

15.24 This problem asks for us to determine how many crosslinks form per isoprene repeat unit when 45.3 wt% sulfur is added, assuming that, on the average, five sulfur atoms participate in each crosslink. If we arbitrarily consider 100 g of the vulcanized material, 45.3 g will be sulfur and 54.7 g will be polyisoprene. Next, let us find how many moles of sulfur and isoprene correspond to these masses. The atomic weight of sulfur is 32.06 g/mol, and thus,

$$\# \text{ moles S} = \frac{45.3 \text{ g}}{32.06 \text{ g/mol}} = 1.41 \text{ mol}$$

Now, in each isoprene repeat unit there are five carbon atoms and eight hydrogen atoms. Thus, the molecular weight of a mole of isoprene units is

$$(5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

Or, in 54.7 g of polyisoprene, the number of moles is equal to

$$\# \text{ moles isoprene} = \frac{54.7 \text{ g}}{68.11 \text{ g/mol}} = 0.793 \text{ mol}$$

Therefore, the ratio of moles of S to the number of moles of polyisoprene is

$$\frac{1.41 \text{ mol}}{0.793 \text{ mol}} : 1 = 1.78 : 1$$

When all possible sites are crosslinked, the ratio of the number of moles of sulfur to the number of moles of isoprene is 5:1; this is because there are two crosslink sites per repeat unit and each crosslink is shared between repeat units on adjacent chains, and there are 5 sulfur atoms per crosslink. Finally, to determine the fraction of sites that are crosslinked, we just divide the actual crosslinked sulfur/isoprene ratio by the completely crosslinked ratio. Or,

$$\text{fraction of repeat unit sites crosslinked} = \frac{1.78/1}{5/1} = 0.356$$