Small-angle X-ray study of particulate reinforced composites

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Small-angle X-ray scattering technique can be used to quantify the microvoids structure within a particulate reinforced composite. An expression for the correlation function of three-phase systems has been derived in terms of the correlation function of the individual phases. By using this expression and the scattered intensities from the damaged and the undamaged composites; it has been show that the volume fraction and the chord length of the microvoids can be obtained, provided no damage occurs to the reinforcement particles. In cases where the microvoids are preferentially oriented within the composites, an approximation scheme based on a linear transformation method has also been developed to measure the aspect ratio of the microvoids provided the volume fraction of these microvoids is much smaller than the other two phases.

Keywords Chord length; composite materials; correlation function; small-angle X-ray scattering; three-phase system

INTRODUCTION

Small-angle scattering techniques, e.g. X-ray, neutron, light, etc., have been used extensively in characterizing the structure of various heterogeneous systems. Most theoretical schemes developed so far have been intended for elucidating certain structure parameters in two-phase systems only. These schemes, for example, are Porod plot for specific interface area[1], chord length determination by integration of the scattered intensity[2] and a Guinier plot for the radius of gyration in dilute systems[2].

Theoretical developments in multiphase systems have been reported; e.g., an expression of the correlation function of three-phase systems was given by Peterlin[3] who introduced an interaction term $\gamma_{12}(\mathbf{r})$ specifying the relative position between components 1 and 2. A correlation function of a specific three-phase case, labelled macromolecules in addition to unlabelled chains in a solvent, was also reported recently[4,5]. It will be shown later in this paper that the final result derived in refs 4 and 5 can easily be obtained using the general expression of a three-phase correlation function reported in the following section. An expression of correlation function of multiple phase systems has also been reported[6]. This expression, however, is valid only at the large scattering angles, provided all the interface area S_{ij} between phases i and j is given.

The purpose of the present work is to provide a theoretical basis for treating the small-angle X-ray scattering (SAXS) data from a particulate reinforced composite containing microcracks. The equations derived herein will enable us to calculate certain structural parameters of the microcracks provided the scattered intensities $I(h)$ and $I_0(h)$ of both the damaged composite and the undamaged one are given. Here h has its normal definition as $(4\pi/\lambda)\sin\theta$, where λ is the wavelength and θ the scattering angle.

THEORY

Correlation function

The general definition of correlation function $\gamma(\mathbf{r})$ is given as

$$\overline{\eta^2}\gamma(\mathbf{r}) = \frac{1}{V}\int_V \eta(\mathbf{x}+\mathbf{r})\,\eta(\mathbf{x})\,d^3\mathbf{x} \tag{1}$$

where $\eta(\mathbf{x})$ is the deviation of electron density at a position $\mathbf{x}$ from the average value within the scattering volume $\mathbf{V}$, and $\overline{\eta^2}$ is the average of the square of the deviation and is called the scattering power. The scattered intensity $I(h)$ is simply the Fourier transform of $\overline{\eta^2}\gamma(r)$. It has been shown[2] that, in a two-phase system, the conditional probability $Z(\mathbf{r})$ is related to the correlation function $\gamma(\mathbf{r})$ by a simple relation:

$$Z(\mathbf{r}) = \varphi_1 + (1-\varphi_1)\gamma(\mathbf{r}). \tag{2}$$

This equation is valid as long as no long range order existed within the system under consideration where φ_1 is the volume fraction of phase 1. The function $Z(\mathbf{r})$ represents the probability that a point in the volume at a distance $\mathbf{r}$ from a point located in phase 1 is itself also located in phase 1. Another function $Z'(\mathbf{r})$, representing the probability that a point at a distance $\mathbf{r}$ from a point located outside phase 1 is also outside phase 1, has an expression:

$$Z'(\mathbf{r}) = (1-\varphi_1) + \varphi_1\gamma(\mathbf{r}). \tag{3}$$

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It is the purpose of this work to derive an expression for the correlation function of a three-phase system in terms of the correlation function of each constituent phase. For example, $\gamma_1(\mathbf{r})$ is the correlation function of phase 1 as if phases 2 and 3 compose a single phase and so on. Following equation 2 the expressions of Z_{ii} can be written as:

$$Z_{ii}(\mathbf{r})=\varphi_i+(1-\varphi_i)\gamma_i(\mathbf{r}) \qquad i=1,2,3 \tag{4}$$

In order to carry out the integration in equation 1 to derive the correlation function of a three-phase system, expressions for $Z_{ij}(\mathbf{r})$ $(i\neq j)$ in terms of $\gamma_i(\mathbf{r})$ are needed. These relations can be obtained from a simple probabilistic consideration as follows:

$$\varphi_2 Z_{23}(\mathbf{r})=\varphi_3 Z_{32}(\mathbf{r})= (\varphi_2+\varphi_3)Z'_{11}(\mathbf{r})-\varphi_2 Z_{22}(\mathbf{r})-\varphi_3 Z_{33}(\mathbf{r}) \tag{5}$$

where $\varphi_2 Z_{23}(r)$ stands for the probability that a point at distance $\mathbf{r}$ away from a randomly chosen point is inside phase 3 and the starting point happens to be in phase 2. This probability $\varphi_2 Z_{23}(\mathbf{r})$ of $\varphi_3 Z_{32}(\mathbf{r})$ is equal to that of the following condition: both the starting and the ending points of $\mathbf{r}$ are not within phase 1, and the condition that both ends located in either phase 2 or 3 is not allowed. The probability of the condition described above is expressed on the right side of equation 5. With the same argument, $Z_{12}(\mathbf{r})$, $Z_{21}(\mathbf{r})$, $Z_{31}(\mathbf{r})$ and $Z_{13}(\mathbf{r})$ can also be expressed in terms of $\gamma_1(\mathbf{r})$, $\gamma_2(\mathbf{r})$ and $\gamma_3(\mathbf{r})$.

The integration of equation 1 can be written as:

$$\overline{\eta^2}\gamma(\mathbf{r})=\Sigma\eta_i\eta_j\varphi_i Z_{ij}(\mathbf{r}) \tag{6}$$

where $\eta_i=\rho_i-\bar{\rho}$, $\bar{\rho}=\Sigma\rho_i\varphi_i$ and ρ_i is the electron density of phase i.

By substituting equations 2 and 5 into the summation of equation 6, the correlation function can be expressed as:

$$\begin{aligned}\overline{\eta^2}\gamma(\mathbf{r})&=(\rho_2-\rho_1)(\rho_3-\rho_1)\varphi_1(1-\varphi_1)\gamma_1(\mathbf{r})\\&+(\rho_3-\rho_2)(\rho_1-\rho_2)\varphi_2(1-\varphi_2)\gamma_2(\mathbf{r})\\&+(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)\gamma_3(\mathbf{r})\end{aligned} \tag{7}$$

The symmetry in the above expression is highly desirable, and it is trivial to show that the expression of equation 7 can be reduced to the appropriate one of two-phase systems by letting $\rho_1=\rho_2$ or $\varphi_1=0$, etc.

Since the correlation of a three-phase system can be expressed as a summation of that of individual phases, the correlation function $\gamma_i(\mathbf{r})$ represents that of a traditional two-phase system. These schemes evaluating chord length, scattering power, specific interface area, etc., in a two-phase system are now expected to be applicable in a three-phase system with certain modifications.

In the following sections, equation 7 will be used as a theoretical basis to deduce certain structure information of the microvoids within a particulate composite given the scattered intensities $I(h)$ and $I_0(h)$ of the damaged composite and the undamaged one, respectively. Finally, the equation relating the scattered intensity to the conformation of long chain molecules within a specific three-phase system will be deduced from equation 7 as a special case.

Application of equation 7 in SAXS of particulate composites—an isotropic case

In this section a composite material with fine quartz particles as fillers will be the subject of discussion. Inside the damaged region, the matrix phase contains microvoids presumably caused by leaching out some unreacted monomer molecules while the shape and relative position of the fillers remain unchanged. The scattered intensities for both the damaged and undamaged zones were isotropic, i.e., independent of the azimuthal angle μ.

The scattered intensity $I(h)$ for the damaged composite in which fillers, matrix and microvoids constitute the three phases is simply a Fourier transform of equation 7 shown as follows:

$$\begin{aligned}I(h)&=(\rho_2-\rho_1)(\rho_3-\rho_1)\varphi_1(1-\varphi_1)F\gamma_1(\mathbf{r})\\&+(\rho_3-\rho_2)(\rho_1-\rho_2)\varphi_2(1-\varphi_2)F\gamma_2(\mathbf{r})\\&+(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)F\gamma_3(\mathbf{r})\end{aligned} \tag{8}$$

where F denotes Fourier transform defined as $\int_V(\sin hr/hr)\,4\pi r^2\mathrm{d}r$ for isotropic cases, and henceforth the subscripts 1, 2, 3 denote the filler, matrix, and microvoids, respectively. For the undamaged portion of the composite, the scattered intensity can be expressed as:

$$I_0(h)=(\rho_2-\rho_1)^2\varphi_1^0(1-\varphi_1{}^0)F\gamma_1{}^0(r)= (\rho_2-\rho_1)^2\varphi_2^0(1-\varphi_2{}^0)F\gamma_2{}^0(r).$$

Given the fillers do not change their shape and relative position from one another, one has the relation:

$$\gamma_1{}^0(r)=\gamma_1(r) \text{ and } \varphi_1{}^0=\varphi_1. \tag{10}$$

It is noteworthy that $\gamma_2{}^0(r)\neq\gamma_2(r)$ because now the microvoids add a third phase inside the matrix which is phase 2.

The volume fraction φ_3, of the microvoids can be calculated from the values of $I(h)$ and $I_0(h)$ using the well known equation[2] relating the scattering intensity to the scattering power $\overline{\eta^2}$:

$$\int_0^\infty h^2 I_0(h)\mathrm{d}h=2\pi^2 I_e(h)\,V(\rho_1-\rho_2)^2\varphi_1(1-\varphi_1). \tag{11}$$

From equation 7 it is trivial to show that:

$$\int_0^\infty h^2 I(h)\mathrm{d}h=2\pi^2 I_e(h)V[(\rho_1-\rho_2)^2\varphi_1\varphi_2+(\rho_2-\rho_3)^2\varphi_2\varphi_3 +(\rho_3-\rho_1)^2\varphi_3\varphi_1] \tag{12}$$

where $I_e(h)$ is the scattered intensity of a single electron. Equations 11 and 12 can be combined to yield an alternative form:

$$\int_0^\infty h^2\Big(I(h)-I_0(h)\Big)\mathrm{d}h=2\pi^2 I_e(h)V\Big((\rho_1-\rho_3)^2\varphi_1+(\rho_2-\rho_3)^2\varphi_2-(\rho_1-\rho_2)^2\varphi_1\Big)\varphi_3 \tag{12'}$$

The value of φ_1 can be obtained from equation 11 and the value of φ_2 or φ_3 can be calculated from equation 12 or 12′ with the additional relation $\varphi_1+\varphi_2+\varphi_3=1$.

The above discussion clearly demonstrates that the value of φ_3 can be obtained from $I(h)$ and $I_0(h)$ only if certain relations such as those given by equation 10 can be assumed. In the high angle region in which Porod's law is applicable[1], the scattering intensity can be approximated by the following equation:

$$I(h)\simeq I_e(h)\frac{2\pi}{h^4}[(\rho_1-\rho_2)^2S_{12}+(\rho_2-\rho_3)^2S_{23}+(\rho_3-\rho_1)^2S_{31}] \tag{13}$$

where S_{ij} is the total interface area between phases i and j within the scattering volume V. The above expression approximating the scattered intensity can easily be derived from equation 7 with the knowledge that[2]:

$$\left(\frac{\mathrm{d}\gamma_1(r)}{\mathrm{d}r}\right)_{r=0}=\frac{-1}{4\varphi_1(1-\varphi_1)}\frac{S_{12}+S_{13}}{V}. \tag{14}$$

Because no *a priori* relation among S_{ij} exists contrary to one such relation $\Sigma\varphi_i=1$ for the volume fraction φ_i, more assumptions will be needed to obtain the value for the individual term S_{ij} from equation 13. Even if one can assume with reasonable confidence that the filler particles do not change their shape and relative position from each other, no apparent relation can be assumed between $S_{12}{}^0$, the interface area of the undamaged region, and S_{ij} of the damaged one. Therefore, Porod's scheme will be useful in estimating interface area of the third phase only if certain assumptions or pre-existent information is available, e.g., all the void occurs inside the matrix, hence $S_{12}=S_{12}{}^0$ and $S_{13}=0$.

The quantity chord length[2] provides an important insight of the average linear dimension of each phase in a two-phase system. This quantity can be measured experimentally by performing the following integration of the experimentally measured data $I(h)$:

$$\int_0^\infty h\,I(h)\mathrm{d}h=4\pi V(\rho_2-\rho_1)^2\varphi_1(1-\varphi_1)I_e(h)\int_0^\infty \gamma(r)\mathrm{d}r. \tag{15}$$

The correlation length of $\bar{l}$ of a two-phase system follows the relation:

$$\bar{l}=2\int_0^\infty \gamma(r)\mathrm{d}r \tag{16}$$

and the chord length is related to the correlation length by:

$$\bar{l}_1=\frac{\bar{l}}{\varphi_2},\quad \bar{l}_2=\frac{\bar{l}}{\varphi_1} \tag{17}$$

For a three phase system, the values of chord lengths can be related to the integral $\int_0^\infty h\,I(h)\mathrm{d}h$ by:

$$\int_0^\infty h\,I(h)\mathrm{d}h=4\pi I_e(h)V\Big[(\rho_2-\rho_1)(\rho_3-\rho_1)\varphi_1(1-\varphi_1)\int_0^\infty \gamma_1(r)\mathrm{d}r+(\rho_3-\rho_2)(\rho_1-\rho_2)\varphi_2(1-\varphi_2)\int_0^\infty \gamma_2(r)\mathrm{d}r+(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)\int_0^\infty \gamma_3(r)\mathrm{d}r\Big] \tag{18}$$

and the chord length $\bar{l}_i$ for each of the three phases can be obtained from the relation similar to equation 17:

$$\bar{l}_i=\frac{2}{1-\varphi_i}\int_0^\infty \gamma_i(r)\mathrm{d}r \tag{19}$$

With the values of ρ_i and φ_i given and the value of the integral $\int_0^\infty h\,I(h)\mathrm{d}h$ determined experimentally, equation 18 will give us the value of certain linear summations of $\bar{l}_i$ instead of the value of each $\bar{l}_i$. By letting the chord length $\bar{l}_1$ (the fillers) stay unchanged, one *a priori* relationship between $\bar{l}_2$ and $\bar{l}_3$ is needed before one can determine their values. A simple relation given by equation 17 relating the chord length and the volume fraction of each phase, i.e., $\bar{l}_1/\varphi_1=\bar{l}/\varphi_2$, is invalid for systems composed of more than two phases. The value of $\bar{l}_3$ can be obtained from equation 18 if, and only if, one more *a priori* information regarding $\bar{l}_2$ is available. However, in case the value of φ_3 is extremely small compared with those of φ_1 and φ_2, one can approximate the following equalities: $\bar{l}_1=\bar{l}_1^0$ and $\bar{l}_2=\bar{l}_2^0$. By using such assumptions, equations 18 and 15 can be combined and rewritten as:

$$\int_0^\infty h(I(h)-I_0(h))\mathrm{d}h\simeq 4\pi I_e(h)V(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)\int_0^\infty \gamma_3(r)\mathrm{d}r=2\pi I_e(h)V(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)\bar{l}_3 \tag{20}$$

Therefore, equation 20 provides the approximating scheme measuring the chord length of isotropic microvoids if their volume concentration is much less than those of either phases 1 or 2.

Estimation of chord length in anisotropic case

Within the specimens damaged by external force with preferentially orientation, the resultant microcracks are also oriented to certain stress direction. Consequently, the quantity $I(h)-I_0(h)$ not only depends on the magnitude of scattering angle θ but also on the azimuthal angle μ. In such cases, the volume fraction of the microvoids or microcracks can be determined again using equation 12 except that the integral $\int h^2(I(h)-I_0(h))\mathrm{d}h$ will be replaced by $\int(I(\mathbf{h})-I_0(\mathbf{h}))\mathrm{d}V_h$ (ref 1) for calculating the so-called scattering invariant. Hence, no theoretical difficulty exists for the measurement of the volume concentration of the microvoids in such a composite specimen.

As for the chord length estimation, equation 20 can no longer be used since the whole scheme in deriving equation 15, the precursor of equation 20, is based on the Fourier inversion scheme for an isotropic case. In the following section, a theoretical scheme will be developed for measuring the chord length of microvoids along certain directions.

Since the quantity $I(\mathbf{h})-I_0(\mathbf{h})$ is anisotropic or azimuthal angle dependent, the corresponding correlation function $\gamma_3(\mathbf{r})$ must be dependent on the direction or $\mathbf{r}$ specified by the azimuthal angles φ and ψ. For the purpose of clarity, the subscription of γ_3 will be dropped in the rest of this section.

To a first degree of approximation, $\gamma(\mathbf{r})$ can be transformed into an isotropic one $\gamma(\mathbf{r}')$ by the following relation between coordinate $\mathbf{r}$ and $\mathbf{r}'$

$$\mathbf{r}=|\lambda_{ij}|\mathbf{r}' \tag{21}$$

where $|\lambda_{ij}|$ is a 3×3 symmetrical matrix.

The scattered intensity difference $I'(h)=I(h)-I(h)$ with the vector $\mathbf{h}$ in θ and μ space can be expressed as:

$$I'(\mathbf{h})=I_e(h)V(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)\int\gamma(\mathbf{r})\mathrm{e}^{-i\mathbf{h}\cdot\mathbf{r}}\mathrm{d}^3\mathbf{r}. \tag{20'}$$

Hereafter, the term in front of the integral of equation 20′ will be replaced by a constant A. In the $\mathbf{r}'$ coordinate, $\gamma(\mathbf{r}')$ is isotropic, i.e., the value of $\gamma(\mathbf{r}')$ depends only on the magnitude of $\mathbf{r}'$, the resultant scattered intensity expressed in a new $\mathbf{h}'$ space must be isotropic also.

The coordinate $\mathbf{h}'$ is simply defined by the relation:

$$\mathbf{h}'\cdot\mathbf{r}'=\mathbf{h}\cdot\mathbf{r} \tag{22}$$

For a transformation given by equation 21, the value of the correlation function remains constant.

$$\gamma(\mathbf{r})=\gamma(\mathbf{r}') \tag{23}$$

This can be visualized easily from the geometric representation of the meaning of $\gamma(\mathbf{r})$ given in ref. 2. The relation expressed by equation 23 is believed to be an essential one in dealing with problems of anisotropic scattering objects.

By substituting equations 22 and 23 into equation 20′ one has

$$\begin{aligned}I'(h')&=A\int\gamma(\mathbf{r}')e^{-i\mathbf{h}'\cdot\mathbf{r}'}\mathrm{d}^3\mathbf{r}'\\&=A\int\gamma(\mathbf{r}')\frac{\sin h'\cdot r'}{h'\cdot r'}4\pi r'^2\mathrm{d}r'.\end{aligned} \tag{24}$$

The chord length expressed in $\mathbf{r}'$ can then be obtained through the integral $\int h'I'(h')\mathrm{d}h'$, and the chord length in real space $\mathbf{r}$ can be calculated later from an inverse transformation of $|\lambda_{ij}|$.

By knowing the deformation history of a specimen, it is possible to position the specimen in such an orientation with respect to the incident X-ray beam that one of the principal strain axes coincides with the X-ray beam direction. Hereafter, only the matrix $|\lambda_{ij}|=\lambda_{ij}\delta_{ij}$ with $\lambda_1\lambda_2\lambda_3=1$ will be treated without losing much generality, where δ_{ij} is the Kroneker delta.

Given the incident beam is in the X_1 direction, the scattering angles ξ and γ of the transformed vector $h'(\xi,\gamma)$ defined in equation 22 will be[7]:

$$\sin\xi=\left[\left(\frac{\lambda_2}{\lambda_1}\sin\mu\right)^2+\left(\frac{\lambda_3}{\lambda_1}\cos\mu\right)^2\right]^{\frac{1}{2}}\frac{\sin\theta}{C} \tag{25}$$

$$\sin\gamma=\lambda_2\sin\mu[(\lambda_2\sin\mu)^2+(\lambda_3\cos\mu)^2]^{-\frac{1}{2}} \tag{26}$$

$$C=\frac{1}{2}\left(\left[\left(\frac{\lambda_2}{\lambda_1}\sin\mu\right)^2+\left(\frac{\lambda_3}{\lambda_1}\cos\mu\right)^2\right](1+\cos\theta)+(1-\cos\theta)\right) \tag{27}$$

and $\mathbf{h}'(\xi,\gamma)=(1-\cos\xi)\mathbf{i}-(\sin\xi\sin\gamma)\mathbf{j}-(\sin\xi\cos\gamma)\mathbf{k}$. (28)

In the transformed coordinate, the term $\mathbf{h}'\cdot\mathbf{r}'$ of equation 24 can be expressed as:

$$\begin{aligned}\mathbf{h}'\cdot\mathbf{r}'=C\lambda_1 r[&\sin\psi\cos\varphi(1-\cos\xi)-\sin\psi\sin\varphi\sin\xi\sin\gamma\\&-\cos\psi\sin\xi\cos\gamma]\end{aligned} \tag{29}$$

From the above equation it is obvious that a new vector $\mathbf{q}$ is needed, the magnitude of $\mathbf{q}$ is $C\lambda_1 r$ and the direction of $\mathbf{q}$ is the same as $\mathbf{r}'$. The corresponding value of the correlation function $\lambda(\mathbf{q})$ still equals that of $\gamma(\mathbf{r})$; furthermore, $\gamma(\mathbf{q})$ is also spherically symmetric. Equation 24 can then be expressed as:

$$I'(h')=\frac{4\pi A}{(C\lambda_1)^3}\int\gamma(q)\frac{\sin h'q}{h'q}q^2\mathrm{d}q \tag{30}$$

Following the rationale in deriving equations 15 and 16, the correlation length expression in $\mathbf{q}$ space is simply:

$$\bar{l}(q)=2\int\gamma(q)\mathrm{d}q=\frac{1}{2\pi A}\int(C\lambda_1)^3h'I'(h')\mathrm{d}h' \tag{31}$$

The value of the correlation length in $\mathbf{r}'$ space can be obtained by the simple relation $\bar{l}(\mathbf{r}')=\bar{l}(q)/C\lambda_1$. Finally, the values of $\bar{l}(\mathbf{r})$ can be derived from the values of $\bar{l}(\mathbf{r}')$ and λ_i.

In performing the integration of the right side term of equation 31 along the meridian and the equator, one denotes the resultant value of $\int I'(h)h\,\mathrm{d}h$ as $E(\mu=0)$ and $E(\mu=\pi/2)$, respectively. Along the meridian ($\mu=0$) one has $C\simeq(\lambda_3/\lambda_1)^2$ and $h'\simeq(\lambda_1/\lambda_3)h$ by letting $\cos\theta\simeq 1$ in equations 25–27. For the angular range encountered in SAXS, this approximation is considered to be justifiable. Similarly, along the equator, i.e., $\mu=\pi/2$, one has $C\simeq(\lambda_2/\lambda_1)^2$ and $h'=(\lambda_1/\lambda_2)h$ also from equations 25–27.

Along the meridian of the scattering pattern while the incident beam $\mathbf{S}_0$ is parallel to X_1 axis, equation 31 can be converted into:

$$\left(\frac{\lambda_3}{\lambda_1}\right)^2 \lambda_1 \bar{l}(r') = \frac{1}{2\pi A}\left(\frac{\lambda_3}{\lambda_1}\right)^6 \int h' I'(h')\mathrm{d}h \qquad (31')$$

Furthermore, in the transformation from **h** to **h**′, the term $I'(h)$ remains the same as $I'(h')$. Equation 31 can be simplified further as:

$$2\pi A\,\bar{l}(r') = \lambda_3^3 \int h\, I'(h)\mathrm{d}h = \lambda_3^3\, E(\mu=0, \mathbf{S}_0=\mathbf{X}_1) \qquad (32A)$$

By similar derivation, the following relations hold:

$$2\pi A\,\bar{l}(r') = \lambda_2^3\, E(\mu=\pi/2, \mathbf{S}_0=\mathbf{X}_1) \qquad (32B)$$

$$2\pi A\,\bar{l}(r') = \lambda_1^3\, E(\mu=\pi/2, \mathbf{S}_0=\mathbf{X}_2) \qquad (32C)$$

$$2\pi A\,\bar{l}(r') = \lambda_3^3\, E(\mu=0, \mathbf{S}_0=\mathbf{X}_2) \qquad (32D)$$

It is obvious that the right hand sides of equations 32A and 32D are identical, i.e., $E(\mu=0,\ \mathbf{S}_0=\mathbf{X}_1)=E(\mu=0,\ \mathbf{S}_0=\mathbf{X}_2)$, therefore, no contradiction is present in the derivations obtaining equations 32A–D.

In the remaining part of this section, these four quantities, λ_1, λ_2, λ_3 and $\bar{l}(r')$ will be expressed explicitly in terms of E_1, E_2 and E_3. Hereafter the quantity E_1 stands for the term $E\left(\mu=\frac{\pi}{2}, \mathbf{S}_0=\mathbf{X}_2\right)$ which is in turn the integral $\int h\, I'(h)\mathrm{d}h$ along an axis parallel to the axis X_1 of the real space **r**. These quantities E_2 and E_3 are similarly defined. The resultant relations for λ_i and $\bar{l}(r')$ are:

$$\lambda_1 = \frac{(E_2E_3)^{1/6}}{(E_1)^{1/3}}, \quad \lambda_2 = \frac{(E_3E_1)^{1/6}}{(E_2)^{1/3}}, \quad \lambda_3 = \frac{(E_1E_2)^{1/6}}{(E_3)^{1/3}} \qquad (33)$$

$$2\pi A\,\bar{l}(\mathbf{r}') = (E_1E_2E_3)^{1/3} \qquad (34)$$

The correlation length $\bar{l}_i(\mathbf{r})$ in the real space along the principal axis X_i is simply $\lambda_i \bar{l}(\mathbf{r}')$ or explicitly:

$$\bar{l}_1(\mathbf{r}) = \frac{1}{2\pi A}(E_2E_3)^{1/2} \qquad (35A)$$

$$\bar{l}_2(\mathbf{r}) = \frac{1}{2\pi A}(E_3E_1)^{1/2} \qquad (35B)$$

$$\bar{l}_3(\mathbf{r}) = \frac{1}{2\pi A}(E_1E_2)^{1/2} \qquad (35C)$$

where A represents $I_e(h)V(\rho_1-\rho_3)(\rho_2-\rho_3)\varphi_3(1-\varphi_3)$ for the composite problems treated herein. The above derivations obtaining 35A–C is equally applicable for a two-phase system problem, and the quantity A represents $I_e(h)V(\rho_1-\rho_2)^2\varphi_1(1-\varphi_1)$ for such cases.

Application of three-phase correlation function (equation 7) to a special case

A theoretical work for determining a single chain scattering factor from polymer solutions has been reported[4,5]. The purpose of the work presented in this section is to demonstrate that an identical result can be obtained simply as a special form of the correlation function expressed in equation 7 for three-phase systems.

The system under consideration is a polymer solution with both hydrogenated and deuterated polymer molecules dissolved, furthermore, these molecules are all of the same length or molecular weight. The correlation function of such a system is:

$$\begin{aligned}\overline{\eta^2}\,\gamma(r) = {} & (\rho_H-\rho_S)(\rho_D-\rho_S)\varphi_S(1-\varphi_S)\gamma_S(r)\\ & +(\rho_D-\rho_H)(\rho_S-\rho_H)\varphi_H(1-\varphi_H)\gamma_H(r)\\ & +(\rho_H-\rho_D)(\rho_S-\rho_D)\varphi_D(1-\varphi_D)\gamma_D(r) \qquad (36)\end{aligned}$$

where the subscripts S, H and D denote solvent, hydrogenated and deuterated species composed of the three phases discussed herein. The scattered intensity of such a system is simply a Fourier tranform of equation 36, i.e., $F\,\overline{\eta^2}\,\gamma(r)$; hereafter, the Fourier transform of each term of the right hand side of equation 36 will be discussed separately.

For the hydrogenated polymer chains, the Fourier transform can be written in the well known Zernicke Prins[2] form:

$$\begin{aligned}&F\varphi_H(1-\varphi_H)\gamma_H(r)\\ &= A\frac{\varphi_H}{V_H}\left[\overline{F_H{}^2(h)} - \frac{\overline{F_H(h)}^2}{v_H}\int(1-P_H(r,v_p))\frac{\sin h\,r}{h\,t}4\pi r^2\mathrm{d}r\right]\end{aligned} \qquad (37)$$

where A is the scattering constant as defined before; V_H is the molar volume of an individual chain (hence φ_H/V_H equals to the number of hydrogenated chain per unit volume). $\overline{F_H^2}(h)$ is the mean value of the square of the single chain form factor in h space, $\overline{F(_H(h)}^2$ is the square of the mean value of $F_H(h)$ which is different from $F_H^2(h)$ in general cases, v_H is the specific volume occupied by each hydrogenated chain (hence $1/v_H$ represents the number of hydrogenated chains per unit volume); $P_H(r,v_p)$ is the pair correlation function of the centres of mass of the hydrogenated chains. The essential point in the derivation given by refs. 4 and 5 is that the pair correlation function $P_H(r,v_p)$ is a function of the total polymer concentration $1/v_p$ instead of the concentration of either H or D species.

The rationale for this essential point can be found elsewhere[4,5]. The pair correlation function $P_D(r,v_p)$ for the D species is then equal to that of the H polymer, and the subscript will be dropped hereafter. Since the single chain form factors of both species are identical because the molecular weight and the confprmtation of these two species are the same, the subscript in these factors will also be dropped. Therefore, equation 37 can be written as:

$$\begin{aligned}&F\varphi_H(1-\varphi_H)\gamma_H(r)\\ &= A\frac{\varphi_H}{V_H}\left[\overline{F^2(h)} - \frac{\varphi_H}{V_H}\overline{F(h)^2}\int(1-P(r,v_p))\frac{\sin h\,r}{h\,r}4\pi r^2\mathrm{d}r\right]\\ &= A\left[\frac{\varphi_H}{V_H}\overline{F^2(h)} - \left(\frac{\varphi_H}{V_H}\right)^2 X(h)\right] \qquad (38)\end{aligned}$$

where $X(h)$ denotes the interaction term among polymer chains and the same quantity $X(h)$ is also applicable in D polymer scattering. The Fourier transform for the second term in the right side of equation 36 is:

$$F\varphi_D(1-\varphi_D)\gamma_D(r)=A\left[\frac{\varphi_D}{V_D}\overline{F^2(h)}-\left(\frac{\varphi_H}{V_D}\right)^2 X(h)\right]. \quad (39)$$

From the well known Babinet principle, the Fourier transform of the solvent term in equation 36 is:

$$F\varphi_S(1-\varphi_S)\gamma_S(r)=A\left[\frac{\varphi_P}{V_P}\overline{F^2(h)}-\left(\frac{\varphi_P}{V_P}\right)^2 X(h)\right] \quad (40)$$

where φ_P is the volume concentration of the total polymer chains and is equal to the sum of φ_H and φ_D; V_P is the molar volume of polymers and equals to both V_H and V_D.

By substituting equations 38–40 into the Fourier transform of equation 36, one has:

$$I(h)=A\left[(\rho_H-\rho_S)^2\frac{\varphi_H}{V_p}+(\rho_D-\rho_S)^2\frac{\varphi_D}{V_p}\right]\overline{F^2(h)}$$

$$+A\left[(\rho_H-\rho_S)\frac{\varphi_H}{V_p}+(\rho_D-\rho_S)\frac{\varphi_D}{V_p}\right]^2 X(h). \quad (41)$$

Equation 41 has the same form as given in refs. 4 and 5, but a quite different approach is used. It is noteworthy that the term $I(h)$ is a function of the total polymer concentration in solution. Therefore, the values of both $\overline{F^2(h)}$ and $X(h)$ can be reduced from two scattering experiments by keeping the total polymer content constant and varying the H to D ratio.

CONCLUSION

A general expression of the correlation function for three-phase systems is derived (equation 7). Applications of this expression were presented for the case of damaged particulate composites. Formulas were derived for measuring the volume concentration (equation 12′) and the average chord length (equation 20) of the microvoids based on the values of $I(h)$ and $I_0(h)$ which are the scattered intensities from the damaged and the undamaged portions of the composite, respectively. Furthermore, for composites with minor amounts of microcracks which were preferentially oriented, equations were derived to measure the correlation length along each principal axis (equations 35A–35C). These equations are also applicable to measure the correlation length in two-phase systems with preferential orientation.

One more example to demonstrate the application of the general expression of the correlation function for three-phase systems was presented for polymer solutions containing both deuterated and hydrogenated chains of same molecular weight. The resultant formulas are consistent with those obtained by others.

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