Analysis of polymer blend morphologies

The impact resistance of semi-crystalline polymers has been shown to be greatly enhanced when blended with rubber particles. However, there seems to be a critical value $L_c$ of the distance $L$ between particles above which the material undergoes brittle fracture when submitted to impact loading; for example, for polyethylene toughened by elastomers, the impact Charpy toughness at 25 Celsius drops from 20kJ/m² for $L = 0.08\mu m$ to 1.5kJ/m² when $L = 0.2\mu m$. In order to determine how the average value of $L$ varies with the average volume fraction and size of the particles, it is necessary to determine the probability distribution of $L$ in the material under consideration, using both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The scope of the present problem is the study of a method which provides such insight. The first part focusses on a method aimed at determining first the probability distribution of rubber particles from TEM and SEM observations.

1. DISTRIBUTION IN PARTICLE SIZE

For TEM observations, thin layers (500-100 nm thickness) of the material are used. What is observed is a bidimensional projection of this thin section. How to reconstruct the true 3D distribution from such observations? This “cross-section” effect also exists in SEM experiments: it arises from the fact that the observed micrograph is a 2D section of of randomly cut particles. In both cases (TEM and SEM), the apparent diameter of the particle is smaller than its true diameter as soon as it is not cut through its center. This is the case of particles 1 and 3 in Fig.1.

Fig. 2(a) shows a typical TEM micrograph of polyamide matrix toughened with 20% particles. In order to determine the size distribution of particles, the image is subsequently binarized (Fig.2(b)), and particles are labeled (Fig.2(c))

An area equivalent diameter $d$ is defined for each particle as the diameter of a circle of same cross-sectional area $A$:

$$d = 2\sqrt{\frac{A}{\pi}}$$

The distribution of particle diameters $d$ is shown in Fig. .

We call $P_A$ the 2D distribution of particle apparent diameters and $P_V$ the 3D distribution of real particle diameters. Practically, $P_A$ and $P_V$ are used in a discrete form. They are divided into the same number of classes, $p$, of equal widths. For each class $i$ ($0 \leq i \leq p$), $P_A(i)$ is the number of particles per
Fig. 1. TEM shows a two-dimensional projection of a thin section (thickness $H$). Particles 1, 2 and 3 have the same diameter $r$. However, the centers of particles 1 and 3 being respectively above and below the thin section, their apparent diameters $a_1$ and $a_3$ are smaller than $r$ (cross-section effect). The center of particle 2 lies within the thin layer, and it appears on the TEM image with its true diameter $r$. In SEM, the same effect exists: it corresponds to a thickness $H = 0$.

Fig. 2. (a) TEM micrograph of polyamide matrix toughened with 20% particles; (b) Binarized image; (c) analyzed image, where particles are identified, numbered and outlined.

unit area with apparent diameter within the range $[i \Delta, (i + 1) \Delta]$. The particle diameter in each class $i$ is represented by its lower limit $i \Delta$. Similarly, for each class $j$ ($0 \leq j \leq p$), $P_V(j)$ is the number of particles per unit volume with real diameter lying within $[j \Delta, (j + 1) \Delta]$.

We distinguish the contribution of particles the center of which is located in the thin layer from the contribution of particles the center of which is located outside the thin layer. For a given class $i$, $P_A$ is decomposed as follows:

$$P_A(i) = P_A^{in}(i) + P_A^{out}(i)$$  \hspace{1cm} (2)
where $P_A^{in}(i)$ and $P_A^{out}(i)$ are the number of particles belonging to class $i$ per unit area the center of which lies respectively inside and outside the thin section.

1- Using Fig.1, find a relationship between $P_A^{in}(i)$, $H$ and $P_V(i)$.

2- $P_A^{out}(i)$ being the number of particles with a real diameter larger than $i\Delta$ and apparent diameter $i\Delta$, show that:

$$P_A^{out}(i) = \sum_{j=1}^{p} P_A(i, j) \quad (3)$$

where $P_A(i, j)$ is the number of particles per unit area with an apparent diameter $i\Delta$ and a real diameter between $j\Delta$ and $(j+1)\Delta$.

Considering that for each couple $(i, j)$, the center of such particles is confined within a narrow strip of thickness $dh$ (Fig. 4), find a relationship between $P_A(i, j)$, $dh$ and $P_V(j)$. Show that $dh$ can be expressed in function of $i$ and $j$ using simple geometry.

3- By replacing $P_A(i, j)$ by this expression in Eq.(3), find the expression of $P_A^{out}(i)$ as a function of $\Delta$ and $P_V$. From this expression, deduce the relationship between $P_A$ and $P_V$. 

Fig. 3. Two-dimensional distribution $P_A(d)$ of particle diameters.
Fig. 4. Correction from the cross-section effect. The idea is to determine the contribution of particles which center is outside the thin section. Consider particles with apparent diameter $j\Delta$ and real diameter in the range $[j\Delta, (j + 1)\Delta[$. Their center is located within a thin strip of thickness $dh$.

Inverting this relationship numerically leads to the experimental distribution $P_Y$ plotted in Fig.5.

These distributions are well fitted with a log-normal distribution. We now use these results to determine the distribution in ligament thicknesses (distance $L_{AB}$ between particles $A$ and $B$, as defined in Fig.6).

2. DISTRIBUTION IN LIGAMENT THICKNESS

We assume the particle distribution to be isotropic, and the particles to be spherical. Furthermore, we will assume that particles are dispersed on a body-centered cubic lattice. Under these conditions, it can be shown that the ligament distribution only depends on the distribution in particle size. We call $P_L$ the probability density in ligament thickness, so that $P_L(x)dx$ is the probability per unit length that $L$ lying between $x - \Delta x$ and $x + \Delta x$.

4- Express the probability $P[L_{AB} \leq \mathcal{L}]$ as a function of $P_L$. Because $L_{AB}$ can be linked to the particles radii $d_A$ and $d_B$ (see Fig. 6), one can write:

$$P[L_{AB} \leq \mathcal{L}] = P[d_A + d_B \geq 2(D - \mathcal{L})]$$  (4)
Fig. 5. Distribution in particle size for two samples of polyamide toughened with elastomer. **Left:** 10wt% elastomer, particle size $\sim 130$nm. **Right:** 10wt% elastomer, particle size $\sim 340$nm. In both cases (left and right): (a) TEM micrograph. (b) Distribution in particle diameter before and after reconstruction for various section thicknesses ($\Delta=10$nm on the left; $\Delta=50$nm on the right; $H=0, 60$ and $100$nm). Negative values are obviously spurious, and are partly due to the difficulty of detecting the smallest particles in images analysis. The cross-section effect may also be overcorrected, especially when $H=0$.

Fig. 6. Two nearest-neighbored particles $A$ and $B$ separated by a distance $D$. $L_{AB}$ is the ligament thickness. $L_{AB} = D - \frac{1}{2}(d_A + d_B)$.

Deduce from (4) that:

$$P[L_{AB} \leq \mathcal{L}] = \int_{z=2(D-\mathcal{L})}^{+\infty} P_{d+d}(z)dz \quad (5)$$

where $P_{d+d}(z)$ is the probability density of variable $z = d_A + d_B$. 

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Fig. 7. $P_L(L)$, in nm$^{-1}$ is plotted as a function of $L$ expressed in nm, for two values of particle volume fractions $\Phi = 30\%$ and $\Phi = 5\%$.

Considering that particles are supposed to be dispersed on the lattice regardless of their sizes, and that hence, $d_A$ and $d_B$ are independent random variable distributed with the same probability density, show that:

$$P_L(L) = \int_{x=0}^{2(D-L)} P_d(x)P_d(2D - 2L - x)dx$$

This distribution $P_L(L)$ is plotted as a function of $L$ in Fig. 6 for two different volume fractions of particles $\Phi = 30\%$ and $\Phi = 5\%$. Considering Eq. (6), do you understand where this dependency of $P_L(L)$ on $\Phi$ comes from?