A COMPREHENSIVE REVIEW ON THERMAL PROPERTIES OF POLYMER; A MODERN APPROACH

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ABSTRACT

In terms of commercial and industrial applications, polymers exhibit a wide array of functional characteristics due to their chemical stability, thin weight, and low cost. The main technological obstacle is the low thermal conductivity of polymers, despite excellent applications such as electronic packaging and heat transfer. Researchers have been working on improving polymer thermal properties since two decades. Aiming firstly to summarize the molecular level understanding of the polymer heat transfer mechanism and secondly, to highlight the rationale behind the recent efforts to improve the material's thermal properties, this research review article looks at aspects of different inter-chain coupling processes, the length of chains, and the morphological properties of polymers. This review summarizes the main challenges, key advances, and thermal properties of polymer composites.

Keywords: thermal properties, polymer, polymer inter-chain, morphological properties, interfacial properties, heat transfer.

1. INTRODUCTION

In the study of thermal properties of the composite polymer having higher value of their commercial level in daily life in both electronic products with their different structural materials due to their low cost, high functionality, lightweight, and their outstanding chemical stability. The main technological obstacle in certain fields of daily life such as electronic products and heat transfer can limit the thermal properties of composites polymer [1-2]. The higher value of thermal

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conduction properties of polymer with heat exchanger properties are designed having features of compact structure, corrosion resistance, easy processing, and the lightweight and low-cost polymer can be manufactured. In turn, many applications can be found in the energy industries, water, and electronics [3-4]. For two decades, the researcher is trying to improve the thermal properties of polymer composite. This basic concept of the heat transfer process can be studied on a smaller length scale of both nano and micro level scale for improving the thermal conduction of polymer. In the present review, our goals are a) By linking the morphology of polymer chains with the coupling between chains, systematically summarizing the understanding of the physical mechanisms that control polymer heat transfer; b) Emphasis on the rationale for efforts to increase the thermal properties of polymers. The polymer structure consisted of both crystalline domains and amorphous domains that were randomly entangled. It is crystal clear that thermal conductivity is solely dependent on its morphology. As a result, low thermal conduction is caused, if amorphous domains were dominant then its vibrational modes lean towards localization in the polymer. Although, polymer chain alignment is the main improving agent for the enhancement of the thermal properties of the polymer. By using nanoscale templates, electrospinning, and mechanical stretching for the aligning of polymer chains to enhance thermal properties. Polythiophene nanofiber's thermal properties having 50nm fiber diameter could be prepared by templating electro polymerization that has been increased by more than 20 times [5]. In this experimental work, with the help of molecular dynamics simulations can understand the effect of nanoscale structures on their thermal conduction. The backbone and side chain is the deciding factors for the improvement of the thermal conduction of polymer. The carbon and graphene foams having three-dimensional fillers have attracted widespread attention. The basic heat transfer mechanism and recent synthesis work of two nanocomposites are reviewed.

1.1 PRISTINE POLYMERS AND THEIR THERMAL PROPERTY

Morphology of polymer plays a significant role in controlling heat transfer. Chain alignment contributes a major role in improving the thermal properties of polymers that are also proven experimentally. Additionally, chain morphology is also significantly playing a key role in the determination of polymer thermal conduction. The method of operating heat transfer by designing a chain structure including the main chain and a side chain is discussed earlier. The method can be enhanced through the introduction of strong hydrogen bonding interaction forming inter-chain coupling and are cross linked through the covalent bond that results in tuning the polymer thermal conductivity.

1.2 CHAIN ORIENTATIONS ALIGNMENT

Both amorphous domains and crystalline domains are playing a deciding role in the thermal properties of the polymer. The crystalline domains are aligned chains while amorphous domains are entangled chains randomly twisted. The amorphous domain suppresses the thermal conductivity due to the lack of periodicity that makes the vibrational modes localized. Therefore, chain alignment is directly proportional to thermal conduction. As one increases the other will directly increase. Thermal conductivity is measured in a crystalline nanofiber of polyethylene (PE) that is 104-105 $W \cdot m^{-1} \cdot K^{-1}$ [5]. The degree of chain alignment is experimentally been proven that they are contributing factor to thermal conduction enhancement [6]. Experimentally, the example of polymer poly(vinylidene fluoride-trifluoro ethylene) [P(VDF-TrFE)] film is annealed above its melting temperature of about 421K, the thermal conductivity increases about 300-400% the reason is that of chain alignment [7]. Its substrates can also have played a significant role in the synthesis of chain alignment during the melting and recrystallization process. Chain-alignment enhancement can be discussed below experimentally.

1.3 Mechanical stretching

By increasing the chain orientation sequences, the polymer thermal conduction is automatically increased with mechanical stretching. The first experimental demonstrations were carried out by Choy et al. they found that polyethylene (UHMW-PE) having ultra-high molecular weight, might exceed 40-42 $Wm^{-1}K^{-1}$ when the stretch proportion exceeds 300 [8]. Shen et al. used a bi-stage heating methodology, by obtaining a higher draw ratio (400) and obtained nanofibers of PE with a diameter of 50-500 nm were produced, which gives 104 $Wm^{-1}K^{-1}$ thermal conductivity. The author said that by increasing the fiber crystallinity, the result is the enhancement of thermal

conduction. The thermal properties of polymer could be improved by mechanical stretching through chain orientation which is confirmed in some experimental work [9]. Sometimes, higher crystallinity does not increase due to the polymer chain alignment. The reason is that chain alignment and thermal properties are solely dependent on each other. An example that supports this understanding is shown that the thermal conductivity of thermally drawn UHMW-PE ultrafine fibres is close to 50 $Wm^{-1}K^{-1}$, and its crystallinity decreases from 91% to 82% during the stretching process [10]. Liu and Yang [11] showed that the stretching of polymer can affect the conductance of PE, which means that the conductance increases.

1.4 TEMPLATING ON NANOSCALE

Nanoscale templating is an important method for the study to arrange chains polymer. The polymer is first heated till melting is achieved and then infiltrates the spongy anodic alumina. NaOH can be used for the removal of this porous anodic alumina, leaving behind the polymer nanofiber array. The polymer chain is enhanced by melting the polymer in a nonporous template which results directly in the efficiency of their thermal properties. The length of polythiophene fibres could be modified by passing the charges over the electrochemical cell. The pores' templating diameter is to be controlled. Polythiophene nanofiber's thermal conductivity is enhanced and resultantly improved by $4.5Wm^{-1}K^{-1}$ which is about 20 times more than that of the bulk polymer due to the chain alignment. Since the possibility of chain entanglement is reduced, the thermal properties can be enhanced by reducing the fibre diameter using a nano-level template method [12].

1.5 ELECTROSPINNING

Electrospinning is an important method for production by using electrostatic forces that pull charged filaments of the polymer solution. The polymer is firstly liquefied and then dissolved completely in the solution and std it. A syringe with a sharp and pointed tip is usually needed to dispense polymer filaments. The electrostatic force of attraction is developed between the collector plate and the tip, the polymer solution is sucked into fibres with nanometre diameter [13]. Electrospolymer'smers chain morphology is affected by two experimental parameters. The first parameter is the electric field strength electric field strengthening is favourable for the enhancement of the chain alignment during the electrospinning procedure, thereby improving the PE electro spun thermal property [14]. Jet speed is another parameter that affects the chain alignment of polymer composite. Because the evaporation speed outside the jet is faster in

electrospinning, the core-shell morphology can be formed in the electrospinning fibres [15], which helps to improve the thermal conductivity.

2. POLYMER CHAINS ATOMIC STRUCTURE

Polymer structure plays a significant role in the thermal conductivity of composite material. Chain entanglement can be affected by both angular bending and bond stretching strength respectively. Similarly, the rotation of the chain segments can be greatly affected by dihedral bending strength. Moreover, thermal properties are also significantly affected by the rotation of chain segments and entanglement of the chain as well. Furthermore, backbone and side chain branching from the main chain also play a role as well.

2.1 BACKBONE

The example of PE takes as a reference to elucidate that the chain conformation energy and its backbone structure are subsidized by different vibration modes. There are various intermolecular forces of attraction such as van der Waals forces that are playing a significant role in the thermal properties of the polymer. There is can be classified as hydrogen bonding and Coulomb interaction. They are solely dependent on covalent bond conformational energy and non-bonding energy. As we know that covalent forces are larger than non-bonding forces, so it is not so important that the covalent bond in disturbing the thermal properties of the uninterrupted single chain, now our discussion is focused on the conformational energy related to the covalent bond. Based on vibrational modes, the covalent bond is decomposed into three fragments. First is due to the stretching of the bond i.e., the two-body stretching energy $Ebond$ of the connecting two atoms. There are many bodies interaction that are contributing to the conformation energy in a two-body bond stretching. Generally, higher bond stretch and angular bending stiffness will result in developed thermal conduction. We took the example of PE as a reference, there is a strong bond forces in PE polymer, and having a higher value of both bending and stretching that makes them hard and stiff are make them good thermal conduction [16]. Generally, the presence of sp^2 hybridized double-C=C-bond leads to a greater value of thermal conduction. There are the basic reasons:

- The bond energy of sp^2 -C=C-bond is 2.7-2.9 times greater than that of sp^3 hybridized –C-C- bond;

- Secondly sp^2 electron is delocalized above and below the plane and as a resulting stiffness is increased by segmented rotation. This show that polyacetylene π-conjugated thermal conductance is greater than that of PE [17].

2.2 POLYMER COMPOSITE SIDE-CHAINS

Side chains are branching out from the main polymer chain that determines the whole topological structure of the polymer. The vibration dynamics and thermal properties will change by changing the side chains [18]. Side-chains have a direct link with thermal properties. They are inversely proportional to each other. When the number of side chains increases their thermal properties will automatically decrease. Similarly, when two neighboring side chain distance is decreased from 75 to 50 segments then their thermal conductivity automatically decreases. As soon as the density of side chains increases, the decreasing trend of thermal properties will be seen. A large number of side chains may result in a lower value of thermal conductivity for side chain alignment.

3. COUPLING OF INTER-CHAIN

The coupling of the Inter-chain plays a significant role in thermal conduction. When these inter-chain couplings are weak then it has a bottleneck for polymer thermal conduction. Increasing the coupling strength between chains may result in a greater value of the thermal properties of the polymer. The thermal conduction of the poly (vinyl sulfonate calcium salt) may be high i.e. $0.67 Wm^{-1}K^{-1}$. Because the polymer chain has strong electrostatic force among them. In addition to the coupling between ionic chains, hydrogen bonding (H-bond) is another comparatively strong coupling between chains, that is a hundred times stronger than that of the Vander Waals forces. Hence, a large number of hydrogen bonds can significantly increase the value of the thermal conduction of polymer. Moreover, cross-linking in the formation of chemical bonds is also a contributing factor to the enhancement of thermal conductivity [19].

3.1 HYDROGEN BONDING AND THERMAL PROPERTIES

A hydrogen bond is a kind of electrostatic force of attraction of a hydrated proton with highly electronegative atoms such as O, N, and F atoms. Hydrogen bonding is responsible for the enhancement of thermal conductivity. Hydrogen bonds enhance inter-chain coupling leading to the formation of continuous thermal networks and providing different pathways for heat transfer. Therefore, the synthesis of high thermal conductivity polymers usually requires a high density of

H bonds [20]. The density of the hydrogen bond is enhanced through polymer blending. In this case, one polymer can provide the donating group and the other will provide the accepting group respectively. Biopolymers with widespread H-bond molecular groups having a functional group such as amide, aldehyde, amino group, and hydroxyl group are responsible for the intermolecular force of attraction [21]. Thus, hydrogen bonding is responsible for the high thermal properties of the polymer.

3.2 CROSSLINK

Cross linkage of any polymer molecule has a direct relation with thermal conductivity like hydrogen bond. More cross linkage will be thermal conductivity of polymer molecule and less cross linkage leads to the low thermal conductivity of polymer molecule. In crosslinking, the polymers are strongly bonded through a covalent bond and are highly effective for the conduction of heat. Naturally, increasing the networking of the polymer will automatically increase the thermal properties of the polymer. PE polymer thermal properties were experimentally determined by Tonpheng et al. [22] that at higher crosslinking density has been increased by 50% its thermal conduction. Similarly, Kikugawa et al. reported that cross-linking density is directly proportional to thermal conductivity. It can be intuitively considered that the thermal property enhancement is mainly due to strong covalent bonds. Although, Rashidi et al. [23] explain that only considering covalent bonds cannot fully explain the increased thermal conductivity of cross-linking. For all crosslink number densities, covalent bonds only account for 20% of the total thermal conductivity. More interestingly, not only do non-bonding interactions account for most of the total conductance but their contribution to the increasing number of cross-linking densities can cause the enhancement of thermal properties. Therefore, when there are more cross-links in the polymer, the non-bonded coupling (vdw, H bond, or Coulomb) becomes stronger, which in turn increases the thermal conductivity significantly.

CONCLUSION

In the above review, we focus on factors influencing polymers' thermal properties. They are concisely summarized. Increased crystallinity or alignment enhances thermal conductivity. To further improve thermal properties, it is important to choose the right polymer with an appropriate

chain structure. Both bending and stretching of the bond have higher values of thermal properties when they have greater strength, whilst smaller dihedral strength results in smaller thermal property values. The thermal properties of the pristine polymer's molecule can also be enhanced by inter-chain coupling (H bonds and covalent cross-linking). Additionally, nanofillers have high thermal properties, so even at low concentrations the thermal conductivity increases. However, surface functionalization that reduces filler aggregation may also enhance thermal resistance at the interface.

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