Calculation of Crystallinity Index by Correlation Method\cite{193,206}

Let, at a common Bragg angle $2\theta$,

$I_S = \text{normalised intensity from the sample},$

$I_{CS} = \text{normalised intensity from the crystalline standard, and}$

$I_{AS} = \text{normalised intensity from the amorphous standard.}$

Assuming the validity of two-phase model for semicrystalline polymers and applying Vainstein's law of conservation of intensity\cite{214}, we can write

$$I_S = f I_{CS} + (1-f) I_{AS} \quad \text{or},$$

$$f = \frac{(I_S - I_{AS})}{(I_{CS} - I_{AS})},$$

where $f$ is the fraction of crystalline material in the sample.

At each increment $2\theta_i$, the numerical value of the intensity differences, say,

$$(I_S - I_{AS})_i = Y_i \quad \text{and} \quad (I_S - I_{CS})_i = X_i$$

can be used to calculate the linear regression of $Y_i$ on $X_i$ from

$$f = \frac{(I_S - I_{AS})}{(I_{CS} - I_{AS})}_i = Y_i / X_i.$$ 

Thus, the crystallinity index ($f$) is given by the slope of the regression line

$$Y_i = f X_i$$

as
\[
\begin{align*}
  r &= \frac{\sum_{i=1}^{N} x_i y_i - \frac{1}{N} \left( \sum_{i=1}^{N} x_i \sum_{i=1}^{N} y_i \right)}{\left( \sum_{i=1}^{N} x_i^2 - \frac{1}{N} \left( \sum_{i=1}^{N} x_i \right)^2 \right)^{1/2} \left( \sum_{i=1}^{N} y_i^2 - \frac{1}{N} \left( \sum_{i=1}^{N} y_i \right)^2 \right)^{1/2}},
\end{align*}
\]

where \( N \) = the total number of pairs of observations.

The spread of the data about the regression is given by

\[ 1 - r^2, \]

where \( r \) is the correlation coefficient. \( r \) is defined as

\[
  r = \frac{\sum_{i=1}^{N} x_i y_i - \frac{1}{N} \left( \sum_{i=1}^{N} x_i \sum_{i=1}^{N} y_i \right)}{\left( \sum_{i=1}^{N} x_i^2 - \frac{1}{N} \left( \sum_{i=1}^{N} x_i \right)^2 \right)^{1/2} \left( \sum_{i=1}^{N} y_i^2 - \frac{1}{N} \left( \sum_{i=1}^{N} y_i \right)^2 \right)^{1/2}}.
\]

A FORTRAN IV program (given on the next page) was written in ATIRA for use in IBM 360 computer for the calculation of crystallinity index.

**Computer Input:**

- \( N \) = total number of intensity values read at equal intervals of 26.
- \( EM = (N-1) \).
- \( Area \) = an arbitrary value (say, 5000) to which the area under various diffractograms can be reduced as a result of normalization.
- \( I = 1, 2, 3, \ldots N \).
- \( CS(I) \) = intensity from the crystalline standard.
- \( AS(I) \) = intensity from the amorphous standard.
- \( S(I) \) = intensity from the sample.

The title cards for the headlines of \( CS(I), AS(I), \) and \( S(I) \)
Computer Program:

FORTRAN IV  MODEL 44 MFT  VERSION 3, LEVEL 4  DATE 76/331  /MFIN44

0001     DIMENSION CS(500),JS(500),S(500),HEAD(20),CSP(500),SP(500)
0002     1 FORMAT(215,F10.0)
0003     2 FORMAT(20F4.1)
0004     3 FORMAT(20A4)
0005     6 FORMAT(I1,H,20A4,2F0.4)
0006     7 FORMAT(I1,H,20F6.1)
0007     8 FORMAT(I1H)
0008     PRINT 8
0009     READ1,N,NM,AREA
0010     READ3,HEAD
0011     PRINT6,HEAD
0012     READ2,CS(I),I=1,N
0013     PRINT7,CS(I),I=1,N
0014     READ3,HEAD
0015     PRINT6,HEAD
0016     READ2,AS(I),I=1,N
0017     PRINT7,AS(I),I=1,N
0018     SCS=.5*CS(I)+CS(I)
0019     SAS=.5*AS(I)+AS(I)
0020     DO25I=1,NM
0021     SCS=SCS+CS(I)
0022     25 SAS=SAS+AS(I)
0023     CN=AREA/SCS
0024     ASN=AREA/SAS
0025     DO35I=1,N
0026     AS(I)=AS(I)*ASN
0027     CSp=CS(I)*CS(I)
0028     35 CSP=CSP(I)+CS(I)
0029     PRINT7,(AS(I),I=1,N)
0030     PRINT7,(CSP(I),I=1,N)
0031     PRINT7,ICSI(I),I=1,N
0032     READ3,HEAD
0033     PRINT6,HEAD
0034     READ2,SL(I),I=1,N
0035     PRINT7,SL(I),I=1,N
0036     SSM=.5*SL(I)+SL(I)
0037     UD45I=2,NM
0038     45 SSM=SSM+SL(I)
0039     SMN=AREA/SSM
0040     SCS2=0.
0041     SSM2=0.
0042     SCSSM=0.
0043     DO55I=1,N
0044     SPl=SPI(I)*SSM
0045     SPI=SPI(I)-AS(I)
0046     SCS2=SCS2+CS(I)**2
0047     SSM2=SSM2+SL(I)**2
0048     55 SCSSM=SCSSM+CS(I)**2
0049     R=SCSSM/SQRT(SCS2*SSM2)
0050     F=SCSSM/SCS2
0051     PRINT6,HEAD,R,F
0052     PRINT7,(SPI(I),I=1,N)
0053     PRINT7,(SL(I),I=1,N)
0054     GO TO 103
0055     END
are also provided in the input.

Computer Output:

Normalized values of the intensities.

R = the correlation coefficient.

F = the crystallinity index.

In the present work, the x-ray diffraction intensities were read off at equal intervals of 0.5° over 2θ = 10 to 40°.