JOINT INSTITUTE FOR NUCLEAR RESEARCH

Frank Laboratory of Neutron Physics

FINAL REPORT ON THE INTEREST PROGRAMME

Investigation and modeling of neutron/x-ray reflection by thin films of polymer nanocomposites

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Abstract

Polymer nanocomposites (PNCs) contribute alot in research of condensed matter physics. Due to the dependence of the properties of materials on the distribution state of nanoparticles inside the material, reflectometry experiments are used to determine the effect of distribution of nanoparticles inside thin films on its properties, this can be obtained by tracing the SLD value of the film which is done by modelling films and fitting experimental data. It's concluded that the mass content of nanoparticles inside thin film can affect the indistinguishability of distribution of nanoparticles.
Keywords: Thin film, SLD, Polymer, Nanocomposites, Reflectometry.

Introduction & Literature Review

In the 1830s, the foundation stone for modern polymer science was laid by the work of Henri Braconnot and his team, where he was working on a derivative of natural cellulose polymer, and in 1833 the term "polymer" was appeared by Jöns Jakob Berzelius, and work continued in this field over a period of 100 years until polymers science become basic and productive science. polymers science reached its peak in the early 1900s, when polymers were used in many industries, and this caused the outbreak of the Second World War, which was using all known sources at the time. Because of the importance of a science such as polymer science, many Nobel Prizes in Physics and Chemistry have gone to related works in this field over the course of the development of this science.

Recently, it has been found that polymeric materials have multiple uses in various fields, especially in applications related to thin film. In general, these materials are used in the case if the characteristic length of the system in which they will be used is comparable to the dimensions of the polymer. The thin film is one of the most important discoveries made by humans, as it helped human civilization advance many steps in various fields itself. The thin film enters into many modern technological industries, so the thin film is used to reduce the prices of solar cells, as thin film photovoltaic cells are used, thin film is also used in medical applications in addition to being an essential factor in building telescopes. One of the most important purposes for which a fine film is used is neutron and x-ray reflectometry experiments which are building block of determining the properties of different martial, with thin film interference phenomenon, and this is the main theme of this report.

This report aims to determine the effect of the adding nanoparticles to thin films which change the the whole properties of the film. these changes can be determined with neutron/x-ray reflectometry experiments. All curves, thin film modeling, and data fitting is done by *Igor Pro* software with *Motofit* package.

The report is structured as follows: it starts with data fitting for some results of reflectometry experiments, which has a variable media -either fronting or backing- and the experiments aim to determine the what is the variable media based on the obtained SLD value for this variable media after fitting the data, *section 1.* Then, different thin films which is doped with nanoparticles are modeled with different properties to investigate factors affecting the nature of the film, *section 2* , and *section 3.* Finally, thin films are modeled with specific properties to be able to determine when reflectometry experiment can't distinguish distribution state of nanoparticles.

1 Data Fitting

In this section of the report some experimental data -Scattering wave vector $Q(\mathring{A}^{-1})$ verses Reflectivity R- were extracted from reflectometry experiments, which contains backing and fronting media only and there is no existences for a thin films. These experiments aim to obtain SLD value for the variable media -either backing or fronting- in order to determine the variable media. data from six experiments were extracted and fitted as a reflectivity curve using *Igor Pro* software with *Motofit* package, and the obtained results were as follows:

1.1 Experiment I

In this experiment air was used as the fronting media and an unknown liquid was used as the backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q, and the obtained fitting for the data appears as follows:

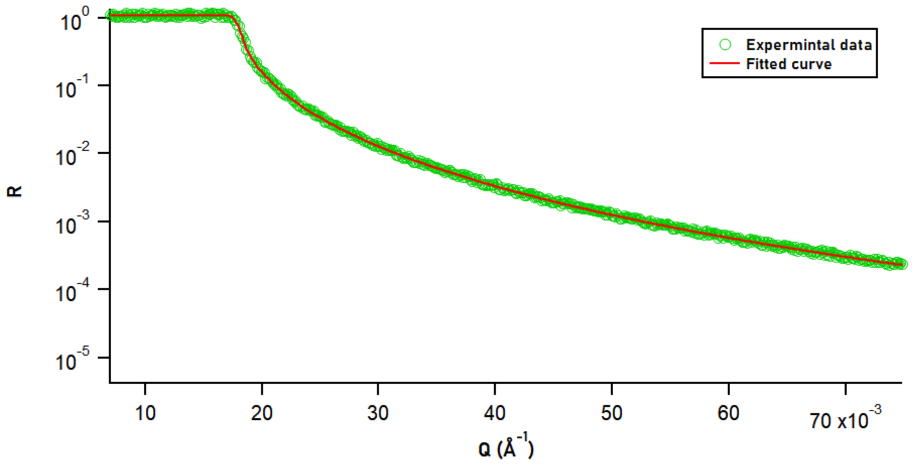


Figure 1: Reflectivity curve, with air as fronting media and an unknown liquid as backing

Based of the fitted curve the obtained value of SLD of backing media is $6.3352 \times 10^{10} cm^{-2}$, with $\chi^2 = 3.67 \times 10^{-4}$. The SLD value indicate that the used liquid as backing media in this experiment is $\mathbf{D_2O}$

1.2 Experiment II

In this experiment air was used as the fronting media and an unknown solid was used as the backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q, and the obtained fitting for the data appears as follows:

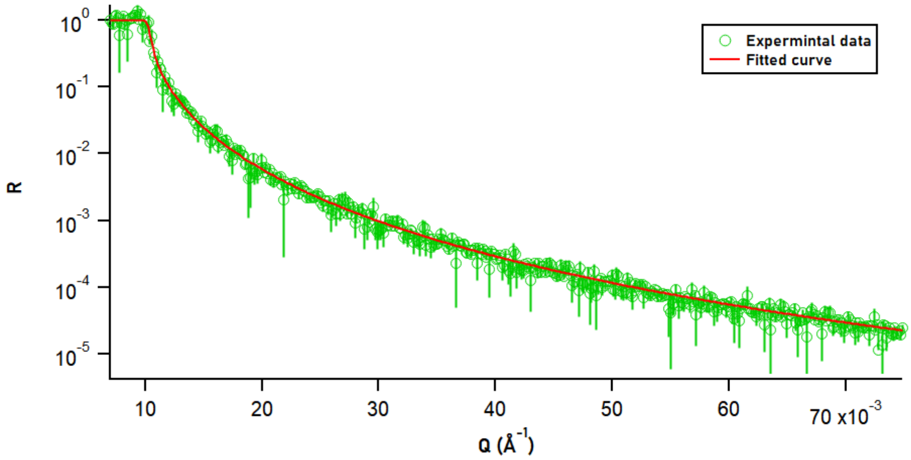


Figure 2: Reflectivity curve , with air as fronting media and an unknown solid as backing

Based of the fitted curve the obtained value of SLD of backing media is $2.0975 \times 10^{10} cm^{-2}$, with $\chi^2 = 1.735 \times 10^{-3}$. The SLD value indicate that the used solid as backing media in this experiment is **Si**

1.3 Experiment III

In this experiment the crystal that was used as the backing media in **experiment II** is taken to be the backing media in this experiment, and an unknown liquid was poured on the crystal, to be used as the fronting media Reflectivity R values was recorded for 500 different value for scattering wave vector Q, and the obtained fitting for the data appears as follows:

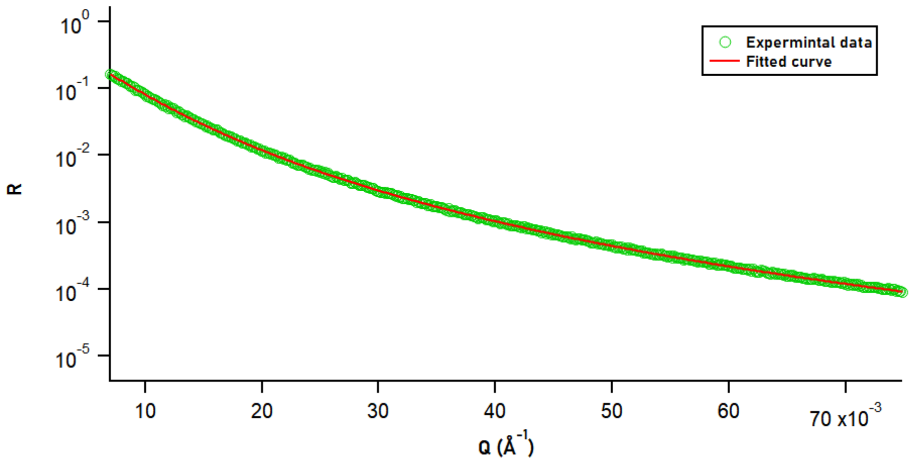


Figure 3: Reflectivity curve , with an unknown fronting media and Si crystal as backing

Based of the fitted curve the obtained value of SLD of fronting media is $6.35 \times 10^{10} cm^{-2}$, with $\chi^2 = 3.35 \times 10^{-7}$. The SLD value indicate that the used liquid as fronting media in this experiment is $\mathbf{D_2O}$

1.4 Experiment IV

In this experiment an unknown crystal was used as the backing media, and D_2O was poured on the crystal to be used as fronting media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q, and the obtained fitting for the data appears as follows:

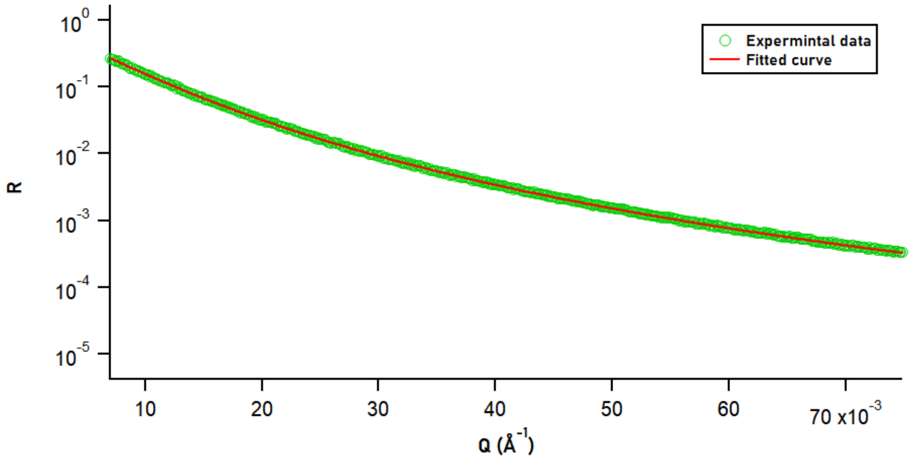


Figure 4: Reflectivity curve , with D_2O as fronting media and an unknown crystal as backing

Based of the fitted curve the obtained value of SLD of fronting media is $-1.88 \times 10^{10} cm^{-2}$, with $\chi^2 = 1.169 \times 10^{-6}$. The SLD value indicate that the used liquid as fronting media in this experiment is **Ti**

1.5 Experiment V

In this experiment an unknown liquid -that was used as the fronting media- was poured on Ni crystal that is used as a backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q, and the obtained fitting for the data appears as follows:

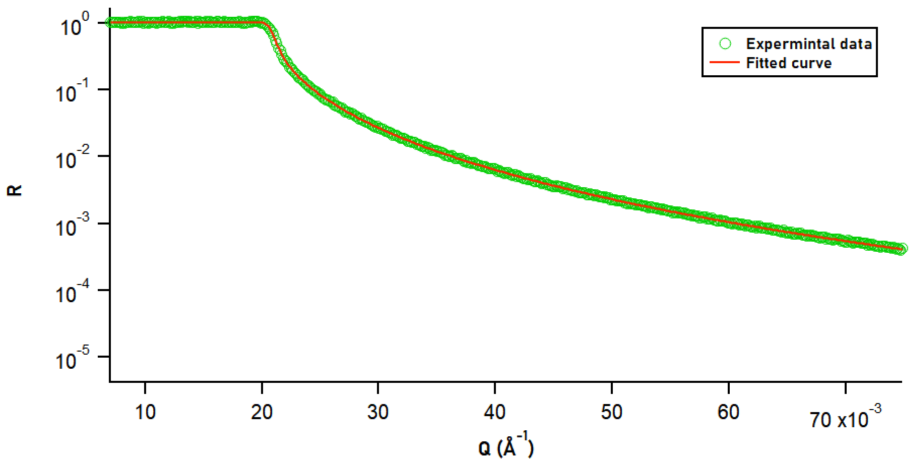


Figure 5: Reflectivity curve , with unknown liquid as fronting media and an Ni crystal as backing

Based of the fitted curve the obtained value of SLD of fronting media is $0.94 \times 10^{10} cm^{-2}$, with $\chi^2 = 7.62 \times 10^{-5}$. The SLD value indicate that the used liquid as fronting media in this experiment is **toluene**

1.6 Experiment VI

In this experiment an unknown liquid -that was used as the fronting media- was poured on Ni crystal that is used as a backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q, and the obtained fitting for the data appears as follows:

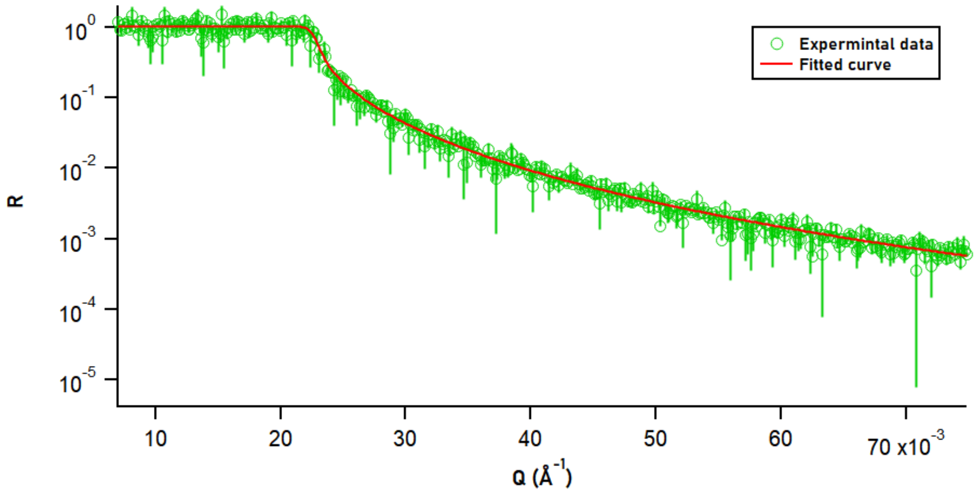


Figure 6: Reflectivity curve , with unknown liquid as fronting media and an Ni crystal as backing

Based of the fitted curve the obtained value of SLD of fronting media is $-0.56 \times 10^{10} cm^{-2}$, with $\chi^2 = 7.7 \times 10^{-3}$. The SLD value indicate that the used liquid as fronting media in this experiment is $\mathbf{H_2O}$

2 Thin Film Modelling (Without Roughness)

2.1 Modelling

In this section of the report different versions of 500 $\mathring{A}$ polystyrene thin films which are doped with 5% mass of fullerene NPs C_{60} are modeled. Every model is characterized by NPs[1] distribution inside the film either uniform, or substrate and air with 100% NPs content in layer. The reflectometry experiments are designed such that the fronting media is the air with $\rho_{film} = 0$, and Si crystal as backing media with $\rho_{film} = 2.07 \times 10^{10} cm^{-2}$, and the film is inserted in between. A reflectivity curve is generated for every case by generating 500 point in the range between $Q = 0.007\mathring{A}^{-1}$ and $Q = 0.075\mathring{A}^{-1}$, also SLD curves are generated for every case

The polystyrene thin film has scattering length density $\rho_{PS} = 1.35 \times 10^{10} cm^{-2}$, When the film doped with fullerene NPs, the SLD value changes according to the following relations:

- in the case of uniformly distributed NPs

$$\rho_{eff} = \rho_{film} + \phi(\rho_{NPs} - \rho_{film}) \tag{1}$$

- in the case of dense layer (substrate and air)

$$\rho_{layer} = \rho_{film} + \phi_L(\rho_{NPs} - \rho_{film}) \tag{2}$$

Such that the length of the dense layer of NPs δ_{layer} is given in terms of the length of the film δ_{film} as follows:

$$\delta_{layer} = \frac{\phi}{\phi_L}\delta_{film} \tag{3}$$

Such that ϕ is fullerene mass content, and ϕ_L is content of NPs in the dense layer

[1] NPs refares to nano-particles

2.1.1 Uniformly Distributed NPs

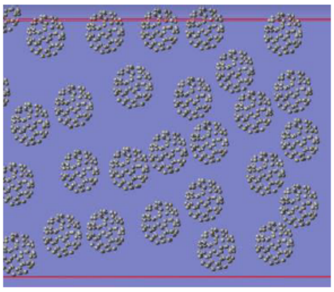
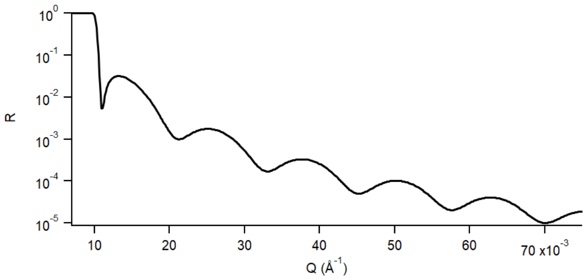
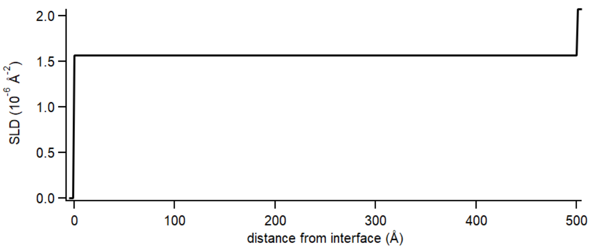


Figure 7: Structural organization of uniformly distributed NPs in thin film

A 500 $\mathring{A}$ polystyrene thin film that is doped with 5% mass of fullerene NPs which are distributed uniformly is designed. According to equation 1 the effective SLD value of the film is $\rho_{film} = 1.569 \times 10^{10} cm^{-2}$. The reflectivity curve and SLD curve appears as follows:



(a) Reflectivity curve



(b) SLD curve

Figure 8: Reflectometry results of 500 $\mathring{A}$ polystyrene thin film, with uniformly distributed fullerene NPs

2.1.2 Substrate layer

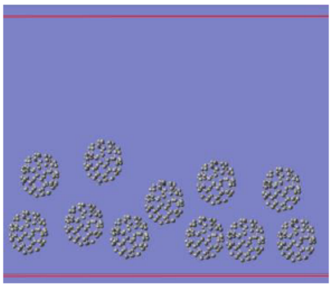
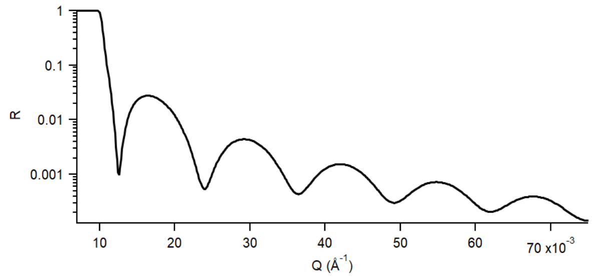
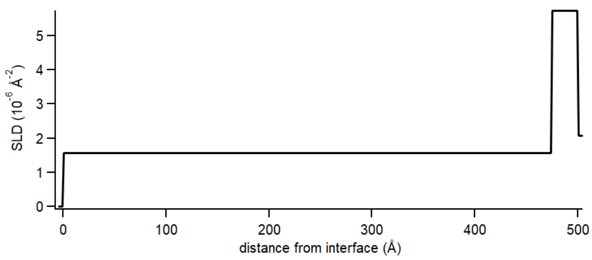


Figure 9: Structural organization of substrate layer in thin film

A 500 $\mathring{A}$ polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length $\delta_{layer} = 25\mathring{A}$, that is close to the backing media. As the content of NPs in the layer $\phi_L = 100\%$, according to equation 2 this layer has SLD value $\rho_{layer} = 5.73 \times 10^{10} cm^{-2}$, then the film can be considered as two layers; the first one is polystyrene layer which has length $\delta_{PS} = 475\mathring{A}$, and the second one is fullerene layer which has length $\delta_{C_{60}} = 25\mathring{A}$, This makes The reflectivity curve and SLD curve appears as follows:



(a) Reflectivity curve



(b) SLD curve

Figure 10: Reflectometry results of 500 $\mathring{A}$ polystyrene thin film, with substrate layer of fullerene NPs

2.1.3 Air layer

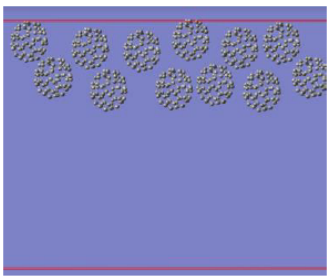
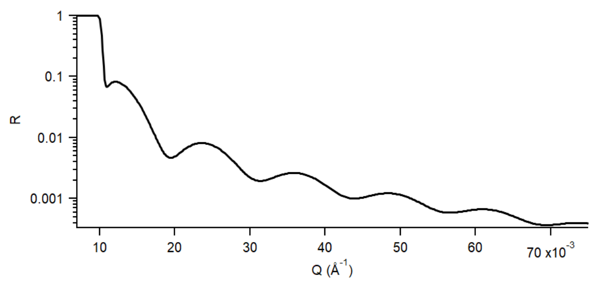
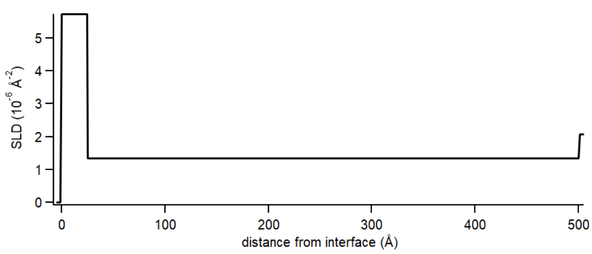


Figure 11: Structural organization of uniformly distributed NPs in thin film

A 500 $\mathring{A}$ polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length $\delta_{layer} = 25\mathring{A}$, that is close to the fronting media. As the content of NPs in the layer $\phi_L = 100\%$, according to equation 2 this layer has SLD value $\rho_{layer} = 5.73 \times 10^{10} cm^{-2}$, then the film can be considered as two layers; the first one is fullerene layer which has length $\delta_{C_{60}} = 25\mathring{A}$, and the second one is polystyrene layer which has length $\delta_{PS} = 475\mathring{A}$, This makes The reflectivity curve and SLD curve appears as follows:



(a) Reflectivity curve



(b) SLD curve

Figure 12: Reflectometry results of 500 $\mathring{A}$ polystyrene thin film, with air layer of fullerene NPs

2.2 Verifying data

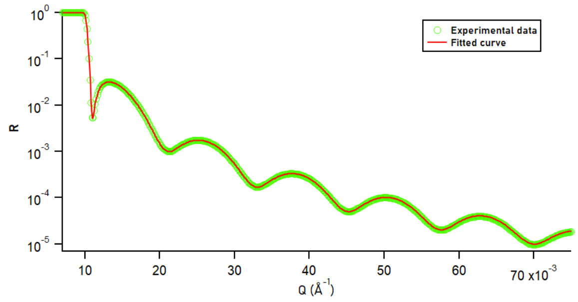
In this part of the report, the data that is generated for the three thin films which are modeled previously are fitted as a reflectivity curve after introducing 10% error bars are introduced these error bars are symmetric, which means that it represent a systematic error. Results and graphs are found to be as follows for the three films:

2.2.1 Uniformly Distributed NPs

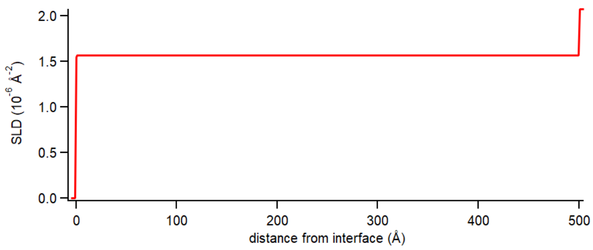
Based of the fitted curve the film where NPs are distributed uniformly, has the following specifications:

- Film thickness: 499.86$\AA$
- Film SLD: $1.5619 \times 10^{10} cm^{-2}$
- Film roughness: 0.0175$\AA$
- Backing roughness: 0.0114$\AA$

with a value of $\chi^2 = 6.64 \times 10^{-11}$. Also, reflectivity and SLD curves appears as follows:



(a) Reflectivity curve



(b) SLD curve

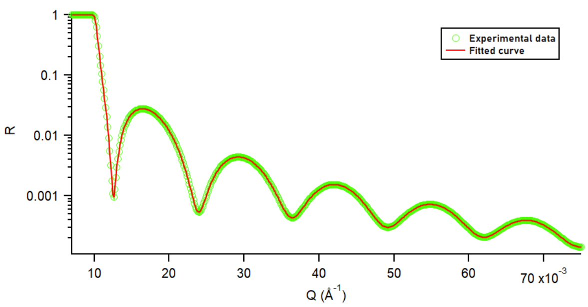
Figure 13: Fitted reflectometry curves of 500 $\AA$ polystyrene thin film, with uniformly distributed fullerene NPs

2.2.2 Substrate Layer

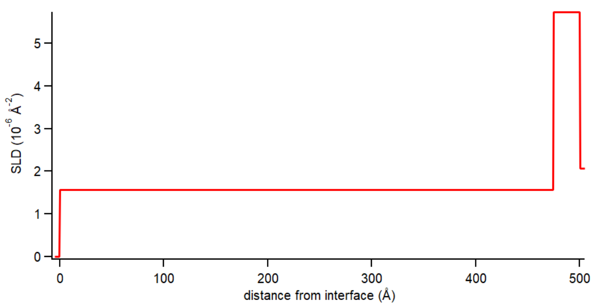
Based of the fitted curve the film where NPs are substrate layer, has the following specifications:

- Film thickness: Film thickness: 499.999$\AA$
- First layer thickness: 475$\AA$
- Second layer thickness: 25.003$\AA$
- First layer SLD: $1.35 \times 10^{10} cm^{-2}$
- Second layer SLD: $5.7301 \times 10^{10} cm^{-2}$
- First layer roughness: 0$\AA$
- Second layer roughness: 0$\AA$
- Backing roughness: 0$\AA$

with a value of $\chi^2 = 1.27 \times 10^{-10}$. Also, reflectivity and SLD curves appears as follows:



(a) Reflectivity curve



(b) SLD curve

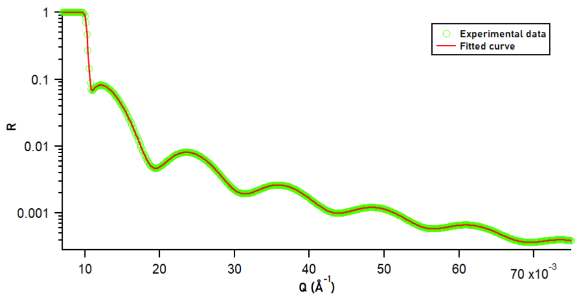
Figure 14: Fitted reflectometry curves of 500 $\AA$ polystyrene thin film, with substrate layer of fullerene NPs

2.2.3 Air Layer

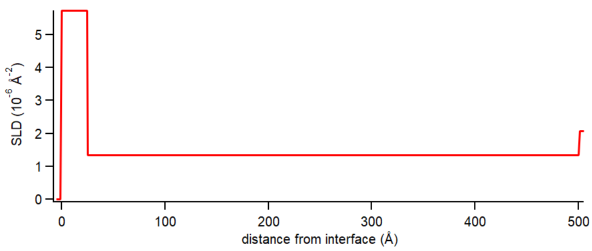
Based of the fitted curve the film where NPs are substrate layer, has the following specifications:

- Film thickness: Film thickness: 499.999$\AA$
- First layer thickness: 24.999$\AA$
- Second layer thickness: 475$\AA$
- First layer SLD: $5.77305 \times 10^{10} cm^{-2}$
- Second layer SLD: $1.35 \times 10^{10} cm^{-2}$
- First layer roughness: 0$\AA$
- Second layer roughness: 0$\AA$
- Backing roughness: 0$\AA$

with a value of $\chi^2 = 1.27 \times 10^{-10}$. Also, reflectivity and SLD curves appears as follows:



(a) Reflectivity curve



(b) SLD curve

Figure 15: Fitted reflectometry curves of 500 $\AA$ polystyrene thin film, with air layer of fullerene NPs

3 Thin Film Modelling (With Roughness)

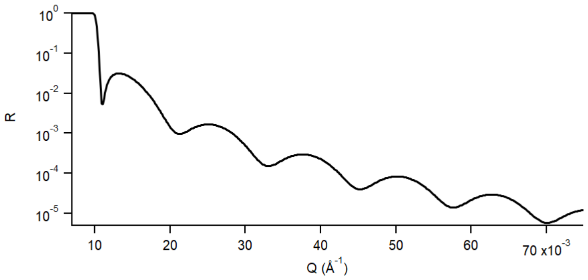
3.1 Modelling

In this section of the report different versions of 500 $\AA$ polystyrene thin films which are doped with 5% mass of fullerene NPs C_{60} are modeled. Every model is characterized by NPs distribution inside the film either uniform, or substrate and air with 100% NPs content in layer. The reflectometry experiments are designed such that the fronting media is the air with $\rho_{film} = 0$, and Si crystal as backing media with $\rho_{film} = 2.07 \times 10^{10} cm^{-2}$ and roughness 5$\AA$, and the film is inserted in between, such that the polystyrene layer has roughness 10$\AA$, and the fullerene layer has roughness 10$\AA$, also . A reflectivity curve is generated for every case by generating 500 point in the range between $Q = 0.007\AA^{-1}$ and $Q = 0.075\AA^{-1}$, also SLD curves are generated for every case

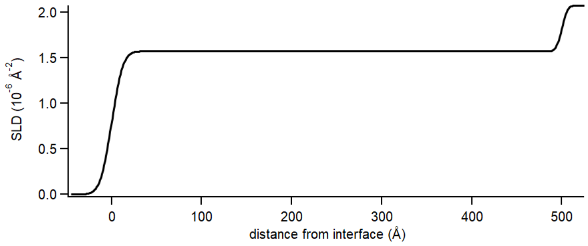
The polystyrene thin film has scattering length density $\rho_{PS} = 1.35 \times 10^{10} cm^{-2}$, When the film doped with fullerene NPs, the SLD value changes according equations 1, 2 ,and 3

3.1.1 Uniformly Distributed NPs

A 500 $\AA$ polystyrene thin film with roughness 10$\AA$ that is doped with 5% mass of fullerene NPs which are distributed uniformly is designed. According to equation 1 the effective SLD value of the film is $\rho_{film} = 1.569 \times 10^{10} cm^{-2}$. The reflectivity curve and SLD curve appears as follows:



(a) Reflectivity curve

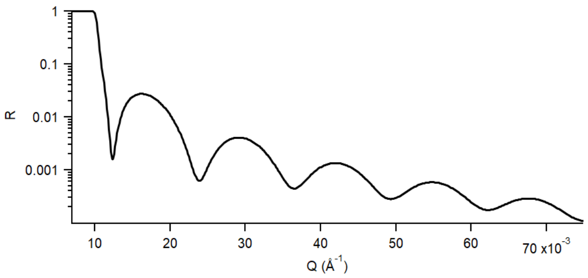


(b) SLD curve

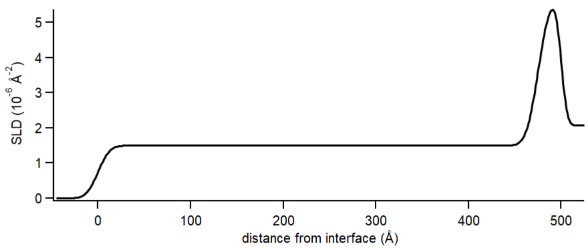
Figure 16: Reflectometry results of 500 $\mathring{A}$ polystyrene thin film, with uniformly distributed fullerene NPs

3.1.2 Substrate layer

A 500 $\mathring{A}$ polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length $\delta_{layer} = 25\mathring{A}$, that is close to the backing media. As the content of NPs in the layer $\phi_L = 100\%$, according to equation 2 this layer has SLD value $\rho_{layer} = 5.73 \times 10^{10} cm^{-2}$, then the film can be considered as two layers; the first one is polystyrene layer which has length $\delta_{PS} = 475\mathring{A}$ and roughness $10\mathring{A}$, and the second one is fullerene layer which has length $\delta_{C_{60}} = 25\mathring{A}$ and roughness $10\mathring{A}$, This makes The reflectivity curve and SLD curve appears as follows:



(a) Reflectivity curve

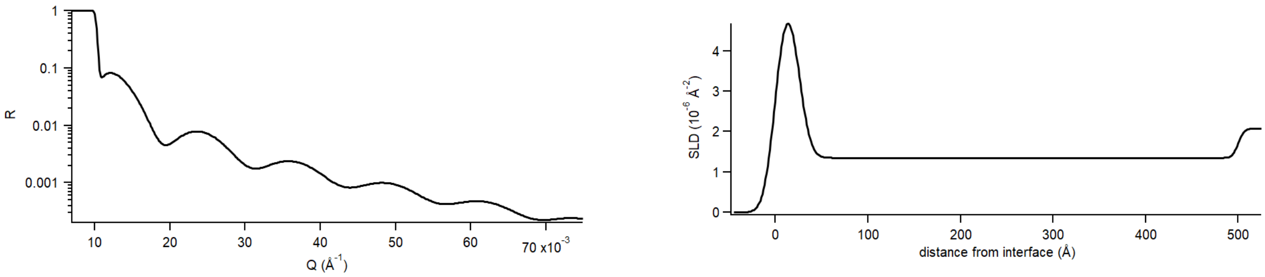


(b) SLD curve

Figure 17: Reflectometry results of 500 $\mathring{A}$ polystyrene thin film, with substrate layer of fullerene NPs

3.1.3 Air layer

A 500 $\mathring{A}$ polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length $\delta_{layer} = 25\mathring{A}$, that is close to the fronting media. As the content of NPs in the layer $\phi_L = 100\%$, according to equation 2 this layer has SLD value $\rho_{layer} = 5.73 \times 10^{10} cm^{-2}$, then the film can be considered as two layers; the first one is fullerene layer which has length $\delta_{C_{60}} = 25\mathring{A}$ and roughness $10\mathring{A}$, and the second one is polystyrene layer which has length $\delta_{PS} = 475\mathring{A}$ and roughness $10\mathring{A}$, This makes The reflectivity curve and SLD curve appears as follows:



(a) Reflectivity curve

(b) SLD curve

Figure 18: Reflectometry results of 500 $\mathring{A}$ polystyrene thin film, with air layer of fullerene NPs

3.2 Verifying data

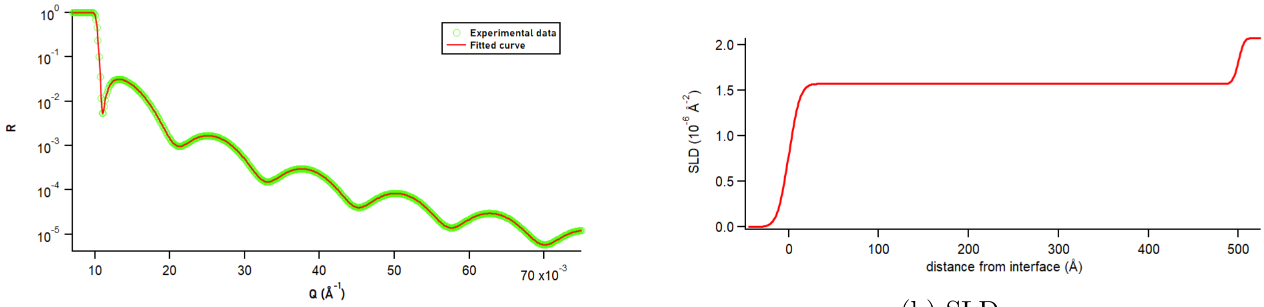
In this part of the report, the data that is generated for the three thin films which are modeled previously are fitted as a reflectivity curve after introducing 10% error bars are introduced these error bars are symmetric, which means that it represent a systematic error. Results and graphs are found to be as follows for the three films:

3.2.1 Uniformly Distributed NPs

Based of the fitted curve the film where NPs are distributed uniformly, has the following specifications:

- Film thickness: $500\mathring{A}$
- Film SLD: $1.569 \times 10^{10} cm^{-2}$
- Film roughness: $10.001\mathring{A}$
- Backing roughness: $4.99\mathring{A}$

with a value of $\chi^2 = 1.84 \times 10^{-15}$. Also, reflectivity and SLD curves appears as follows:



(a) Reflectivity curve

(b) SLD curve

Figure 19: Fitted reflectometry curves of 500 $\mathring{A}$ polystyrene thin film, with uniformly distributed fullerene NPs

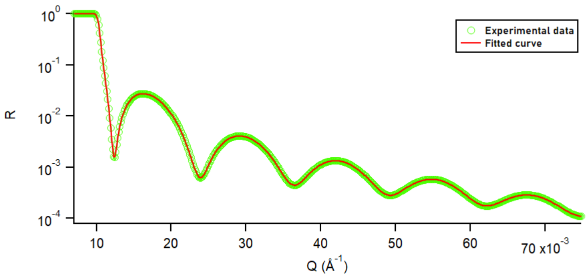
3.2.2 Substrate Layer

Based of the fitted curve the film where NPs are substrate layer, has the following specifications:

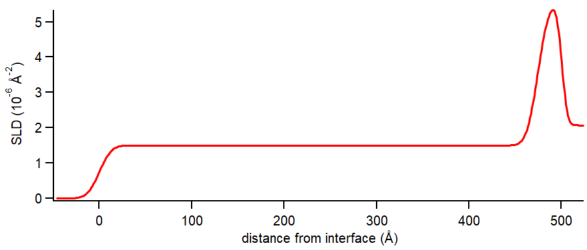
- Film thickness: Film thickness: $500.32\mathring{A}$
- First layer thickness: $474.39\mathring{A}$
- Second layer thickness: $25.962\mathring{A}$

- First layer SLD: $1.4997 \times 10^{10} cm^{-2}$
- Second layer SLD: $5.583 \times 10^{10} cm^{-2}$
- First layer roughness: $10.39 Å$
- Second layer roughness: $9.53 Å$
- Backing roughness: $4.73 Å$

with a value of $\chi^2 = 1.1 \times 10^{-11}$. Also, reflectivity and SLD curves appears as follows:



(a) Reflectivity curve



(b) SLD curve

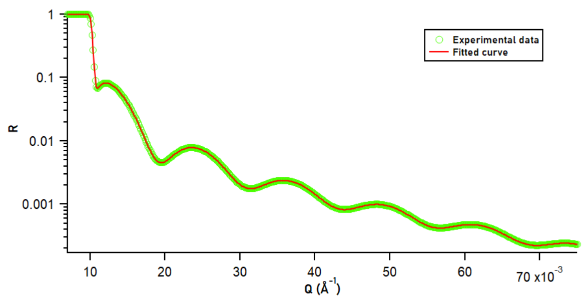
Figure 20: Fitted reflectometry curves of 500 Å polystyrene thin film, with substrate layer of fullerene NPs

3.2.3 Air Layer

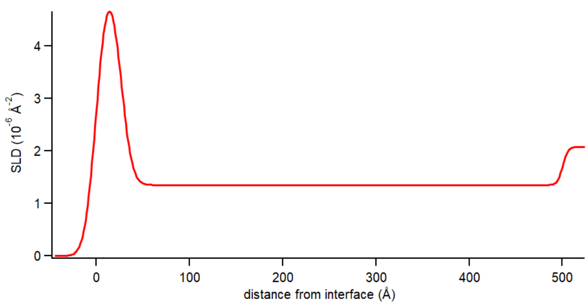
Based of the fitted curve the film where NPs are substrate layer, has the following specifications:

- Film thickness: Film thickness: $499.999 Å$
- First layer thickness: $24.999 Å$
- Second layer thickness: $475 Å$
- First layer SLD: $5.77305 \times 10^{10} cm^{-2}$
- Second layer SLD: $1.35 \times 10^{10} cm^{-2}$
- First layer roughness: $0 Å$
- Second layer roughness: $0 Å$
- Backing roughness: $0 Å$

with a value of $\chi^2 = 1.27 \times 10^{-10}$. Also, reflectivity and SLD curves appears as follows:



(a) Reflectivity curve



(b) SLD curve

Figure 21: Fitted reflectometry curves of 500Å polystyrene thin film, with air layer of fullerene NPs

4 indistinguishability of distribution state of NPs

Sometimes a reflectometry experiment fails to determine the distribution state of NPs, this is due to the nature of the thin film itself and the percentage of NPs in it. The indistinguishability appears by plotting the reflectivity curve of different films and it is found that these curves are approximately identical, this happens due to the small content of fullerene in the film, as the smaller the percentage of fullerene in the film, the closer the value of SLD of the film (with fullerene) to the original value of SLD of the film (without fullerene), this result seems very intuitive as if the content of fullerene is very small the film will behave as if it's a film without fullerene. Five different thin films are generated with different content of fullerene (3%, 1%, 0.5%, 0.2%, 0.1%) and the curves of the reflectivity for every case appears to be the same with slight differences. When content of fullerene approaches 0%, reflectivity curves become identical as the effective SLD value of the film approaches SLD value of polystyrene. Reflectivity curves appears as follows:

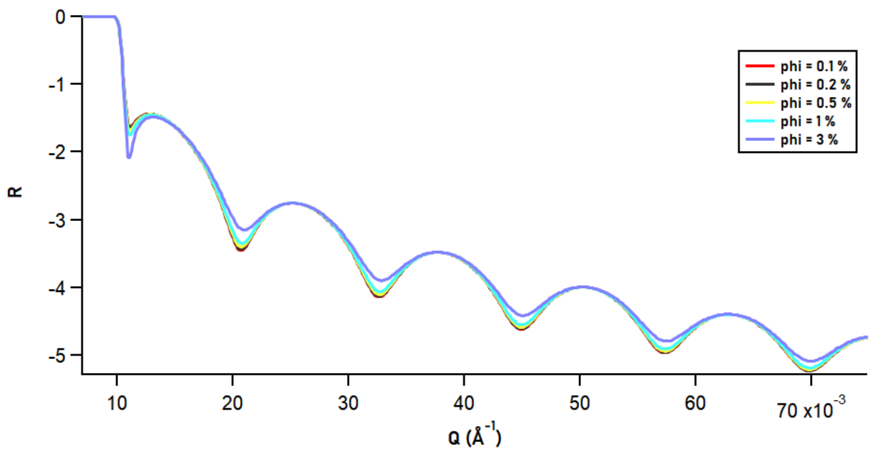


Figure 22: Reflectivity curves for different content of fullerene (3%, 1%, 0.5%, 0.2%, 0.1%)

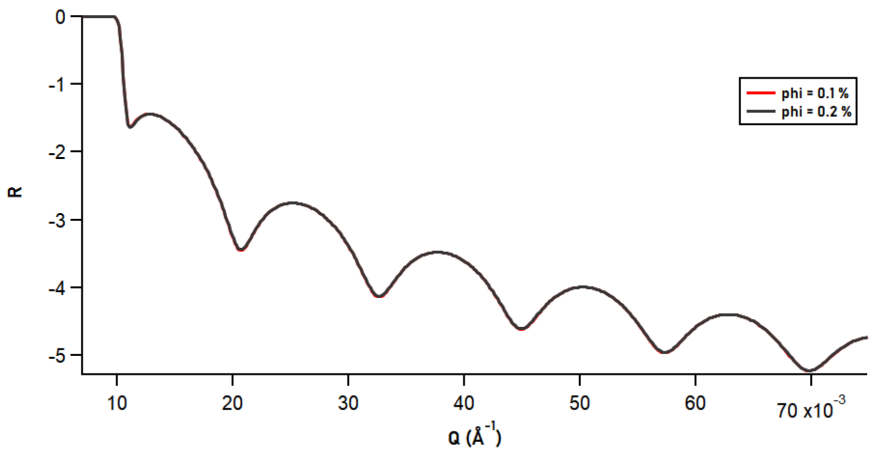


Figure 23: Reflectivity curves for $\phi = 0.2\%$, and $\phi = 0.1\%$

5 Conclusion & Summary

In conclusion, polymer nanocomposites has a great impact in many field. these nanoparticles strongly affect the properties on matters, as it has several organization ways in side the matter. these changes can be detected by reflectometry experiments of neutron/x-ray reflection by thin films which are doped with these polymer nanocomposites. the report discuss the effects of adding the fullerene nanoparticles to a polystyrene thin films. The produced modeled of thin films and the fitted curves shows that the smaller the content of the nanoparticles in the film, the closer the value of SLD of the film (with fullerene) to the original value of SLD of the film (without fullerene). which means that the used reflectometry experiments cannot make a conclusion about the properties of the film.

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References

- Mackay, M. E.; Tuteja, A.; Duxbury, P. M.; Hawker, C. J.; Van Horn, B.; Guan, Z.; Chen, G.; Krishnan, R. S. General Strategies for Nanoparticle Dispersion. Science (80-.)., 2006, 311 (5768), 1740–1743. https://doi.org/10.1126/science.1122225.

- Mackay, M. E.; Tuteja, A.; Duxbury, P. M.; Hawker, C. J.; Van Horn, B.; Guan, Z.; Chen, G.; Krishnan, R. S. General Strategies for Nanoparticle Dispersion. Science (80-.)., 2006, 311 (5768), 1740–1743. https://doi.org/10.1126/science.1122225.