



Characteristics, Applications and Properties of Polymers

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ABSTRACT

A polymer is any of a class of natural or synthetic substances composed of very large molecules, called macromolecules, which are multiples of simpler chemical units called monomers. Polymers make up many of the materials in living organisms and are the basis of many minerals and man-made materials. polymers are used in almost every area of modern living. Grocery bags, soda and water bottles, textile fibers, phones, computers, food packaging, auto parts, and toys all contain polymers

KEYWORDS: Polymer, nanomaterials, permeability

1. INTRODUCTION

In the recent years, there has been a rapid increase of polymeric materials in domestic and industrial usage due to their peculiar properties such as ease of fabrication into different forms, being light in weight, ductile nature, good strength etc. Moreover, The pore size of polymeric materials can be reduced to such an extent that it can act as barrier for fluids and this barrier performance has made it applicable as packaging material in different industries such as medical, food, chemical etc. Materials that are vulnerable or sensitive to moisture or certain gases certainly demand enhanced barrier performance. Although, polymers are used in aforementioned applications since decades, however, they lack in functionality due to their inherent permeability and degradation. In order to solve this, the addition of fillers micro to nanoscale sizes into the polymeric matrix have been widely employed which greatly enhances the barrier performance. Consequently, the

resultant polymeric composite can potentially block the diffusion of gas, vapors, or water diffusion by following the tortuous pathways. Generally, it has been reported that the migration of gaseous molecules or atoms through the polymer is perpendicular to the orientation of the film. The added filler in the polymer matrix is expected to either block the diffusion of migrating gas or vapor molecules or make the passage more tortuous which will eventually lead to little or no passage of gas or vapors. The high surface to volume ratio as well as high aspect ratio of nanofillers make it highly efficient to use and very small amount of nanofillers is required to be added to large volume of neat polymer to enhance the barrier properties of the latter. Thus, in this regard, to act as fillers in polymers nanocomposites (PNCs) lately graphene and its derivatives have added tremendous attention and the resultant nanocomposite system has been highly efficient in barrier application of gases, vapor, and other fluids.

2. POLYMERS

Polymer is combination of the two Greek words *i.e.*, 'Poly' which refers to many (numerous) and 'Mer' which refers to units. A polymer is fundamentally a long-chain molecule derived from the smaller but identical structural units; the so-called "monomers" covalently bonded with each other in any tenable pattern (Kumar and SANTOSH 1978). It is a long chain molecule of several repeating units of identical structure units or "mers" each consists of either simple two or three atoms or complex ring-shaped structures comprises of several atoms. The monomers often referred to as the "building block" possess several bonding sites which links them together to form a polymer chain.

In the recent past, the polymeric materials have almost entered every sector of domestic and industrial usage and have replaced many conventional materials due to their peculiar properties such as low cost, ease of functionality or fabrication, being light in weight *etc.* (Cui, Kundalwal et al. 2016). However, properties of most of the polymers are modified to yield composites to make them suitable for various applications. In this context, the barrier performance of these polymer is very important, particularly, in food packaging, medical, electronic, and chemical industries.

3. THERMOPLASTIC POLYMERS

Thermoplastic polymers comprise of a large range of plastics. These types of polymers find wide variety of application in different fields due to their good mechanical characteristics, electrical and thermal properties (Giboz, Copponnex et al. 2007). Some of these can sustain up to 250 °C, (*e.g.*, polyetheretherketone PEEK), while, the polymers like perfluoroalkoxy (PFA) can resist the aggressive chemicals including the acids, solvents and alkaline solutions (Heckele and Schomburg 2003). The Van der Waal's forces or the inter-molecular forces hold these long chain polymers together. At elevated temperatures, these polymers exhibit thick fluid like morphology that can form a hard mass upon cooling. Moreover, these can be easily shaped by heating or by using of bonds owing to the exclusion of any cross-bond in them, *e.g.* Polystyrene or PVC, which is used in the pipes *etc.* (Shenoy 1996, MacDermott and Shenoy 1997), and the changes are reversible. On

increasing the temperature above the softening point of these polymers, the thermal motion of the polymer segments becomes vibrant and strong and at a critical temperature it overcomes the inter- and intra-molecular forces.

4. THERMOSET POLYMERS

Thermoset polymers possess low molecular mass and semi-fluid in nature, which upon heating gets cross-linked and become hard and infusible. Although, they can be heated to a point where they can be softened once under stress. However, the heat induced reaction is irreversible which means that they undergo a "curing" reaction, that gives rise to the three-dimensional structures (Brazel and Rosen 2012).

5. POLYMER NANOCOMPOSITES

PNCs are composite materials in which the polymer matrix contains nanorange organic or inorganic fillers in which at least the dimension of one of the constituents is <100 nm. The filler is dispersed inside the polymeric matrix by physical or chemical means which significantly enhances the properties of pristine material (Manias 2007). The synergistic hybridization of nanofillers and the polymer matrix yield exceptional properties which cannot be realized in the individual constituents (Gaddam, Narayan et al. 2016). These are prepared either by physical blending or chemical polymerization routes. The fillers can be different forms *i.e.* in the form of particles, clusters, fibrous or layered materials that are embedded in the natural or synthetic polymers (Gao 2012).

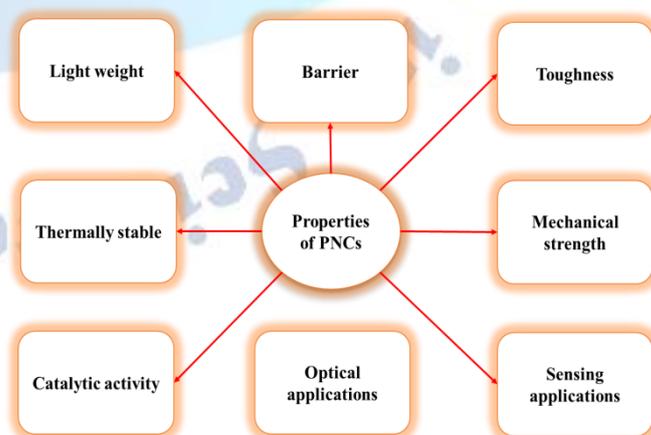


Figure 2.1: Some of the important properties of PNCs (Idumah, Hassan et al. 2019, Karak 2019).

6. BARRIER PROPERTIES OF POLYMERS, DRAWBACKS AND STRATEGIES TO IMPROVE

Barrier polymers are broadly defined as the macromolecules that enable the significant restriction to the passage of gases, vapors, and liquids (Dhoot, Freeman et al. 2002). These barrier polymers have attracted a lot of attention in the recent past due to their wide variety of potential applications in packaging industries, flexible displays, pharma industries, electric and electronic devices etc. (Lange and Wyser 2003).

The permeation of gas/liquid/vapors through a polymeric matrix generally involves four different steps; (i) the absorption of permeating species on the polymeric surface, (ii) secondly, the solubility of permeating species in the polymer matrix, (iii) thirdly, the diffusion occurs through the wall along a concentration gradient and (iv) and finally the desorption from the outer surface of polymer takes place (Salame and Steingiser 1977). It should be noted that the barrier properties are highly dependent on the molecular structure of polymeric backbone and only certain polymeric molecular structure provide efficient barrier properties.

- A good polarity, *e.g.*, in case of halogens such as chlorine or fluorine, nitrile radicals, oxygen, sulfur, ester group, etc.
- High stiffness in polymeric chains.
- A symmetrical closed chain-to-chain packing in long range, ordered orientation of chains and functional groups, good crystallinity, or proper orientation.
- Presence of bonding in chains by strong or weak attractive forces and,
- High glass transition (T_g).

Fillers to Enhance the Barrier Properties of Polymers

A tremendous progress related to the barrier properties of polymers have been made in the past few decades with the production of highly efficient barrier polymers. Further research in this field involves wide variety of different methodologies to improve polymeric barrier properties, but a large number of these methods possesses drawbacks/disadvantages such as low mechanical strength, high cost of preparation, sensitivity to atmospheric conditions such as humidity, temperature etc. (Lange and Wyser 2003). The key two factors namely diffusion rate and

solubility of the small molecules determine their permeation through the polymer films (Nir, Narkis et al. 1998). Diffusion depends on the chains segmental motion and consequently fast redistribution of the polymer free volume at the molecular level.. For instance, Ward *et al.*(Ward, Gaines Jr et al. 1991) improved the gas barrier properties using vermiculite and mica in the polymer film and the results exhibited pronounced reduction in the permeability as shown in Figure 2.2.

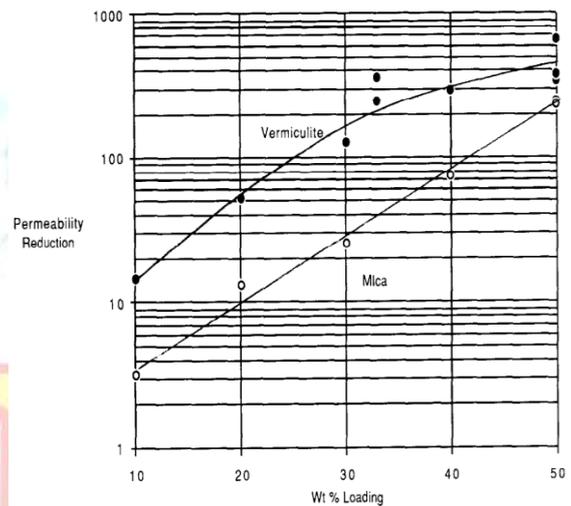


Figure 2.2: Permeability reduction as a function of filler loading (wt%) (Ward, Gaines Jr et al. 1991).

• Nanofillers to Enhance the Barrier Properties of Polymers

Although, the permeability of the polymers improved due to these *micron size* fillers, however, the key characteristics such as flexural and impact strength had to be compromised (Liang and Yang 2007). To address the aforementioned issues, PNCs have been the subject to the extensive research since past three decades. PNCs are a radical replacement of the conventional filled polymers or polymer blends (Galpaya, Wang et al. 2012). Contrary to the conventional composites, the PNCs contain the filler with dimensions less than 100 nm. Since their inception for the first time by the Toyota Group, tremendous efforts have been made to research this field. The importance of PNC technology is not limited to the mechanical enhancement of the pristine polymer or the replacement of the inefficient fillers. Figure 2.3 illustrates the hierarchy of nanoparticles based on their tendency towards improvement and thus, the potential to increase the functionality of the polymer matrix.

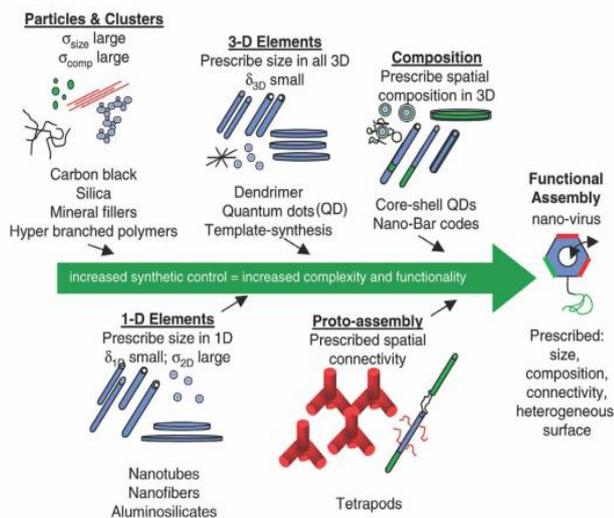


Figure 2.3: Categorization of nanoparticles based on how much they can improve the barrier properties of the polymers (Figure extracted from Ref.(Vaia and Wagner 2004))

- **Properties and Surface Chemistry of Nanomaterials**

The most critical factor in the nanomaterials and PNCs is to acquire the desired properties that should be superior to the bulk and the pristine materials. It should be noted that the properties of nanomaterials or PNCs whether it be physical, chemical, or biological properties are largely different in contrast to the bulk materials. While many especial features are possible to achieve in the desired fields such as electrical, optical, thermal, magnetic, *etc.*

The characteristic difference between nanomaterials and the bulk materials is that the former has much smaller size, large surface area, high aspect ratio and more importantly the number of atoms on the surface of nanomaterials is much higher in contrast to those present in its interior part (Karak 2019). The high surface area, surface energy and large number of surface atoms make nanomaterials highly reactive.. In order to understand this, the parameters which affects the properties of nanomaterials is presented in Figure 2.4 .

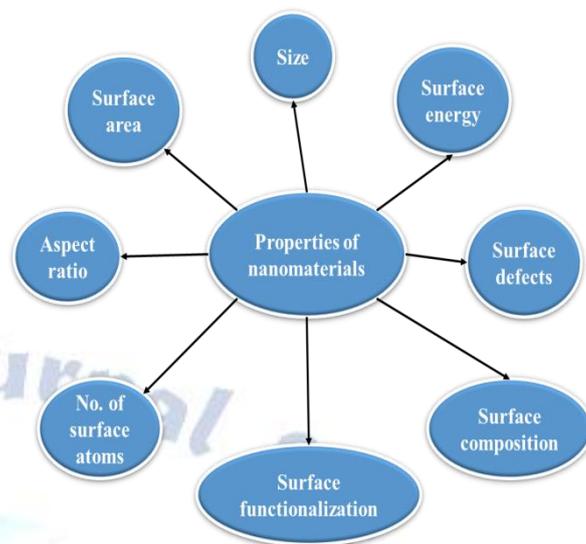


Figure 2.4: Key parameters that influence the characteristics of nanomaterials.

- **Key Aspects in Polymer Nanocomposites for Barrier Properties**

For the designing and fabrication of efficient barrier PNCs, the key points that should be considered are the aspect ratio and the percolation threshold of the nanofiller inside the polymer matrix (Terrones, Martín et al. 2011). For example, it has been reported in literatures that by incorporating nano-platelets with large aspect ratio, permeability gets dramatically reduced (Choudalakis and Gotsis 2009). The nano-platelets decrease permeability by inducing a more tortuous path in or around polymer and around nano-platelets thereby increasing the diffusion path (Damari, Cullari et al. 2018). Generally, the gas barrier performance is largely dependent on three key factors (Möller, Kunz et al. 2012); **(i)** first is the characteristics of the filler (*e.g.* aspect ratio, ability to prevent diffusion of gas and the volume fraction), **(ii)** second is the dispersion quality (*i.e.* uniform dispersion or aggregation/specific interface, free volume generated by mediocre interface management, and the texture/orientation of filler platelets) and the **(iii)** third is the intrinsic barrier properties of the polymer matrix (Cui, Kundalwal et al. 2016).

. Further to this, phenyl isocyanate functionalized crumpled graphene oxide (GO) when added to the polystyrene (PS) matrix showed interfacial interactions between π bonded electrons of the rings of phenyl isocyanate and polystyrene, thereby resulting in very low permeability of oxygen at just 0.02% loading,

while similar permeability was obtained with 1 to 1.5% loading of nanoclays (Compton, Kim et al. 2010). Defects also play key role in barrier properties, and perforated graphene layer as a result of different manufacturing process may show different barrier properties in contrast to the non-defective graphene

- **Recycled Polymers**

As per the report released by Ellen MacArthur Foundation, plastic production in 2014 was 311 million tons which is expected to be doubled in 20 years and quadruple by 2050 (López de Dicastillo, Velásquez et al. 2020). A large quantity of waste polymers is produced every year from industrial, household, and agricultural activities which is accumulated to account for over 12% of the municipal solid waste, a substantial growth since 1960, when plastic counted for only 1% of the waste stream (Zare 2013). Most of these plastics are synthetic materials stem from petroleum or natural gas and owing to their high degradation temperature as well as resistant to UV radiation, they are largely not biodegradable and can sustain on sea and land for years, which ultimately cause pollution (Gürü, Çubuk et al. 2014).



Figure : Schematic illustration of nano reinforcing process of plastics towards a circular economy (López de Dicastillo, Velásquez et al. 2020).

To circumvent these issues, the industry considers blending recycled polymers along with the pristine polymers and/or additives to function as chain extenders, compatibilizers, and stabilizers (Nofar and Oğuz 2019). In this context, nanotechnology has been employed to mitigate the negative effect of recycling on the physical and mechanical characteristics of the

polymers via development of polymer-nanocomposites by incorporating reinforcements at nanoscale size into polymeric matrices.

- **Recycling of Nylon and PET and its effect on properties of polymers**

Polymer recycling, specifically Nylon (PA6 and PA66) and to large extent the PET also, can be broadly classified into four methods. Firstly, primary recycling or depolymerization does repolymerization of original monomers which are obtained from breaking down the long polymer chains. This method retains the quality equivalent to that of the "virgin" polymer (Mihut, Captain et al. 2001). The depolymerization can be carried out using hydrolysis, alcoholysis also referred as methanolysis), glycolysis, aminolysis and solvolysis, or special chemicals (Kamimura and Yamamoto 2007). Secondly recycling recovers the individual components of a polymeric matrix without breaking into the monomers which is usually carried out using a variety of extraction and separation methods (Lu and Hamouda 2014).

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