Composite material characterisation using an advanced small angle x-ray (SAXS) technique

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Abstract. Materials development in the field of composite material spurs the use of advanced characterization technique. As the fillers become in the nanoscale range in size, the effect of agglomeration become apparent and cannot be avoided. The use of Small Angle X-Ray (SAXS) Scattering technique revealed the information on agglomeration based on the value of specific surface (m²/g). Thermoplastic natural rubber composite was found isotropic based on 2D saxs scattering pattern. As the amount of fillers increased from 2-10% wt., the value of specific surface dropped accordingly. This indicated the higher the amount of filler used, the higher the degree of agglomeration. The SAXS system was also tested by Alumina (BAM) powder and yield result which was in good agreement with BET technique.

1. Introduction
The sample is a blend of natural rubber and high density polyethylene or known as NR/HDPE. Both phases are compatibilised with liquid natural rubber (LNR). This LNR fills in the gap between the dispersed phase of HDPE and the matrix phase of NR [1]. Fillers are added in the blend to form composite system which act as radiation shielding material. However, the fillers which in the nanometer size range are very sensitive to moisture and prone to form agglomerates. The fillers were therefore treated with surfactant to minimize agglomeration. The degree of agglomeration of filler inside the blend was then characterized by using SAXS technique.

SAXS is an analytical method to determine the structure of particle systems in terms of averaged particle sizes or shapes. It is a non-destructive method for investigating nanostructures from typically 1 nm to 100 nm in size. In this context, the nanostructures are regarded as the object of interest which scatter the incoming x-rays. The scattered x-rays are captured by the detector (1 or 2 Dimensional) behind the object as shown in figure 1. Information of the object (scatterer in the nano range) is obtained by performing data analysis on the scattered data signal. Comparison of SAXS technique with the other techniques is given in figure 2. SAXS instrument used in the study is shown in figure 3 (a). Differences between SAXS and XRD is shown schematically in figure 3 (b).
Figure 1. X-rays source, nanostructures and detector configuration.

Figure 2. Comparison of SAXS technique with other techniques

Figure 3. (a) SAXS instrument (b) Schematic diagram of differences between SAXS and XRD

2. Materials and method

2.1. Sample preparation
Sample of polymer blend consists of 50% natural rubber (Nr), 10% liquid natural rubber (Lnr) and 40% high density polyethylene (HDPE). Nr (SMR L grade) was supplied by Malaysian rubber research institute, RRI (Malaysia). The density of Nr is 0.95g/cm$^3$. HDPE was supplied by Titan Chemicals Corp. Bhd. (Malaysia) with a density of 0.91g/cm$^3$. Lnr was produced from Nr with weight average molecular weight relative to polystyrene as Mw = 40 x 10$^4$. Nano fillers B$_4$C with the density of 2.52g/cm$^3$ was used and added to the blend starting from 2%wt until 10%wt. Before the fillers were added to the blend, they are treated with surfactant and observed under scanning electron microscope.
2.2. Experimental work
SAXS experiments were performed using Hecus SWAX instrument, operated at 50kV and 1mA with the point collimation geometry. The radiation used was a Ni filtered CuKα radiation of wavelength 0.154nm (Seifert, Ahrensburg, Germany). The intensity profiles are recorded using a CMOS 2-D detector (Pilatus) and the scattering vector q, covers from 0.01 to 0.6Å⁻¹. One-dimensional scans of I(q) were extracted from two-dimensional scattering patterns using the analysis package Fit2D.

Angular calibration of the scattered intensities in the small angle regime for the detector is performed using silver stearate (d = 48.68 Å). Sample to detector distance is 271mm and sample exposure to the source is 600 seconds. All experiments are carried out at room temperature, 20°C. Validation experiment is carried out using a reference material, alumina type 150 (Al₂O₃) CRM BAM-PM-104.

2.3. Data analysis
The principle of SAXS technique is large objects scatter to small angle and small objects scatter to large angle. In this aspect, SAXS complement XRD as the minimum of diffraction angle for XRD is typically 10° which is easily achievable by SAXS. The relationship between the angle and the scattering vector q is given by [5]:

\[ q = \frac{4\pi}{\lambda} \sin \theta \]  

where:
- q = scattering vector, \( \lambda \) = wavelength of the x-rays, \( \theta \) = half of the diffraction angle

Scattered data signal in 2 dimensional is reduced to 1 dimensional data profile by radial averaging and typically plotted in scattered intensity, I (arbitrary unit) versus scattering vector q (nm⁻¹). Data in I and q is used to fit three possible model of the scatterer based on the following equation [2]:

1. \[ I(q) = I_0 e^{-(qR_g^2/2)} \] gives spherical shape  
2. \[ I(q) * q = I_0 * e^{-(qR_c^2/2)} \] gives cylindrical shape  
3. \[ I(q) * q^2 = I_0 * e^{-(qR_t^2/2)} \] gives lamellar shape

where,
- I(q) = scattered intensity, q = scattering vector, I₀ = Initial intensity,  
- R_g = Radius of gyration due to globular, R_c = Radius of gyration due to cross section,  
- R_t = Radius of gyration due to thickness

The calculation could also be performed on samples which contain nanoporous structure to obtain information on specific surfaces based on the following equation [3]:

\[ Si = \frac{\pi \varphi_1 \varphi_2 10^4 k}{\rho A Q} \]  

where:
- Si = specific surfaces, \( \varphi_1 \) = volume fraction of solid, \( \varphi_2 \) = volume fraction of air,  
- \( \rho A \) = apparent density of sample, k/Q = constant in Angström²/Angström³
3. Results and discussion
Figure 4 shows the effect of surface treatment on the nano-filler. The treatment successfully de-agglomerates the raw nano-filler. The success of the treatment is basically stems from the optimum amount of surfactant selected from SEM results. Figure 5-7 clearly show the agglomeration exist when the surfactant is not suffice or in excess. The optimum amount of surfactant was found to be 1.6%wt. Even with the proper selection of surfactant amount, still this does not guarantee that the fillers will not form agglomeration when they are mix with the polymer blend. At this stage SAXS technique plays vital role to probe the fillers condition when they form composite with the polymer blend. In order to have the understanding on the changes of the clustered fillers, some of the treated fillers were subjected to BET test for measuring the specific surface for comparison with SAXS result.

![TEM micrograph of (a) raw nano-filler (x10k) and (b) treated nano-filler (x10k)](image)

Figure 4. TEM micrograph of (a) raw nano-filler (x10k) and (b) treated nano-filler (x10k)
Figure 5. SEM micrograph of treated nano-filler with 0.2%wt surfactant (x10k)

Figure 6. SEM micrograph of treated nano-filler with 1.6%wt surfactant (x10k)
Figure 7. SEM micrograph of treated nano-filler with 2.0%wt surfactant (x10k)

Figure 8 shows an example of comparison between composite with 10%wt nano-filler and polymer blend. Both of them have the same linear scaling in the q range of $0.01 < q < 0.25$ Å$^{-1}$. Exposure time was 600 seconds and the beam centre was at pixel $x = 274$, $y = 99$. Fillers or $B_4C$ particles are clearly visible by the excess SAXS signal (A). There is no preferred orientation of the nanostructure within the plane of the samples. This does not exclude the possibilty that a preferred nematic type orientation exists perpendicular to the surface. Rings at larger angles (B) are due to Be window.

Figure 8. SAXS 2D scattering pattern (a) composite with 10%wt nanofiller (b) polymer blend
Figure 9 shows 1D scattering profiles of some of the samples. These profiles are subjected to analysis using Guinier plot, Porod plot and Invariant plot [3]. The values obtained from the analysis were substituted in equation 5. The result of this equation were tabulated in Table 2.

![Graph showing scattering profiles](image)

**Figure 9.** Data reduction from 2D scattering pattern results in 1D scattering profiles ready for data analysis

It is clearly seen from table 1 that as the filler loading is increased, the value of specific surface is reduced. This indicates the fillers experience slight agglomeration. The value of specific surface of the treated filler from BET test was found to be 595 m$^2$/g. This proves that the result from Table 2 is very reliable as they are close to BET result.

| Filler loading (%wt) | Treated filler Si/p (m$^2$/g) |
|----------------------|-----------------------------|
| 2                    | 554.6                       |
| 4                    | 509.6                       |
| 6                    | 481.5                       |
| 8                    | 460.3                       |
| 10                   | 457.4                       |

### Table 1. Specific surface of fillers inside the polymer blend

4. **Conclusions**

The result of this study shows the importance of the advanced characterization technique in implementing the R&D in developing countries. The use of small angle x-ray scattering (SAXS) technique revealed the information on agglomeration based on the value of specific surface (m$^2$/g). This lab-scale instrument could be used as a platform to further develop knowledge and skills especially to cater the need of using high flux X-ray or synchrotron facility in the near future.

5. **References**

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[3] Heimo Schnablegger and Yashveer Singh, 2011, The SAXS Guide.