Calculation of WAXS crystallinities in multicomponent polymers: the total correction factor method

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By application of absorptive correction factor and some other improvements, the general procedure for evaluating apparent crystallinity and substantial crystallinity from wide-angle X-ray scattering patterns of binary and ternary copolymers with sufficient thickness was extended to multicomponent polymers with any thickness. The total correction factors of semicrystalline poly(ethylene oxide), amorphous poly(methyl methacrylate), polyacrylate acid, poly(ethyl acrylate), poly(butyl acrylate), poly(dimethylsiloxane), polystyrene, polybutadiene and poly(propylene oxide) were calculated. The results showed that when a diffractometer is used with reflection geometry, the influence of absorption factor can be ignored when $\mu t \geqslant 0.5$, but it should be taken into account when $\mu t < 0.5$ (μ is linear absorption factor and t is sample thickness).

(Keywords: total correction factor; WAXS; crystallinities; multicomponent polymer)

INTRODUCTION

Recently, the author has proposed a general procedure for evaluating crystallinity from wide-angle X-ray scattering (WAXS) patterns of binary and ternary copolymers by defining a total correction factor[1,2]. In those papers, two kinds of crystallinity, the apparent crystallinity X_{ca} relative to the entire sample and the substantial crystallinity X_{cs} relative to the semicrystalline component alone, were evaluated at the same time. Because the method was established under the condition that the samples concerned are sufficiently thick, it cannot be directly applied to evaluate the crystallinities in copolymers that are not thick enough.

In this paper, the total correction factor is redefined after consideration of the influence of absorption factor and atomic scattering factor when using a diffractometer with reflection geometry. With this redefined total correction factor, the general method is extended to multicomponent polymers, such as poly(ethylene oxide) (PEO)-containing multicomponent polymers with any thickness.

THE TOTAL CORRECTION FACTOR METHOD

Based on the theory proposed previously[1,2], the partial weighted average correction factor for amorphous scattering curve, $\bar{C}_p$, and the range correction factor, K_a, are given by the following equations:

$$\bar{C}_p = \frac{\sum_{2\theta=2\theta_0}^{2\theta_p} C_{2\theta} I_{a_{2\theta}}}{\sum_{2\theta=2\theta_0}^{2\theta_p} I_{a_{2\theta}}} \tag{1}$$

$$K_a = \frac{\sum_{2\theta=2\theta_0}^{2\theta_p} C_{2\theta} I_{a_{2\theta}}}{\sum_{2\theta=2\theta_0}^{2\theta_t} C_{2\theta} I_{a_{2\theta}}} \tag{2}$$

in which

$$C_{2\theta}^{-1} = f_r^2 TLP \tag{3}$$

where $2\theta_0$ and $2\theta_t$ are respectively the lower terminal angle and the upper terminal angle of the whole amorphous scattering curve of amorphous homopolymer; $2\theta_p$ is the upper terminal angle of the partial amorphous scattering curve of the amorphous homopolymer; $I_{a_{2\theta}}$ is relative integrated intensity of the area with unit angular step on the amorphous scattering curve of the sample with sufficient thickness; $f_r = f_{2\theta}/f_0$, $f_{2\theta}$ and f_0 are respectively the atomic scattering factor of unit mass at 2θ and 0°; $T = \exp(-2B \sin^2\theta/\lambda^2)$; θ is Bragg angle; λ is X-ray wavelength; $2B = 10$; $LP = (1+\cos^2 2\theta)/(\sin^2\theta \cos\theta)$.

By applying the absorptive correction factor, A_a, the total correction factor F_a for amorphous homopolymers with any thickness is redefined as follows:

$$F_a = \frac{\bar{C}_p}{K_a} A_a \tag{4}$$

When a diffractometer is used with reflection geometry, the absorptive correction factor A_a can be calculated by the following equation:

$$A_a = \frac{\sum_{2\theta=2\theta_0}^{2\theta_p} I_{a_{2\theta}}}{\sum_{2\theta=2\theta_0}^{2\theta_p} A_{2\theta} I_{a_{2\theta}}} \tag{5}$$

where $A_{2\theta}$ is absorption factor; with a flat sample $A_{2\theta} = 1 - \exp(-2\mu t/\sin\theta)$, where μ is linear absorption factor and t is sample thickness (cm). $A_{2\theta} I_{a_{2\theta}}$ is the relative integrated intensity of the samples that are not thick enough.

Substituting $\bar{C}_p$, K_a and A_a, and then reducing, we have:

$$F_a = \frac{\sum_{2\theta=2\theta_0}^{2\theta_t} C_{2\theta} I_{a_{2\theta}}}{\sum_{2\theta=2\theta_0}^{2\theta_p} A_{2\theta} I_{a_{2\theta}}} \tag{6}$$

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Following the same procedure, the total correction factor F_c for the crystalline phase of semicrystalline homopolymer is given by:

$$F_c = \frac{\sum_{j=1}^{T} C_j I_{c_j}}{\sum_{j=1}^{N} A_j I_{c_j}} \quad (7)$$

where T is the total number of crystalline peaks of semicrystalline homopolymer; N is the number of the major crystalline peaks of the semicrystalline homopolymer; C_j and A_j are respectively defined as the same as $C_{2\theta}$ and $A_{2\theta}$ in equations (3) and (5); I_{c_j} is relative integrated intensity of peak j of the semicrystalline homopolymer.

Taking into account the total correction factors, the extended formulas for the apparent crystallinity X_{ca} and the substantial crystallinity X_{cs} in multicomponent polymers can be written as follows:

$$X_{ca} = \frac{\sum_{i=1}^{M} F_{c_i} I_{c_i}}{\sum_{i=1}^{M} F_{c_i} I_{c_i} + \sum_{i=1}^{M} F_{a_i} I_{a_i} + \sum_{k=1}^{P} F_{a_k} I_{a_k}} \times 100\% \quad (8)$$

$$X_{cs} = \frac{F_{c_i} I_{c_i}}{F_{c_i} I_{c_i} + F_{a_i} I_{a_i}} \times 100\% \quad (9)$$

where I_{c_i} and I_{a_i} are respectively the relative integrated intensities of the major crystalline peaks and the amorphous scattering curve of semicrystalline component i over partial angular range; I_{a_k} is the relative integrated intensity of the amorphous scattering curve of amorphous component k over partial angular range; M is the number of semicrystalline components; P is the number of amorphous components; F_{c_i} and F_{a_i} are respectively the total correction factors of the crystalline phase and amorphous phase of semicrystalline component i; F_{a_k} is the total correction factor of amorphous component k.

FORMULAS OF CRYSTALLINITIES FOR PEO-CONTAINING MULTICOMPONENT POLYMERS

For the multicomponent polymers composed of semicrystalline PEO and N kinds of other amorphous components, equations (8) and (9) can be reduced to give:

$$X_{ca} = \frac{F_{c_{PEO}} I_{c_{PEO}}}{F_{c_{PEO}} I_{c_{PEO}} + F_{a_{PEO}} I_{a_{PEO}} + F_{a_M} I_{a_M}} \times 100\% \quad (10)$$

$$X_{cs} = \frac{F_{c_{PEO}} I_{c_{PEO}}}{F_{c_{PEO}} I_{c_{PEO}} + F_{a_{PEO}} I_{a_{PEO}}} \times 100\% \quad (11)$$

where $F_{c_{PEO}}$ and $F_{a_{PEO}}$ are respectively the total correction factors of crystalline phase and amorphous phase of the PEO component; $I_{c_{PEO}}$ and $I_{a_{PEO}}$ are respectively the relative integrated intensities of the major crystalline peaks, $I_{120}+I_{113/032}$, and amorphous curve of the PEO component over partial angular range; F_{a_M} is the total correction factor of a kind of matrix that is composed of other amorphous components; I_{a_M} is the relative integrated intensity of the matrix over the partial angular range.

If X_i is the content of component i of the matrix and F_{a_i} is the total correction factor of component i of the matrix, we have:

$$F_{a_M} = \frac{\prod_{i=1}^{N} F_{a_i}}{\sum_{i=1}^{N} X_i \prod_{\substack{j=1 \\ j \neq i}}^{N} F_{a_i}} \quad (12)$$

Using equations (6) and (7) and with $2\theta_0 = 5°$, $2\theta_p = 35°$ and $2\theta_t = 65°$, the total correction factors at μt ($0 < \mu t \leqslant 2$) of semicrystalline PEO, amorphous poly(methyl metha-

Table 1 Total correction factors of several homopolymers

	Semicrystalline		Amorphous							
μt	PEOc	PEOa	PMMA	PAA	PEA	PBA	PDMS	PS	PB	PPO
$\rightarrow 0$	4.06051	2.80398	3.41444	7.69490	6.22929	5.02060	1.86772	3.29041	6.80053	6.47281
0.01	4.03148	2.81213	3.47182	7.69950	6.30376	5.13999	1.90050	3.34557	6.80884	6.50558
0.05	3.92706	2.82941	3.65714	7.69012	6.52256	5.47219	2.00804	3.51486	6.81987	6.60328
0.10	3.82132	2.82921	3.80615	7.63787	6.66534	5.67626	2.09626	3.64051	6.80064	6.66738
0.15	3.74006	2.81762	3.88970	7.56630	6.72222	5.76000	2.14633	3.70644	6.76408	6.69010
0.20	3.67939	2.80236	3.93168	7.49281	6.73349	5.78742	2.17171	3.73822	6.72319	6.68996
0.25	3.63530	2.78741	3.94945	7.42661	6.72412	5.78994	2.18264	3.75151	6.68502	6.67920
0.30	3.60402	2.77449	3.95434	7.37142	6.70748	5.78276	2.18590	3.75546	6.65264	6.66504
0.35	3.58231	2.76413	3.95309	7.32771	6.69016	5.77300	2.18554	3.75510	6.62679	6.65123
0.40	2.56751	2.75621	3.94945	7.29434	6.67498	5.76370	2.18377	3.75310	6.60701	6.63938
0.45	3.55758	2.75036	3.94532	7.26953	6.66275	5.75600	2.18168	3.75074	6.59233	6.62991
0.50	3.55101	2.74613	3.94153	7.25145	6.65339	5.74993	2.17977	3.74858	6.58168	6.62270
0.60	3.54394	2.74106	3.93594	7.22928	6.64147	5.74219	2.17607	3.74545	6.56872	6.61353
0.70	3.54102	2.73862	3.93272	7.21827	6.63541	5.73826	2.17541	3.74369	6.56240	6.60889
0.80	3.53984	2.73749	3.93102	7.21297	6.63246	5.73637	2.17461	3.74280	6.55940	6.60664
0.90	3.53938	2.73698	3.93016	7.21043	6.63106	5.73548	2.17422	3.74237	6.55800	6.60558
1.00	3.53920	2.73674	3.92974	7.20922	6.63040	5.73506	2.17403	3.74216	6.55704	6.60508
1.20	3.53910	2.73658	3.92944	7.20838	6.62995	5.73478	2.17390	3.74202	6.55690	6.60474
1.50	3.53908	2.73655	3.92936	7.20816	6.62983	5.73472	2.17387	3.74199	6.55679	6.60465
2.00	3.53908	2.73654	3.92935	7.20813	6.62982	5.73471	2.17387	3.74198	6.55677	6.60464

Table 2 Relative changing degree of the total correction factors

	Semicrystalline		Amorphous							
μt	PEOc	PEOa	PMMA	PAA	PEA	PBA	PDMS	PS	PB	PPO
$\rightarrow 0$	14.7335	2.4643	−13.1042	6.7531	−6.0413	−12.4523	−14.0829	−12.0679	3.7176	−1.9961
0.01	13.9132	2.7622	−11.5119	6.8169	−4.9181	−10.3705	−12.5753	−10.5936	3.8444	−1.4998
0.05	10.9626	3.3937	−6.9277	6.6867	−1.6177	−4.5777	−7.6284	−6.0698	4.0126	−0.0206
0.10	7.9748	3.3864	−3.1353	5.9619	0.5418	−1.0192	−3.5700	−2.7116	3.7192	0.9500
0.15	5.6787	2.9626	−1.0091	4.9689	1.3937	0.4411	−1.2665	−0.9499	3.1616	1.2939
0.20	3.9645	2.4052	0.0593	3.9494	1.5637	0.9192	−0.0993	−0.1007	2.5381	1.2918
0.25	2.7187	1.8587	0.5117	3.0310	1.4223	0.9631	0.4034	0.2547	1.9559	1.1290
0.30	1.8350	1.3869	0.6359	2.2654	1.1713	0.8380	0.5536	0.3600	1.4620	0.9146
0.35	1.2213	1.0083	0.6042	1.6589	0.9102	0.6678	0.5370	0.3505	1.0679	0.7054
0.40	0.8031	0.7188	0.5116	1.1959	0.6811	0.5056	0.4554	0.2971	0.7662	0.5259
0.45	0.5227	0.5048	0.4063	0.8518	0.4967	0.3705	0.3594	0.2341	0.5423	0.3826
0.50	0.3371	0.3505	0.3100	0.6010	0.3556	0.2654	0.2715	0.1764	0.3798	0.2734
0.60	0.1372	0.1650	0.1677	0.2934	0.1757	0.1304	0.1431	0.0925	0.1822	0.1346
0.70	0.0546	0.0761	0.0857	0.1409	0.0844	0.0620	0.0710	0.0457	0.0859	0.0643
0.80	0.0214	0.0348	0.0425	0.0671	0.0399	0.0290	0.0341	0.0219	0.0401	0.0303
0.90	0.0083	0.0158	0.0207	0.0319	0.0188	0.0134	0.0161	0.0103	0.0187	0.0141
1.00	0.0032	0.0072	0.0100	0.0151	0.0088	0.0062	0.0076	0.0048	0.0087	0.0066
1.20	0.0005	0.0015	0.0023	0.0034	0.0020	0.0014	0.0017	0.0010	0.0019	0.0014
1.50	0	0.0002	0.0002	0.0004	0.0002	0.0001	0.0002	0.0001	0.0002	0.0002
2.00	0	0	0	0	0	0	0	0	0	0

crylate) (PMMA), polyacrylate acid (PAA), poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), poly(dimethylsiloxane) (PDMS), polystyrene (PS), polybutadiene (PB) and poly(propylene oxide) (PPO) were calculated. The normalized values are listed in *Table 1*.

It can be seen from *Table 1* that there exists an extreme value (the underlined value) for each total correction factor. Although every total correction factor reaches its extreme value at respective value of μt, all the extreme values distribute within the range of μt from 0 to 0.5. In order to study the influence of μt on the total correction factors, the relative changing degree of total correction factor D_f was calculated using the following equation:

$$D_f = \frac{F_{\mu t} - F_\infty}{F_\infty} \times 100\% \qquad (13)$$

where $F_{\mu t}$ is the total correction factor at μt and F_∞ is the total correction factor at $\mu t \rightarrow \infty$. It is suggested from *Table 1* that $F_{\mu t=2}$ can be regarded as F_∞.

It can be seen from the data in *Table 2* that the value of D_f is less than 1% when $\mu t \geqslant 0.5$, but it can reach 14.7% when $\mu t < 0.5$. Thus, with the procedure for calculating crystallinities in multicomponent polymers using a diffractometer with reflection geometry, the influence of the absorption factor can be ignored when $\mu t \geqslant 0.5$, but it should be taken into account when $\mu t < 0.5$.

Compared to the original procedure described in the previous study[2], the extended method discussed here has the following improvements.

1. A relative atomic scattering factor f_r was used, replacing the atomic scattering factor f in the original procedure, to calculate the partial weighted correction factor $\bar{C}_p$ and the range correction factor K_a. With homopolymers and those copolymers whose components have similar chemical compositions, f is equivalent to f_r when calculating $\bar{C}_p$ and K_a. But when the chemical compositions of the components of copolymers vary greatly, f_r should be used to calculate $\bar{C}_p$ and K_a.
2. The total correction factor F_a was redefined by introducing an absorptive correction factor A_a. With the redefined F_a, the general method can be used to calculate the crystallinities in copolymers with any thickness on condition that a diffractometer is used with reflection geometry.
3. With equation (12), the general method was extended to calculate the crystallinities in multicomponent polymers. At least theoretically, the contribution of some amorphous components with lower molecular weight, such as coupling agent and other additives that might exist in copolymers, to X-ray scattering curve can be taken into account by using equation (12).
4. The total correction factors F_c and F_a were calculated following the same procedure. As far as semicrystalline PEO is concerned, a weighted average correction factor $F_{c_{PEO}}$ was used to replace the separate correction factors F_{120} and $F_{113/032}$. Apart from the simplification of calculation, the application of $F_{c_{PEO}}$ may, in part, eliminate the influence of orientation on crystallinity calculation that might exist in copolymers.

Taking into account the discussion above, it can be concluded that the extended method may be used more widely than the original one.

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