# Summary

        Elastomers are polymeric materials that can stretch to over twice their normal length and then, when the stretching force is relieved, return immediately to their original shape. This behavior is called elastic elongation. Most elastomers will also compress to one-half their original size and return again to their original shape after the compressing force is removed. This property is called resiliency. The stress strain curve for most elastomers shows a low initial slope (low modulus) and a long elongation with very little force required.

         If elastomeric materials are crosslinked, they continue to exhibit this elastomeric behavior provided that the number of crosslinks is not too high. The crosslinking or curing of elastomers is called vulcanization. Typically, there is one crosslink for every 100 or so atoms along the polymer backbone. This amount of crosslinking is much less dense than in the thermoset plastic molding resins that were discussed in Chapter 9. The amount of crosslinking in elastomers is sometimes described as lightly crosslinked. The crosslinks have the beneficial effect of giving an ultimate limit to the amount of stretch that the molecules can have, that is, the amount of creep, thus solving one of the most difficult problems confronting the early users of elastomeric materials the softening and creeping that occurred at high temperatures. Another advantage of crosslinks is that the limit to stretching limits the elastic range, thus defining the maximum amount of stretch that can be obtained without permanent deformation.

         Elastomeric materials are usually highly random, aliphatic molecules that have no crystallinity in their relaxed state. These molecules can be pulled into more oriented configurations, which is what occurs during elastic stretching. The most common materials that possess these properties are built on a four-carbon backbone unit with a carbon-carbon bond between the middle two carbons. Some molecules have one or more pendant methyl groups, which add intramolecular and intermolecular interferences that result in higher stiffness, higher strength, and higher hardness. In some applications these interactions are desirable, whereas in other applications they are not. Some elastomers have added bulky comonomers (like styrene) to achieve similar interactions. Chlorine can be added as a pendant group to the basic four-carbon repeating unit to give intermolecular interactions and, in addition, oil resistance.

        Thermoplastic elastomers can be made by copolymerizing materials that create soft and hard segments. The advantage of these materials over crosslinked elastomers is that they can be processed in traditional thermoplastic processes, such as extrusion and injection molding.

        Fluorocarbon polymers can be made that have 200% elongation with full recovery, and these are therefore elastomers. The fluorocarbon elastomers have excellent resistance to oils, acids, alkalis, and most other solvents. This resistance extends over the entire range of use, which is much broader than for other elastomeric materials. The fluorocarbon elastomers also have excellent resistance to oxidation and UV radiation.

         Silicones are polymers based on the silicon atom rather than on the carbon atom. When polymerized, the silicon monomers form repeating silicon-oxygen bonds, which are called siloxane bonds. Therefore, silicon polymers are polysiloxanes or, more normally, silicones. Silicones can be oils, elastomers, or molding compounds, the elastomers being the most important. When these elastomers are cured at room temperature (usually by the absorption of either water or carbon dioxide), the curing system is called room-temperature vulcanization (RTV). When cured at high temperatures, usually with peroxides, the system is called high-temperature vulcanization (HTV).

         To achieve good durability, as would be needed in automobile tires, fillers need to be added to elastomers. The most common filler is carbon black, which also imparts resistance to UV radiation. This carbon black must be well dispersed in the elastomeric batch. To accomplish this task, high-intensity and high-shear mixers have been developed. The most common type of mixer for this purpose is the Banbury mixer.

        Two mixing steps are normally required when using a Banbury mixer. The filler and other minor constituents are added in the first mixing step, which is usually done at high temperatures. A second step to mix in the curing agent is done at lower temperature so that the mixture will not prematurely crosslink. After mixing is completed, the elastomeric batch is preformed, usually on a two-roll mill, and is then molded and cured.

         One of the key functions of elastomeric materials is to toughen other plastics. The effect varies depending on the primary nature of the base plastic and its compatibility with the toughening rubber agent. Because toughness depends on both strength, elongation, and, in the case where tougheners are added, compatibility of the polymers, it is difficult to understand and relate the toughness of one plastic to another. A chart is given in Appendix 4 to assist in comparing the toughness of several representative plastics.

## 10.8.1. Questions

1. What are the key polymeric structural features common to most elastomeric materials?

2. What is the mechanism and thermodynamic explanation for why elastomers recover to their original shape after being elastically stretched?

3. Why is the cis form of polyisoprene softer than the trans form?

4. Explain why polybutadiene is softer than polyisoprene.

5. Explain why silicones have higher gas permeability than do carbon-based molecules with equivalent pendant groups.

6. Describe the changes in properties that are likely to occur when the temperature is lowered below the Tg for an elastomer. What does this indicate about the usable lower temperature range for elastomers?

7. What is the effect of crosslinks on an elastomer and what is the structural explanation for their effect? What would happen to the amount of stretch, hardness, strength, and creep in an elastomer if the crosslink density were increased?

8. Explain why copolymers of ethylene and propylene can be elastomers when the pure polyethylene and pure polypropylene are not elastomeric. Discuss whether you would expect a blend (instead of a copolymer) of polyethylene and polypropylene to be elastomeric.

9. Explain what may happen to the properties of a rubber material if the carbon black filler is poorly mixed into the batch.

10. Why would fluorocarbon elastomers be so effective in resisting solvents?

11. (a) Explain why stretching an elastomer causes an unstable state and, therefore, when the stretching force is removed, why the elastomer recovers. (b) Explain why stretching of some polyethylene molecules results in "blushing," a situation not eliminated when the stretching force is removed.

12. Explain why a rubber band fails after having been wrapped very tightly around an object for several months.

13. Explain why a rubber washer stops sealing tightly after several years.

14. What is the effect of chlorinating rubber?

15. Using molecular explanations, discuss the differences in mechanical, physical, and chemical properties of natural rubber and butadiene.

## 10.8.2. References

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