An Insight to the Interphase in Polymer Nanocomposites

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Abstract. Nanocomposites has floated in the market as the best in class material related to many sectors of manufacturing. Base material is embedded with nanoparticles to form nanocomposites. Afterwards, layered formation known as interphase starts to take place. It is the link (interface) between the base material (polymer) and the nanoparticle. Up till now, the problem of finding the material properties in this interphase has become a challenge for researchers and scientists. This piece of work corresponds to analyzing the possible types of variations in properties within interphase. Some power law may govern the distribution of material properties in nanocomposites and unit cell of same may be investigated. For getting the values of final properties of polymer nanocomposites, ideation of variation in the interphase area is quite essential. The huge improvement in the material properties in nanocomposites is observed just because of the zone of interphase. As it is a very difficult area, as far as its property analysis is concerned, So extensive literature survey is required for proceeding ahead. Nanocomposites have nowadays also coined in the form of novel materials for various processes like additive manufacturing.

1. INTRODUCTION: Contemporarily, the requirement of engineering materials is getting increased regularly. These are the materials having higher strength as well as lighter weight. Nowadays in the field of Aerodynamics, Medical Science, these materials are of prior importance. Polymer nanocomposites are also among these engineering materials.

Polymer nanocomposites are prepared by doping a polymer with higher strength Nano filler. On doing this, the strength of the new material gets considerably increased. These are formed by embedding some nano sized particles to a polymer matrix. The nano sized particles are called as filler material and the matrix (polystyrene, PVC, polyurethane etc.) is called as base material. The nano filler materials are having the mechanical properties quite much superior to the Base material. But on addition of a very small amount of nano sized filler material particles, the mechanical properties, e.g. Elastic Modulus, Poisson Ratio etc., of the combination i.e. the polymer nanocomposites gets improved significantly. Overwhelming results are obtained and observed by synthesizing the nanocomposites. Hence these prove to be a very important kind of novel material.

On mechanically or chemically combining the base polymer with nano sized filler materials( of the order of 100 nm), a combination of layers gets formed between the base material and nano filler particles at local areas surrounding the particles scattered in the base material, which is known as interphase. Interphase lies within nano filler and polymer matrix. The peculiarity about the interphase can be described as the variation in material properties. The properties in this area are not constant hence undefined. These neither correspond to base polymer nor to the filler material. The work is intended to predict and investigate the nature of variation of these properties corresponding to the interphase area. This is required because the final mechanical properties of the nano composites also
depend on the interphase property variation. Different type of variation will lead to different properties of polymer nanocomposites. The role of the interface (interphase) in the strength of composite materials has been addressed in the early study of composites by Tsai and Hahn (1980) [1]. The tempting feature of these materials is that significant improvement in the properties of nanocomposites is obtained by doping a very low scale amount of the filler material to the base polymer. Due to this insignificant level of doping, the base polymer doesn’t sacrifice its original properties like: manufacturability, ductility, malleability etc. which also coins to be an asset of nanocomposites. The light weight and easy processing of the base polymer is retained completely. Because of all the mentioned points, nanocomposites are used in various sectors of the society like: industries, automotives, aerospace, shipbuilding, medico equipments and space exploration etc. various types of the nanoparticle morphology is available like: spherical (silica), platelets (graphite etc.), nanotubes, like CNTs etc [2].

The purpose of the work is to analyze interphase property variation influence on the final properties of the nanocomposites. In this interphase zone, the properties (elastic modulus, Poisson ratio etc.) vary in the form of a certain function. Now depending on the type of function, we get various overall properties for various kinds of functions. Also the final properties depend on various parameters like thickness of interphase layers, number of interphase layers, volume fraction of the inclusion, type of inclusion etc. Available data on the interphase zones has proven, not to be sufficient to formulate the law of variation of the interphase properties across the thickness.

To find the various effects, a unit cell model should be considered and it should be analyzed for various parameter values, various conditions etc. In the view of continuum mechanics, the interphase is characterized by constrained polymer chains around Nano-particles (Yung et al., 2006). According to the Hierarchical Multi Interphase Model (HMM), The interaction between the inclusion and the matrix is not direct but through the interphase. On extensive study it was found that, the interphase region can be formed due to the interaction of matrix polymer chains with filler molecules either by covalent bonds (Smith et al., 2002; Yung et al., 2006) or through Van Der Waals forces (Jiang et al., 2006).

Ratio of elastic modulus of filler material and base polymer is termed as stiffness ratio. It has been observed that the efficiency of property enhancement increases with stiffness ration is a non linear fashion. Studies have found that for the range of stiffness ratio and the enhancement in mechanical properties are correlated as per following table 1.

| Stiffness Ratio (Range) | Enhancement in Properties |
|-------------------------|---------------------------|
| 1-100 (Range 1)         | Slow                      |

Table 1
As per table 1, we can figure out that enhancement efficiency approaches its asymptotic limit, and it cannot be enhanced further by increasing the stiffness ratio. Generally the traditional composites fall in Range 1 and nanocomposites are covered under Range 2.

The need of contribution of interphase properties is felt in explaining the remarkable change in the viscoelastic properties. Its challenging to gather the exact information regarding interphase properties. Using experimental setups, it is contemporarily very difficult to measure the interphase properties foolproof. Some backing assumptions are required altogether. On the other hand, the numerical calculation of molecular dynamics (MD) can capture some structural and dynamical details of interphase only at the molecular time and length scale, while the continuum modeling requires material properties in many orders of magnitudes longer.[3-8]

Even addition of inorganic material in particulate form as a filler to some polymers has proved to be an effective way to improve mechanical properties. But the typical filler requirement for this purpose may be as high as 10 to 20 \% v/v, which proves to be extremely difficult from processing point of view. Also the asset of light weight also gets buried, as the filler is having significantly high density, while nanocomposites can fulfill the very same purpose on addition of filler material as low as 1 to 4 \% v/v, attracting attention of the industries.

Industries dealing with plastics, generally use inorganic filler materials to improve mechanical properties of thermoplastics like: stiffness, hardness, toughness and heat distortion temperature etc. The effect on the properties is according to the particle size, shape, dispersion of the filler material. It is observed that the properties of composites with micro sized particles are inferior to the properties obtained by nano sized filler inclusion, in the case of same filler material.

Improvements in numerous properties such as yield strength, hardness, bulk modulus, shear modulus, optical properties, magnetic properties, electrical conductivity etc are found by introducing nano fillers in base polymer. In addition to mechanical and rheological properties, the development of nanocomposites filled with carbon Nano-tubes and graphene sheets is particularly effective in modifying electrical properties of Nano-composite materials.[9]

2. VARIATION OF INTERPHASE PROPERTIES (MATHEMATICAL MODEL):

| Range      | Property  |
|------------|-----------|
| 100-10000  | Rapid     |
| >10000     | Again Slow|

In the interphase area, in between the inclusion and the base polymer, property variation can be assumed in the form of various functions, like: parabolic function, exponential function, hyperbolic function etc. All the types of variations are to be assumed by us, because the peculiar nature of the
interphase is still under research and it is not clear that how the properties of the material are going to change in the interphase area.

Suppose the property variation in the interphase takes place in exponential manner. Both Poisson’s ratio ($\nu$) and Young’s modulus ($E$) are varying exponentially towards the thickness of the interphase, in the case of Polypropylene (matrix) and Alumina (inclusion), the Poisson’s ratio is exponentially increasing towards the thickness while Young’s modulus is exponentially decreasing. There are 3 interphase layers and the properties are calculated in those as per the exponential variation.

$$y = ae^{bx}$$  \hspace{1cm} (1)

Where $y$ is the corresponding mechanical property ($\nu$ or $E$) and $x$ is the distance of the interphase point from the inclusion, $a$ and $b$ are constants.

Now suppose the variation of mechanical properties takes place in parabolic manner. With the thickness of the interphase area, the properties are either parabolically increasing or decreasing.

$$y^2 = 4ax + b$$  \hspace{1cm} (2)

Where $y$ is the corresponding mechanical property ($\nu$ or $E$) and $x$ is the distance of the interphase point from the inclusion, $a$ and $b$ are constants.

This nature of variation can be taken in the form of various other functions too, like hyperbolic function, quadratic function or power law or any the type of function. Prime objective of research revolves around obtaining the overall mechanical properties of the polymer nanocomposites on assuming different kinds of variation of the interphase properties. In the literature review, the findings obtained after studying the vast literature available on the topic till now are studied. A number of researches have been done in the field of polymer nanocomposites and the proceedings are available in the form of papers. On thoroughly studying the paper we noted certain points related to the work that is shown in the literature review. As there is a need of having the basic knowledge of the subject matter before doing any kind of work in any field, therefore after literature review, the theoretical study of the area dealing with polymer nanocomposites is presented. Various aspects of the concepts related to the field are explained under this section, this will make any person familiar with the area of the work [10].

The results are shown in the form of various tables and plots. Thus on observing the results, we come to certain concluding remarks. The further future scope of the present work is shown in future plan of work. It covers all the possibilities of the work that can be further done in the corresponding field.

M. Quaresimin et al [11] have worked on the strategies for finding out the mechanical properties of Polymer Nanocomposites. They studied about Micro-mechanical modeling strategy, Nano-structural modeling strategy and Molecular modeling strategy. They studied the maximum about the
micromechanical model, hence further they gave an indication that Nano-structural and molecular models will offer better results. Overall this work is known as three stage strategy. They observed that the molecular model is having an advantage that it deals with the chemical interaction phenomenon too, while the others are mainly focused on the mechanical interactions. In this way this work provides a proper guideline to work further for deciding the mechanical properties of polymer nanocomposites. As per the study of Yaning Li et al. [12] ,the Mori Tanaka model for the polymer nanocomposites fails to determine all the mechanical properties properly, because it doesn’t have any involvement of the interphase, a finite zone of material that surrounds the inclusions and is a main structural feature of nanocomposites, significantly contributing to the enhancement mechanisms of nanocomposites, it is based on simple two phase model. Along with this, there is a serious issue in the above mentioned model: that is being independent of size. Influence of size can be observed in a way that for same volume fraction of a filler material, on decreasing the size of the filler particle, the properties enhance extraordinarily. The properties of nanocomposites are evaluated with inclusion and without filler material.

R. Qiao, L. Catherine Brinson [13] studied about the effect of the interphase zone on the visco-elastic behavior of the polymer nanocomposites. They found that the percolation of the interphase zone has an important role in deciding the mechanical properties of the nanocomposites. They did the simulations using various volume fractions, various thicknesses of interphase layers and other conditions. They basically studied about the thermo mechanical behavior of polymer nanocomposites, that revolves around the glass transition temperature (T_g) of the nanocomposites.

Nanocomposites are a special kind of composites, in these, the filler constituent is in the scale of Nano-meters, means the main matter is the size of the filler constituent [14].

Nanocomposites are further of three kinds:
1. Ceramic matrix nanocomposites
2. Metal matrix nanocomposites
3. Polymer matrix nanocomposites

In all of the above, the main part of the volume of Nano-composite is occupied by Ceramic, Metal and Polymer respectively.

When the size of the high strength inclusion or filler particles is of the scale of 1 nm to 100 nm, and these particles are added to the polymer matrix, then due to higher surface area interaction between filler and matrix, there is improvement in the properties of polymer nanocomposites and an interphase gets formed in between the filler and matrix [15].
Figure 1: Unit cell of a Nanocomposite

Figure 1 illustrates the formation of unit cell of polymer nanocomposites. Now the interphase formation phenomenon is shown in figure 2, it shows the interphase as a whole and in the form of various number of layers. It depends on us that how much number of layers we are going to take. Interphase is a 3rd phase, other than matrix and inclusion, in which the properties vary so much peculiarly [16].

Figure 2: Interphase Layers Formation

**Filler Material:** The filler material or inclusion is high strength inorganic material having a comparatively higher value of young’s modulus then the polymer matrix. Few of the primly used Nano-fillers are Alumina, Silica, Mg(OH)$_2$, Carbon Nano-tubes, Silicates etc. Additional Nano-fillers include carbon Nano-tubes, graphite platelets, carbon Nano-fibers[17].

3. RESULTS AND DISCUSSIONS:

*Calculation of properties at layers:*
In the study, Polystyrene is taken as the matrix and alumina as the filler material. The Poisson ratio of polystyrene and alumina is 0.42 and 0.21 respectively [18]. The values of Young modulus of the two constituents are 1.5 GPa and 390 GPa respectively. Afterwards, the calculations are described in the following section:

**Parabolic Variation:**

| Zone                  | Poisson Ratio, $\nu$ | Young Modulus, E(GPa) |
|-----------------------|-----------------------|-----------------------|
| Inclusion             | 0.21                  | 390                   |
| Interphase Layer 1    | 0.2572                | 356.02                |
| Interphase Layer 2    | 0.3320                | 275.77                |
| Interphase Layer 3    | 0.392874              | 159.22                |
| Matrix                | 0.42                  | 1.5                   |

On considering variation to be parabolic (figure 3), we got the various values of properties at various layers in the RVE[19], using the developed mathematical relations, viz. eq. (2), calculated data are as mentioned in table 2:

![Figure 3: Parabolic Variation](image)

**Exponential Variation:**

| Zone                  | Poisson Ratio, $\nu$ | Young Modulus, E(GPa) |
|-----------------------|-----------------------|-----------------------|
| Inclusion             | 0.21                  | 390                   |
| Interphase Layer 1    | 0.2357                | 154.372               |
| Interphase Layer 2    | 0.297                 | 24.1867               |
Now on considering variation to be exponential, properties were found referring eq. (1), which are mentioned in table 3.

| Interphase Layer 3 | 0.3742 | 3.79 |
|--------------------|--------|------|
| Matrix             | 0.42   | 1.5  |

4. CONCLUSION: We can conclude on the basis of results obtained from the mathematical model that the properties obtained in the various layers of the interphase are different. In this interphase layers, value of the properties lie between the corresponding values of the base polymer and the filler material. So the power law, which is going to govern the interphase area, can indicate the distribution of properties in various layers, as we can see from the comparison of parabolic distribution and exponential distribution. Now as the properties of interphase will be distributed in an element of the polymer nanocomposite, the overall properties will also be varying accordingly. Because the consolidated representative volume element will be indicating the overall properties of the nanocomposite. Further mathematical modeling may be done for different power laws, which may
govern the interphase and which may be concluded from latest literature reviews. Ultimately these will help the researchers to get exact idea of overall properties and will help in making the synthesis of nanocomposites more productive. Many more researchers from different domains have also worked out in the corresponding fields [20-25] and have given significant outcome which is also utilized in this work.

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