,300	740	145,000
Natural rubber (carbon black reinforced and cured)	28,200	560	48,000
SBR synthetic rubber (carbon black reinforced and cured)	29,800	590	45,000

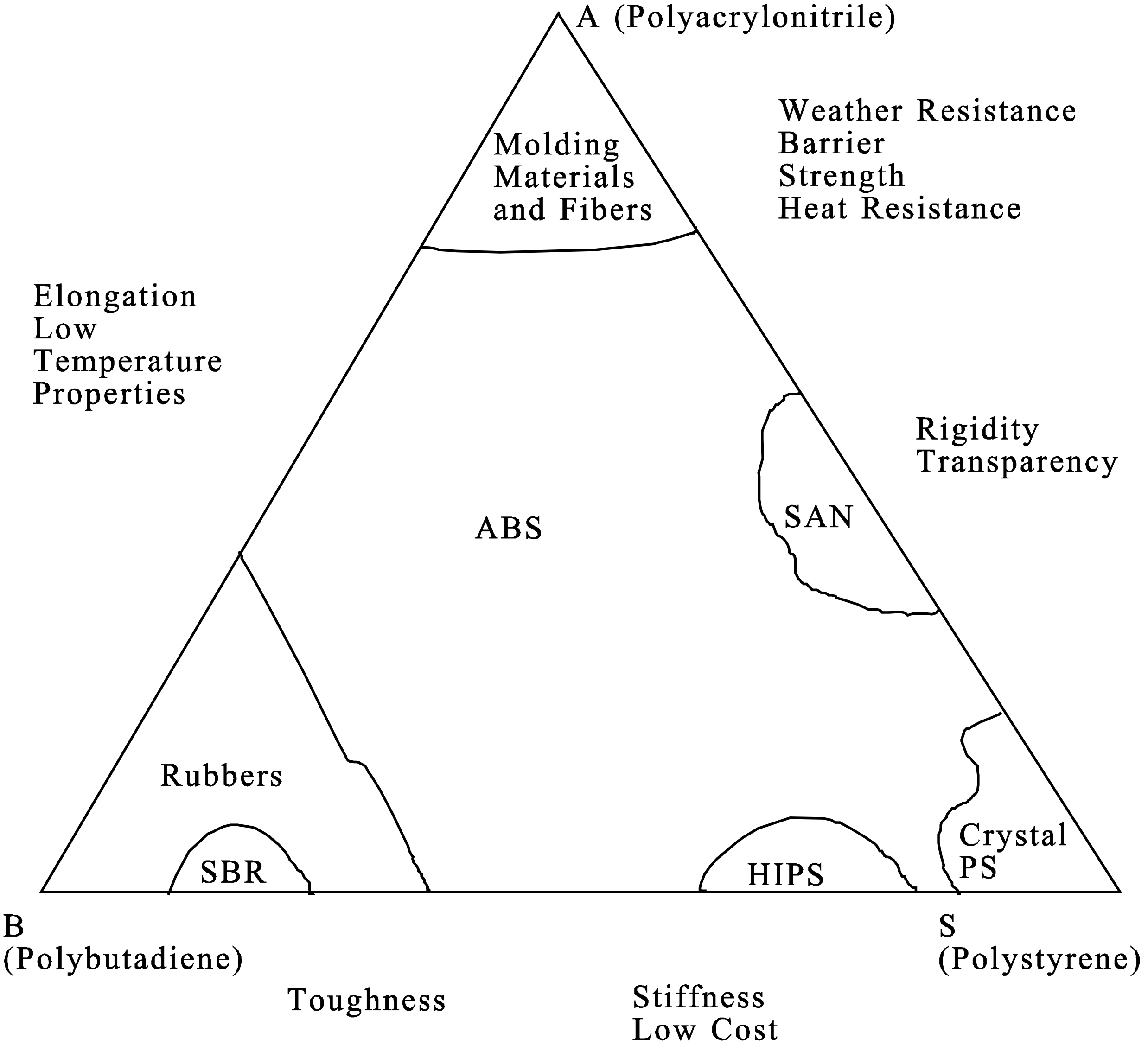
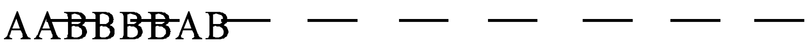


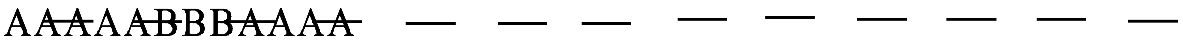
Figure 1
Representation of the changing properties among polyacrlonitrile, polybutadiene, polystyrene and ABS.

Fig1.wpg

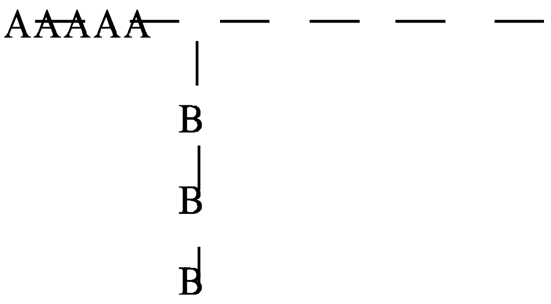
a) Regular (alternating)



b) Random



c) Block



d) Graft

Figure 2
Types of Copolymers

Copoly.wpg

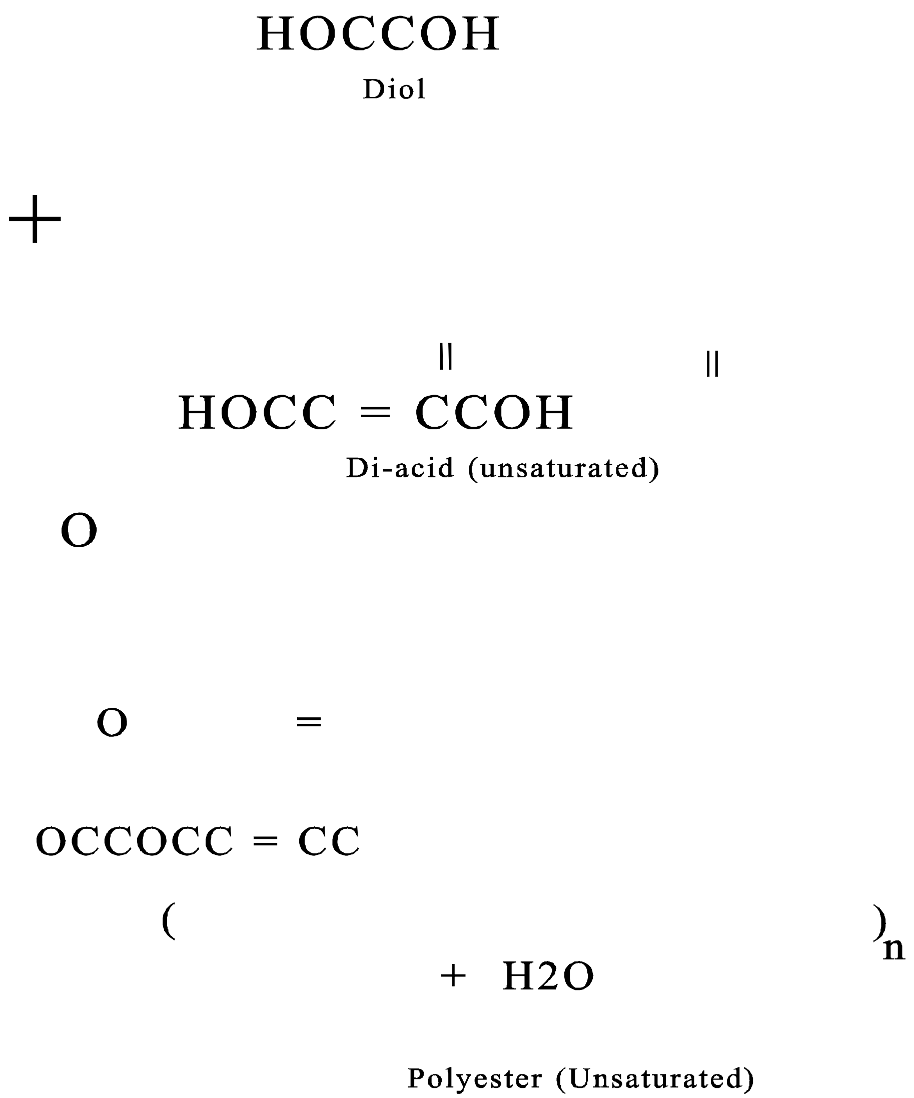


Figure 3
Reaction of a diol and an unsaturated di-acid to form a polyester.

Fig3.wpg

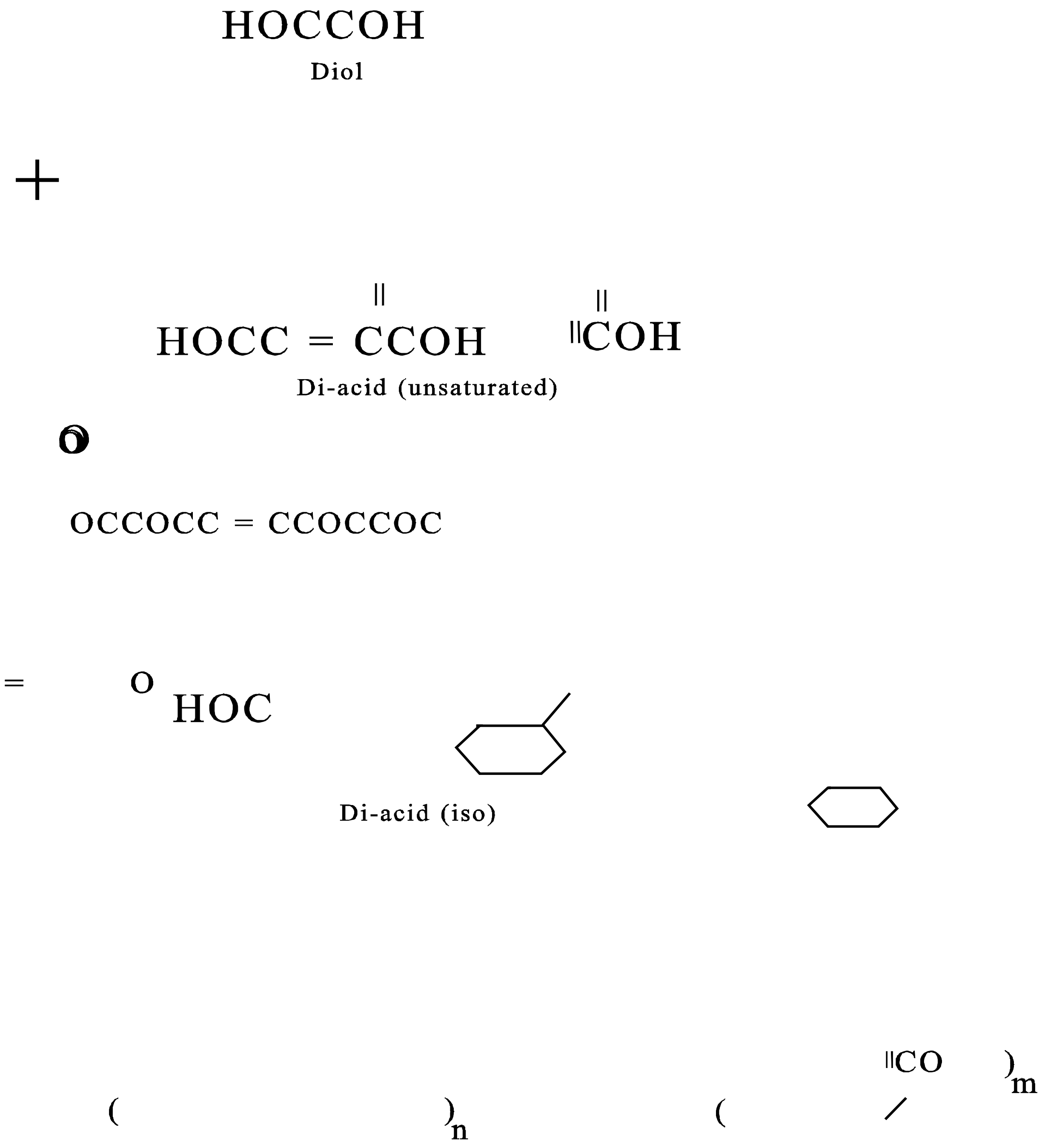


Figure 4
Reaction of a diol with two types of di-acids.

Reaction.wpg

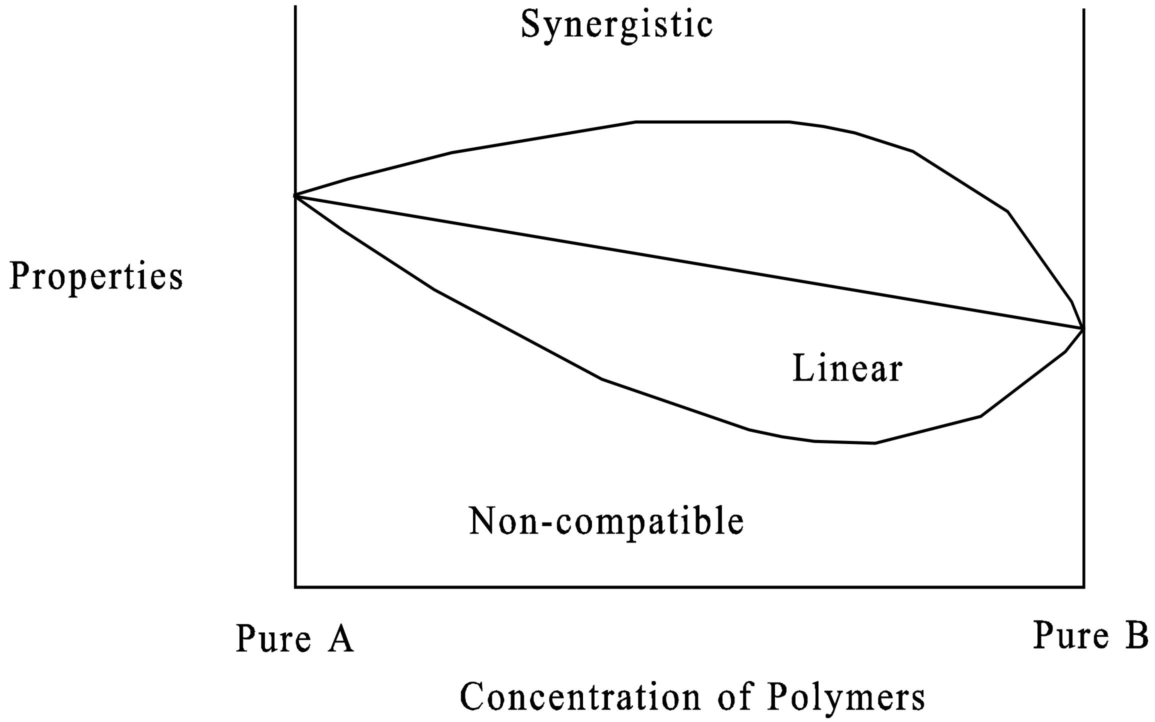


Figure 5
Types of alloys and blends possible when mixing two polymers (A and B).

Alloys.wpg

Added material—

Page 6, bottom of page, new paragraph

Although not a copolymer in the usual sense, the reaction of the material with an additional monomer, isocyanate, qualifies the much discussed polyester/urethan for consideration in this paper. This product is Xycon, a resin developed by Amoco and now sold by Cook Composites. This resin is a polyester/polyol that is reacted with isocyanate to extend the chain far beyond what would normally be possible. The material can then be crosslinked using standard styrene crosslinking. The advantages of this resin over standard polyesters are associated with the higher linear molecular weight and include higher elongation, high heat distortion temperature, and higher toughness.