

Materials and technology 112



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Question For each of the following pairs of polymers, decide which is more likely to have the greater tensile strength, and then give reasons for your choice:

(a) Lightly cross-linked polyethylene; network Bakelite

A network Bakelite has a greater tensile strength than a lightly cross-linked polyethylene. 1 Crosslinking hinders the re-organization of molecules during crystallization; hence, a lightly cross-linked polyethylene has a lower degree of crystallinity as compared to its linear form. A decrease in crystallinity makes crosslinked polymers less rigid and weaker. On the other hand, a network of Bakelite, though it has a highly crosslinked structure, often produces hard, impervious, black, and tough solids².

(b) High density polyethylene; low density polyethylene

High density polyethylene has high levels of crystallization. 3 The crystallization process is less likely to hinder because of low level branching in its structure. Crystallization markedly enhances strength, rigidity, and opacity of a polymer. High density polyethylene, then, is the stiffest of all types of polyethylene due to its high degree of crystallinity. Thereby, high density polyethylene has a greater tensile strength than low density polyethylene.

(c) 95% crystalline and linear PTFE; 95% crystalline and branched PTFE

Branching tends to impede crystallization, making a polymer less rigid, more easily to deform, and weaker⁴. Thus, a 95% crystalline and linear polytetrafluoroethylene (PTFE) has a greater tensile strength than a 95% crystalline and branched PTFE.

Question 2:

Molecular weight data for some polymer are tabulated below. Compute (a)

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the number-average molecular weight, and (b) the weight-average molecular weight. (c) If it is known that this material's degree of polymerisation is 477, which one of the polymers listed in Table 14. 3 of the lecture notes is this polymer? Why?

Number-Average Molecular Weight (M_n)

Mass per molecule, M_i (g/mol)

Number fraction, X_i

$X_i M_i$ (g/mol)

14, 000

0. 05

700

26, 000

0. 15

3, 900

38, 000

0. 21

7, 980

50, 000

0. 28

14, 000

62, 000

0. 18

11, 160

74, 000

0. 10

7, 400

86, 000

0. 03

2, 580

Mn

47, 720

$$M_n = \sum X_i M_i$$

$$= 47, 720 \text{ g/mol}$$

Weight-Average Molecular Weight

Mass per molecule, M_i (g/mol)

Weight fraction, W_i

$W_i M_i$ (g/mol)

14, 000

0. 02

280

26, 000

0. 08

2, 080

38, 000

0. 17

6, 460

50, 000

0. 29

14, 500

62, 000

0. 23

14, 260

74, 000

0. 16

11, 840

86, 000

0. 05

4, 300

Mw

53, 720

$$M_w = \sum W_i M_i$$

$$= 53, 720 \text{ g/mol}$$

n_n = number-average degree of polymerization

m = molecular weight of a mer unit

$$n_n = M_n / m$$

$$n_n = 477 \text{ Mn} = 47, 720 \text{ g/mol}$$

$$n_n = 47, 720 \text{ g/mol}$$

477

$$n_n = 100. 042 \text{ g/mol}$$

This value is closer to the molecular weight of the mer unit of PTFE/Teflon.

Question 3:

The density and associated % crystallinity for two polypropylene materials are as follows:

ρ (g/cm³)

Crystallinity (%)

0. 904

62. 8

0. 895

54. 4

(a) Compute the densities of totally crystalline and totally amorphous polypropylene.

Crystallinity = $C \rho = \text{density}$

$C = \% \text{ crystallinity} / 100$

$= \rho_c (\rho_s - \rho_a)$

$\rho_s (\rho_c - \rho_a)$

by rearrangement:

$\rho_c (C \rho_s - \rho_s) + \rho_c \rho_a - C \rho_s \rho_a = 0$

where:

ρ_c and ρ_a are unknown

Since ρ_c and C are specified in the problem, two equations can further be derived:

$\rho_c (C_1 \rho_{s1} - \rho_{s1}) + \rho_c \rho_a - C_1 \rho_{s1} \rho_a = 0$

$\rho_c (C_2 \rho_{s2} - \rho_{s2}) + \rho_c \rho_a - C_2 \rho_{s2} \rho_a = 0$

where:

$\rho_{s1} = 0.904 \text{ g/cm}^3$ $\rho_{s2} = 0.895 \text{ g/cm}^3$

$C_1 = 0.628$ $C_2 = 0.544$

$\rho_a = \rho_{s1} \rho_{s2} (C_1 - C_2)$

$C_1 \rho_{s1} - C_2 \rho_{s2}$

$= (0.904 \text{ g/cm}^3) (0.895 \text{ g/cm}^3) (0.628 - 0.544)$ __

$(0.628) (0.904 \text{ g/cm}^3) - (0.544) (0.895 \text{ g/cm}^3)$

$\rho_a = 0.841 \text{ g/cm}^3$

$\rho_c = \frac{\rho_{s1} \rho_{s2} (C_2 - C_1)}{\rho_{s2} (C_2 - 1) - \rho_{s1} (C_1 - 1)}$ __

$\rho_{s2} (C_2 - 1) - \rho_{s1} (C_1 - 1)$

$= \frac{(0.904 \text{ g/cm}^3) (0.895 \text{ g/cm}^3) (0.544 - 0.628)}{(0.895 \text{ g/cm}^3) (0.544 - 1) - (0.904 \text{ g/cm}^3) (0.628 - 1)}$ _____

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0.895 g/cm³ (0.544 - 1.0) - (0.904 g/cm³) (0.628 - 1.0)

$$\rho_c = 0.946 \text{ g/cm}^3$$

(b) Determine the density of a specimen having 74.6% crystallinity.

ρ_s = density of specimen

$$\rho_s = \frac{C \rho_c + (1 - C) \rho_a}{C(\rho_c - \rho_a) + \rho_c}$$

$$C(\rho_c - \rho_a) + \rho_c$$

$$= \frac{0.746(0.946 \text{ g/cm}^3) + (1 - 0.746)(0.841 \text{ g/cm}^3)}{0.746(0.946 \text{ g/cm}^3 - 0.841 \text{ g/cm}^3) + 0.946 \text{ g/cm}^3}$$

$$= \frac{0.704(0.105 \text{ g/cm}^3) + 0.946 \text{ g/cm}^3}{0.0746(0.105 \text{ g/cm}^3) + 0.946 \text{ g/cm}^3}$$

$$\rho_s = 0.917 \text{ g/cm}^3$$

Question 4:

Carbon dioxide diffuses through a high density polyethylene (HDPE) sheet 50 mm thick at a rate of 2.2×10^{-8} (cm³ STP)/cm²-s at 325 K. The pressures of carbon dioxide at the two faces are 4000 kPa and 2500 kPa, which are maintained constant. Assuming conditions of steady state, what is the permeability coefficient at 325 K?

$$50 \text{ mm} = 5 \text{ cm}$$

$$Q / t = PA (P_1 - P_2) / l$$

Q - quantity of permeant
P - permeability
A - area

t - time
P₁ - P₂ - drop in pressure

$$2.21 \times 10^{-8} \text{ cm}^3 / \text{cm}^2\text{-s} = P (14.8038 \text{ atm})$$

$$5 \text{ cm}$$

$$P = 7.4643 \times 10^{-9} \text{ cm}^3\text{-cm}$$

$$\text{cm}^2\text{-s-atm}$$

Bibliography

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Sperling, Leslie Howard. Introduction to Physical Polymer Science. Hoboken, NJ: Wiley, 2006.