Polymer/Filler Interactions: A Critical Review

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Abstract

Development in the era, needs cost effective structural and functional materials with diverse properties. Material science is an interdisciplinary area concerned with invention of new materials and improving the already known and existing materials for their better use in present scenario. Materials form the basis of human life with more emphasis given to polymer composites. In this mini review authors describe the role of fillers in enhancing properties of polymer composites with principles governing their distribution and interaction within polymer composite materials.

Introduction

Fillers [particulate fillers and fibers] irrespective of their sources are gaining importance in manufacturing of technical goods and products for structural and functional applications. The increase in their importance is attributed to their fundamental and practical behaviour. Hence it is vital to understand the complex behaviour of fillers when they are practically used in solid [polymer], liquid or gaseous media[1]. This short review focuses on the behaviour of these fillers particularly to polymers. Behaviour of fillers with polymers requires the knowledge on physical and chemical characteristics of fillers; as these characteristics determine the enhancement level in performance of the final product[2]. In general, polymer mixed with fillers [with respect to concentration] is termed as polymer composite material. There are various classifications for polymer composite materials depending upon the source of polymers and fillers, but in this review we shall only focus on the organization of phases within polymer composite material and principles governing filler distribution and interaction.

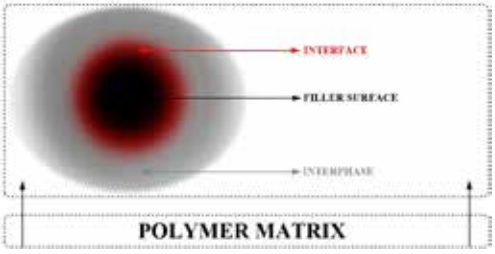

Figure 1: Schematic representation of molecular dimensions zones in filled polymer composites (Interface and Interphase)

"Interface" and "Interphase" are two molecular dimensions within the polymer composite material and are used sometimes in replacement to each other or as a synonym to each other; but rather there is a huge difference between their actual presence in the polymer composite material, as seen in **Figure 1**. The molecular dimension in the vicinity of the polymer is termed as "interface" and the dimension extending from the polymer surface which is influenced by the polymer surface is "interphase"[1]. "Interface" and "Interphase" are the two molecular dimensions within polymer composite materials responsible for properties of the final polymer composite material under stress during application.

Filling polymers with fillers is one of the most widely used methods in manufacturing of structural and functional materials with required set of mechanical, physical and functional properties for any practical application[2]. Fillers are those materials in polymer composite which are distributed near to uniformity (with isotropic and anisotropic alignments) as shown in **Figure 2**, with appropriate means of processing, after knowing the physical and chemical properties of the polymers as well as fillers.

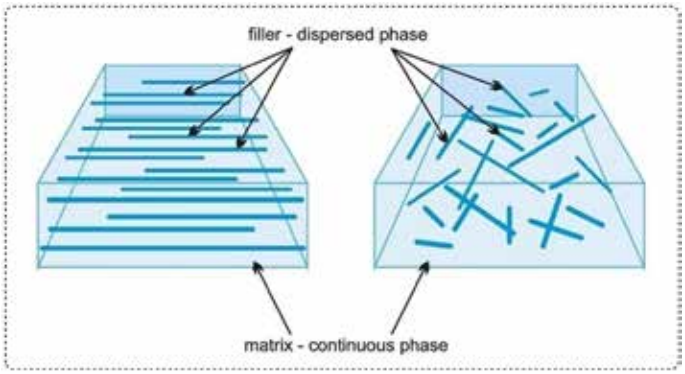

Figure 2: Schematic representation of phases in polymer composite "Macrostructure of a polymer composite"

Reinforcement of polymers with fillers is a process that indicates the compatibility of the fillers with the polymers, thereby having a distinct phases (i.e. interface and interphase) with the polymer phase[2]. As we already discussed, polymer composite materials are

"heterophasic" [two or more phases] wherein phases interact with each other. Proportion of the constituents phase is an important parameter, giving rise to different properties in polymer composite materials, but formation of two molecular dimensions (i.e. interface and interphase) cannot be neglected. Following the definition of composites, on a broader aspect the polymer composite materials may be ordered and structured into "particulate or fibrous filled polymer composite" and "long fiber reinforced polymer composite". Further on following the dimensional aspects, of fillers as we can order polymer composites into "dispersed particles", "short cut fibers" and "long fibers"[2]. Several physical characteristics of fillers influence the properties of the polymer composite materials, to name a few - shape, dimension, size distribution, orientation and composition, out of which "mean values of particle size" is considered as the important property relating to the property of polymer composite material; that contributes to the total surface of the phase border between phases[2]. Particle size along with the shape predicts the performance of the polymer composite material. Effectiveness of the filler action is determined by the "specific surface area" of the filler; specific surface is important wherein fillers are modified by utilizing any of the available chemical methodologies of modification. Packing of fillers within the polymer composite material is dependent on the shape of filler used, i.e. hybrid effect wherein smaller size fillers are used to fill in gaps between larger size fillers within polymer composites. Fillers having tendency to enhance the mechanical properties of base polymer are termed as "active fillers"[2]. "Inactive fillers"[2] intend to give a particular color or rather makes the final product cost effective. As physical properties are important, chemical characteristics of the fillers also have an important role in determining the final properties of the polymer composite material; free surface energy is one such chemical property – as interfacial interactions [between polymer and filler] within polymer composite is dependent on the ratio of "free surface energy" of polymer and filler. Fillers in polymer cannot introduce change in only one particular property[2] as addition of filler into polymer results in formation of new material, with properties completely different from the polymer, it shall be accounted to "micro and macro heterogeneities" and "physical and chemical interactions at molecular dimensions zones". Strong chemical interactions (strength of interface) within polymer composite material increases the stiffness of polymer composite material. Strong physical interactions (strength of interphase) contributes to elastic modulus within polymer composite material and enhances toughness. Having a balance between "stiffness" and "toughness" is of great importance in research area of polymer composite materials. Distribution of phases within polymer composites has a great influence on the properties of the polymer composite materials. Polymer matrix in any polymer composite material is "primary continuous phase"[2]; continuous fibers in a polymer composite material is termed as "secondary continuous phase"[2] whereas particulate fillers in polymer composites are termed as "secondary dispersed phase"[2]. As mentioned about the properties of fillers for polymer composite material, polymer material should possess properties to be used in polymer composite material out of which "good ability to wet the filler surface" is essential. "Area of application" of polymer composite material, determines the choice of polymer and fillers. Fillers activity into polymers, can be classified as "structural"[2] "kinetic"[2] and "thermodynamic"[2]. Changes in polymer structure on a molecular or sub molecular level by a filler is termed as structural activity[2]; ability to change the viscoelastic and relaxation properties of polymer chains in contact with filler (i.e. chain mobility) is kinetic activity[2] and ability of filler to influence the phase state and thermodynamic parameters (enthalpy and entropy) important for filled "polymer blend" is termed as thermodynamic activity of filler[2]. "Influence of filler"[2] can be arbitrarily determined by relating the changes in properties per unit content of filler. In the above text we described the important physical and chemical factors of fillers and polymers, formation of molecular dimension zone and their influence on properties of polymer composite materials, now in the further text we shall discuss on the principles governing filler distribution and interaction within polymer composite materials.

Factors governing the organization of fillers within the polymer composite materials are related to physical and chemical nature of the fillers and the polymers, and further determine the performance and properties of the polymer composite materials. Through this mini review we attempt to discuss interactions and the factors governing them, within a polymer composite material, for readers to consider them during their next additive formulation of polymers with fillers. First of all it is the particle size distribution[3,4] of filler within the matrix, that depends on the surface availability and potential for interaction with the polymer matrix with respect to filler; with considerations for polymer – polarity, crystallinity and viscosity are the parameters; finally processing methods also determines the filler distribution within polymer matrix. Filler distribution in polymer matrix is subjected to "area of application", polymer composite materials intended to be used in electrical conduction, adhesive may decrease in performance if uniform distribution of fillers occurs in polymer matrix. Morphological analysis for distribution of filler in polymer matrix may appear identical but may differ in their properties, this may be

attributed to the molecular motions within the polymer matrix. The "intensity"[3] and "extensity"[3] factors should be considered to have a uniform distribution of filler within polymer, intensity factor i.e. reduction to the smallest particle size determining the property; and extensity factor i.e. uniform inter particle distance[3] determining the uniformity of the properties. Then comes the orientation of fillers in a polymer matrix. Particle shape and concentration of filler and viscosity of polymer matrix are the material factors determining the orientation of fillers in a polymer matrix[3]. Orientation of fillers within polymer matrix is also determined by the processing as distribution of fillers is. Processing factors like rate of flow, characteristics of die, residence time and mold characteristics[3] also effect orientation of fillers within polymer matrix. Orientation within polymer matrix can be induced by controlling the shear forces or by simultaneous shearing and electric fields[3]. "Area of application" also determines the best orientation of fillers within the polymer composite materials. Further comes important dimension in the polymer composites "Void", void if "macro" sized would reduce the mechanical performance of the polymer composites, hence void minimization is taken care of; in some applications "micro" voids are created to enhance the toughness of the polymer composite materials[3]. "Polymer – filler interaction" forms the basis of all set of experimental observation through any means of characterization as reported in past and current literatures. Physical interaction and chemical interaction within the polymer composites are responsible factor for "polymer – filler interaction". Chemical interaction between polymer functional groups and surface groups on fillers, physical interaction through Vander Wal forces and hydrogen bonding between polymer – polymer, polymer – filler and filler – filler, mechanical interlocking between polymer chains are responsible factors for "polymer – filler interaction"[3]. Ionic interactions, acid base interactions are other interactions responsible[3]. Changes in morphology of interacting components also confirms the "polymer – matrix interaction". Molecular dimension zones (interface and interphase) formed due to molecular transformation is a static phenomenon dependent on the concentration of fillers. These molecular transformation forms molecular dimension zones which have properties different from the bulk of the polymer and hence usually improves the material properties. Chemical interactions also play a role in organization of fillers within polymer matrix. Chemical interactions are chemical reactions occurring at the surface of filler and with filler surface. Interactions within polymer composites materials are complex and their quantification is difficult; however the structural characterizations e.g. FTIR, RAMAN, NMR and ESCA are used to determine the type of interactions i.e. physical or chemical, occurring within polymer composite materials[3,FR3]. All the factors governing filler distribution and interactions are inter – related to each other. Further interfacial adhesion and interphase thickness can be roughly estimated through tensile test. Filler chain links, polymer chain dynamics and bound polymer[3] are few experiments which may give an inference on organization of fillers within the polymer matrix.

Conclusions and Outlook

This mini review address, distribution and dispersion of fillers; and interactions between polymer and filler within polymer composite material. Physical and chemical properties of the polymers and fillers should be taken into consideration depending on the potential application. Processing techniques also is an important parameter to be considered. Specific and required level of distribution and dispersion of fillers within the polymer matrix plays a vital role in the final properties imparted to the polymer composite product.

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Further Reading

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