Future Scope of Silicone Polymer based Functionalized Nanocomposites for Device Packaging: A Mini Review

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Abstract

Organic electronic devices, such as conducting polymer [1,2] based or perovskite [3,4] based solar cells are flexible, lightweight, and more economical than traditional silicon devices, but cannot be commercialized/marketed due to device failure caused by atmospheric moisture/oxygen [5] and hence protection of those devices are very critical. Silicone polymer based composite encapsulants are attractive to this purpose because of its easy processability, wide range of curing temperatures (room temperature to moderately higher temperature), low shrinkage, high thermal stability, low volatility etc. All these properties of silicones partly coincide with the requirements of an ideal device encapsulant. Even though, silicone polymers are moisture resistant, but the oxygen barrier properties of silicones are not desirable to fulfill organic device requirement. If the barrier properties of silicone polymers are further improved, then it may find an important application towards encapsulation of those devices.

Silicone polymers are an important class of polymer that are used in numerous applications such as drug-delivery vehicle, biomedical implants, lubricants, cosmetics industries and lot more [6-8]. These polymers are flexible, attributed to the Si-O-Si linkages at the backbone of the polymer chain. This Si-O-Si can flip easily from one configuration to another due to long bond lengths (163 pm) and high bond strengths (~452 KJ mol⁻¹) and low activation energy of Si-O-Si bond rotation, are responsible for its flexibility. The excellent thermal stability also arises out of the siloxane linkages in the structure. Due to the overlap of O '2p' electrons in the vacant Si '3d' orbitals, a 'n' bond character arises, in addition to the strong Si-O 'o' bond. This increased bond multiplicity of the Si-O-Si linkages makes the polymer thermally stable.

These polymers can be easily modified by chemical reactions and the physical properties can be tailored/ altered. Hydrolysislation reaction is one of the important reactions that are used to modify/conjugate other chemical functionality with silicone polymers at the Si-H sites of the "polydimethylsiloxane (PDMS)" backbone. Due to chemical inertness, these are used in several biological applications [9] such as, drug delivery [10] etc. The mechanical properties of silicones are poor, but reinforcement with nanoparticles can improve the mechanical properties to a desired extent. Various nano fillers have been introduced in the composites such as clays, carbon nanotubes, oxide nanoparticles etc. in order to modify/enhance the properties of pristine silicones. Nanofiber reinforced PDMS by using femtosecond laser irradiation have also been carried out [11]. Flexibility and transparency of silicones are also exploited in electronic device packaging. The processability of these polymers are also simple, coupled with the above mentioned physic-chemical properties, leads the polymer for the applications in various fields of material science and technology.

Various oligosiloxane based hybrid materials has also been synthesized for the encapsulation of organic devices [12-14]. Reactive and functionalized nanoparticles are supposed to provide a tortuous pathway towards an incoming gas molecule and hence will reduce the permeability to a greater extent (Scheme 1). Recently, it has been shown covalently attached silicones with functionalized nanoparticles like alumina/silica to fabricate composite films fabricated by an in-situ technique, can be used for organic device encapsulation [15-18]. In this context, it is also important to mention that conductive carbon based material such as graphene, carbon nanotubes [19], are also promising for the improvement in the barrier properties [20,21] of polymers.

Keywords: Curing; Organic devices; Nanocomposite; Functionalization; Silicone polymer

Introduction

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This mini-review encompasses (1) various in-situ strategies to fabricate polymer/nanocomposites with silicones towards organic electronics encapsulation, (2) a brief comparison between ‘in-situ’ method with solution casting and melt-processing technique, and, (3) some future directions toward the synthesis of new barrier composites with silicone polymers.

**In-situ Curing Technique for the Fabrication of Polymer Nanocomposites**

In this section, various methods/techniques have been discussed for the fabrication silicon polymer based nanocomposites. Functionalized silica/alumina has been used as a filler material for silicone polymers. The functionalizations were carried out to make the surface more compatible with the polymer matrix and the reactive surface functional groups were supposed to participate in the curing reaction with the specific functional groups in polymer matrix to enhance the interfacial interaction. The intended inorganic phase was also supposed to reduce the gas permeability through providing a tortuous pathway.

**Functionalized mesoporous silica as filler materials for silicone polymers**

Mesoporous silica nanoparticle (MSN) is an important class of mesoporous material that is used in various applications such as in targeted drug delivery as a ‘drug loaded vehicle’ because of its biocompatibility [22,23], filler material in polymer nanocomposites, active catalyst support, adsorbent, separation and bio-sensing [24] applications etc. Large surface area and pores of these particles has been exploited for various applications. In addition, the surface functionality of these particles can be tuned through functionalization by silane coupling chemistry (Scheme 2). Silanes can be represented as (R’O)SiR in general, where R’O- is either EtO- or, MeO- which undergo condensation with the surface Si-OH groups of mesoporous silica surface. This provides different functional groups at the surface. Basically it generates ‘Si(surface-core)OSiR’, where R is the organic functionality and ‘Si(surface-core)Osi’ bond generate after the silane coupling at the surface. This provides a platform to conjugate various bio-molecules or polymers. The functionalization makes the surface either polar or non-polar depending on the organic functional groups present.

MSN’s with higher pore diameters also serves as a critical filler material for the reinforcement of polymer matrix. Large pore sized mesostructured silica (MSU-I, pore size 5.3) was observed to improve tensile properties like tensile modulus, toughness etc. of rubbery-epoxy polymer [25]. A significant improvement has been observed in the composites as compared to the neat epoxy polymer system. The reinforcement effect in this case was comparable to that of exfoliated organo nanoclay. The improvement can be explained by the segmental confinement of the polymer chains in the mesopores at the inter-phase region of the silica particles [26,27]. This segmental confinement of the polymer chains imparts a profound impact on the properties of the polymer composite materials. Hence the organic inorganic interface is very critical for these composites. The chemical bonding between the polymer and the silica particles also plays a vital role in the enhancement of the thermal [28] and mechanical properties as through these covalent chemical bonding the load transfer to the inorganic filler is possible. Recently it has been reported that mesoporous silica can enhance the thermal stability of polymethylmethacrylate (PMMA), may be due to the radical scavenging activity of silica.

**Allyl functionalized silica with internal hydride containing siloxane: Hydrosilylation strategy**

In this study, the composites were fabricated by platinum catalyzed hydrosilylation reaction. Internal hydride containing silicone polymer has been covalently grafted over allyl decorated mesoporous silica (MSU-H, 2D hexagonal with a pore diameter of ~7 nm) by hydrosilylation reaction [18]. Mesoporous silica was functionalized by allyltrimethoxysilane, which provides allyl fragments at the particle surface. This organic modification also makes the surface hydrophobic. The grafting was carried out in dry toluene reflux condition to avoid the self-condensation of the silane and this functionalization was determined from FTIR and solid state NMR spectroscopy (13C and 2H). Two different wt% (0.6 and 1.5) of these functionalized mesoporous silica have used to fabricate the composites. The curing temperature of this system was estimated from differential scanning calorimetry (DSC), which showed a broad exothermic peak around 135°C. For a curing mixture it is very important to understand the curing behavior as the mixture needs thermal treatment for the application purpose. In addition to DSC studies, rheological experiments were also carried out to understand the curing behavior of the mixture, which showed a self-coupling reaction of ‘Si-H’ between the same polymer chains at the beginning, followed by the true curing (cross-coupling) i.e. hydrosilylation reaction between the allyl groups of the functionalized nanoparticles surface and the Si-H of the polymer. Energy of activation (Ea) was calculated from DSC by heating at various heating rates by Kissinger method and was found to be 15.9 kJ mol-1. Contact angle measurement of the composite an increase in contact angle with the increase in allyl functionalized silica content (98.7° for lower loadings and 102.5° for the higher loadings). This indicated an increased hydrophobicity, which is important for an encapsulant material. Even though the oxygen barrier properties of the silicone polymers are not good, but the impregnated silica particles were supposed to reduce the oxygen barrier property through tortuous pathway. Swelling study of the composites was carried out in dry toluene medium, which is a good solvent for silicones. This study showed that the composite with higher silica loadings is having weight

![Scheme 1: Reduction in gas permeability due to tortuous pathway, created by the inorganic phase](image)
Functionalized alumina as filler materials for silicone polymers

Various functionalized (amine and allyl functionalized) alumina particles have been used as a filler material for silicone polymers. The surface functionalization of alumina was carried out by silane coupling chemistry where, ‘Al_{surface-core}O’ bond formation takes place at the surface, instead of ‘Si_{surface-core}O’ (as discussed in the section Functionalized mesoporous silica as filler materials for silicone polymers). The composite fabrication with these functionalized nanoparticles with the silicone polymers are discussed below.

(A) Amine functionalized alumina with epoxy-terminated siloxane: ‘Amine–Epoxy’ curing strategy: Amine functionalized alumina nanoparticles has been used as a filler in the polymer [poly(dimethylsiloxane) diglycidyl ether terminated] matrix [15] to fabricate composites. Hydride terminated polydimethylsiloxane (PDMS) is used as a precursor for the synthesis of [poly (dimethylsiloxane) diglycidyl ether terminated]. Surface functionalization of the nanoparticles were thoroughly studied through various techniques like, FTIR (Fourier transformed infrared), XPS (X-ray photo electron spectroscopy), TGA (thermogravimetric analysis), Brunauer–Emmett–Teller (BET) isotherm and CHN analysis. Various other functionalities can be also attached onto the hydride terminals of PDMS to get desired properties or for further conjugation with specific surfaces/polymers.

swelling ratio (Q_t) lower than the composite with lower filler loadings. This is due to the increased cross-linking density with the increase in the allyl terminated silica loadings of the composite that prevented the permeation of toluene molecules through the composite matrix. Density of the composites also increases with the increase in the silica loadings as observed from density gradient column. This supports that there is a better integrity and cross linking density with increased filler loadings. Nanoindentation and dynamic mechanical analysis (DMA) of the composites indicated an increase in the modulus values with the increase in mesoporous silica loadings. An increase in the coefficient of thermal expansion was also observed as the filler loading was increased. The composites were observed to be thermally stable up to ~300°C, which is an important property for the composites as it has to protect active and sophisticated device components from harsh environmental conditions. All the properties of the composites indicated that it can be used as a potential encapsulant for organic devices. The curing mixture (liquid polymer dispersed with allyl functionalized silica particles and platinum catalyst) can be easily spin coated or drop casted over the devices and finally cured by thermal treatment to get the in-situ encapsulated device. As compared to the complex, high-cost and laborious multilayered type construction/architecture for encapsulation [29], the ‘in-situ’ curing technique of encapsulation will be cost effective, easy and a faster method.
It has been shown that surface amine groups can react with the epoxy terminals of the polymer and forms the flexible composite. Differential scanning calorimetry analysis indicated the curing reaction between amine at the surface and epoxy at the polymer end group, apart from curing of the polymer with the additional curing agent present in the system. This covalent modification is to provide enhanced reinforcement of the nanoparticles with the polymer matrix. The dispersed alumina is expected to provide a torturous pathway for the incoming gas molecules and hence reduces the permeability of incoming gas molecules like moisture vapor/oxygen and hence to form a gas barrier encapsulant, which are critical for organic devices. Atomic force microscopy showed an increased in roughness with the increase in the particle loadings in the matrix. The thermal stability of those composites are found to be high (–305°C) till the optimum loadings of alumina. The optimum loading plays a key role for fabricating a composite as after that important property deteriorates.

(B) Allyl functionalized alumina with hydride terminated siloxane: Hydrosilylation strategy: In this study, silicone polymer/functionalized alumina nanocomposites have been also prepared by chemical attachment of the silicone polymer (hydride terminated polydimethylsiloxane) with allyl functionalized alumina through hydrosilylation reaction catalyzed by Karstedt platinum catalyst, where the impregnated nanoparticles in the matrix can reduce the permeability of gases [16]. The alumina surface terminated with allyl groups that make the nanoparticles non-polar and hence compatible in the polymer matrix and cross-links with Si-H of the silicone polymer chains by platinum catalyzed hydrosilylation reaction. It is important to understand the nature of curing, as these materials will be treated thermally for application purpose. The curing behavior of the system was analyzed in details, from non-isothermal rheology and DSC analysis [17]. The mechanistic model for the system was also proposed, based on the two studies. It was observed that an initial self-coupling of the polymer chains occurs first, followed by hydrosilylation reaction occurs in the curing system. Since the oxygen barrier, properties of silicones are not good so the dispersed nano-phase can reduce the permeability of such gases through a torturous pathway. Nano-indentation of the composites indicated the flexible nature of the films. The composites were good electrical insulators and thermally stable up to ~400°C. The FTIR of the composites showed that all the Si-H groups have been reacted. In order to achieve the best performance of the composite material it is important to introduce optimum concentration of fillers in the matrix. The fractured surfaces of the composites reflected the presence of interfacial bindings within the matrix. With the increase in the filler loadings an increase in the contact angle was observed, indicating the increase in hydrophobicity of the matrix. The composites were also stable at two extreme pH values, reflects that the matrix is effectively protecting the alumina nanoparticles from dissolution. This indicates a robust and cross-linked composite matrix.

It is important to note, in this study since hydride terminated silicone polymer have been used for composite fabrication, so the cross-linking density will be much less than the composites (discussed in the section Functionalized mesoporous silica as filler materials for silicone polymers), where internal hydride terminated silicone polymer was used. The improved cross-linking density helps in the improved interfacial interactions within the composites. The increase in cross-linking density is important to reduce the gas permeability further. For all these cases, the liquid polymer dispersed with nanoparticles can be easily spin coated or drop casted over the devices and cured to get an in-situ encapsulated device (Scheme 3).

Advantages of in-situ curing over solution casting and melt processing

In this section, a solution casted film fabrication method have been shown, where amine functionalized mesoporous silica particles were used as a filler material and the composite properties are also discussed briefly. Finally the advantages of in-situ curing technique over solution casting and melt-processing for device encapsulation application are compared.

Hybrid organic-inorganic composite films can be fabricated by solution casting [30-32] methodology (Scheme 4B). A solution casted composite film of polyvinyl butyral (PVB) as a base polymer matrix and amine functionalized mesoporous silica as a filler material has been synthesized, where ethanol was used as a solvent [31]. A polyol was also used for the composite fabrication to increase the polar content in the polymer matrix. In this study, mesoporous silica was used as a filler material, which was supposed to reduce the permeability by providing an extended pathway. The surface of the mesoporous silica particles were functionalized withaminopropyldimethoxyxsilane (APTMS), which generates –NH₂ groups at the surface (Scheme 2D). This makes the surface hydrophilic and helps in better mixing in the PVB polymer matrix. The functionality reduces (~84% reduction was observed) the surface area as compared to the pristine silica, as observed from the BET analysis. Previously it has been shown that amino-propyl functionalized mesostructured silica acts as better reinforcing agent for epoxy polymer [33]. Nanoscale mesoporous silica (NMS)/polyimide nanocomposites have been synthesized [34], in which silica was functionalized withaminopropyldimethoxyxilane. A homogeneous dispersion of nanostructured mesoporous silica was observed in the composites. Due to which substantial improvement in the thermostability and moisture absorption properties were observed for the composites, as compared to neat polyimide. Homogeneous dispersion is an important criteria for the improvement of the properties of composites. Incorporation of –Si(CH₃)₃ modified MCM-48 particles (hydrophobic and compatible to the polymer matrix) in the Polyvinylacetate (PVAc) was also observed to improve mechanical properties resulting composites [35].

In this case the polar –NH₂ groups can also help in forming hydrogen bonding with incoming moisture molecules, to trap the moisture. Hence it was anticipated that the synergistic effect of tortuosity and the trapping effect can reduce the permeation rate to a greater extent. Three different wt% of functionalized mesoporous silica (0.25 wt %, 0.5 wt %
and 1.5 wt %) were intended in the composite matrix. The moisture permeability was determined from the calcium degradation test. This indicated a huge reduction in the moisture permeability with the increase in the increase in silica loadings in the matrix. The permeability value was reduced by an order in case of the composites as compared to the neat polymer matrix. But this reduction was significant till an optimum loading. This amine functionalized silica can also form hydrogen bonding with the polar groups (alcohol and acetate) of PVB, which helps to enhance the interfacial interactions (this was observed for the composites from the fractured surface SEM images which showed higher crack density as compared to the neat polymer matrix). The mechanical property (as obtained from tensile and DMA analysis) and thermal properties (as observed from TGA analysis) showed deterioration. Hence the critical loading or the percolation threshold plays a vital role in fabricating a composite. After the critical loading, aggregation of silica nanoparticles predominates as observed from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) which is responsible for the degradation in the important properties. The composites were used to encapsulate Schottky diodes by sealing with additional glue and tested under accelerated aging conditions. It was observed that the diodes encapsulated with the pristine PVB polymer matrix exhibited almost two times reduction in the current density, as compared to the devices encapsulated with the composite films. This reflects the mesoporous silica loaded composites can be used a gas barrier layer for organic devices.

However, solution casting method suffers from several drawbacks. In-situ curing is a single step process, while solution casting or melt processing needs multiple steps. In solution casting, step 1 is the evaporation of solvent to get films and step 2 is the use of a glue to encapsulate the device with the as obtained film (Scheme 5). Unfortunately, solution casting can generate pinholes during the evaporation of the solvents. While in-situ curing method does not use any solvent and hence, less chance of pinhole generation. Melt processed films [36] also requires an additional glue to seal the device.

Hence, there are several advantages that can take silicone polymers to the forefront towards the advancements of various technologies.

**Future Directions towards New Gas Barrier Composites Preparation**

Furthermore, the incorporation of oxygen/moisture scavengers in the composites can further reduce the permeability of such composites. It is important to note that silicones are very good moisture resistant, but oxygen barrier properties are not desirable. Hence, in addition to the mixing of nanoparticles, a moisture/oxygen reactive component will reduce to a much greater extent and will be much fruitful for the encapsulation of organic devices.

Several other strategies can be also developed to form the composites such as, ‘azide-ene click- chemistry’ and ‘thiol-ene click chemistry’. In which the inorganic surface should have reactive azide, alkyne or thiol groups [illustrated in Scheme 2(A) and (C)], while the silicone should have the counter-functional group to couple through click-reaction. Functionalized mesoporous silica is a critical choice as a filler material towards the design and fabrication of composites for various important future applications. Apart from the other potential
applications of this important porous material, a suitable and optimized mesoporous silica loaded composite with high gas barrier properties can play a major role in device packaging, in the near future. Until now, the films have been made by using silicas as a base polymer matrix, which are easy to cure. One of the important features regarding ‘in-situ curing’ method is, it involves no solvent. These composites will further find applications in other potential areas where moisture and oxygen permeation is disadvantageous such as, food/beverage packaging.

Conclusions

Siloxanes are smart material for the purpose of encapsulation because of its easy processability, wide range of curing temperatures, low shrinkage, high thermal stability, low volatility etc. Furthermore, the properties for an encapsulant material such as, (1) hermetic and conformal coating, (2) good chemical, electrical, environmental and thermal stability, (3) compatibility with mass production techniques, and (4) minimum shrinkage of the encapsulant upon curing, coincide with the critical properties of a suitable organic device encapsulant. Unfortunately, the oxygen permeability of silicones is relatively high, so dispersion of nanofillers and oxygen scavengers will be critical for low gas barrier applications. This will open up a new application for silicones in the field of organic device packaging. In comparison to the existent atomic layer deposition or molecular layer deposition route, the in-situ casted silicone polymers having an improved barrier properties will be cost effective, easy to fabricate and will capture the market of organic device packaging industries in near future.

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References

1. Silva WJ, Kim HP, Yusoff ARM, Jang J (2013) Transparent flexible organic solar cells with 6.87% efficiency manufactured by an all-solution process. Nanoscale 5: 9324-9329.
2. Sea JH, Gutacker A, Sun Y, Wu H, Huang F, et al. (2011) Improved High-Efficiency Organic Solar Cells via Incorporation of a Conjugated Poly(ether ether ketone) Interlayer. J Am Chem Soc 133: 8416-8419.
3. You J, Hong Z, Yang Y, Chen Q, Cai M, et al. (2014) Low-Temperature Solution-Processed Perovskite Solar Cells with High Efficiency and Flexibility. ACS Nano 8: 1674–1680.
4. Luo S, Daoud WA (2015) Recent progress in organic–inorganic halide perovskite solar cells: mechanisms and material design. J Mater Chem A.
5. Pietro RD, Fazzi D, Kehoe TB, Sirringhaus H (2012) Spectroscopic Investigation of Oxygen- and Water-Induced Electron Trapping and Charge Transport Instabilities in n-type Polymer Semiconductors. J Am Chem Soc 134: 14877-14889. 
6. Duffy DC, McDonald JC, Schueller OJA, Whitesides GM (1998) Rapid Prototyping of Microfluidic Systems in Poly(dimethylsiloxane). Anal Chem 70: 4974-4984.
7. Leclerc E, Sakai Y, Fuji T (2003) Cell Culture in 3-Dimensional Microfluidic Structure of PDMS (poly(dimethylsiloxane)). Biomed Microdevices 5: 109-114.
8. Cong H, Pan T (2008) Photopatterning Conductive PDMS Materials for Microfabrication. Adv Funct Mater 18: 1912–1921.
9. Abbas F, Mirzaheh H, Khatib AA (2001) Modification of polysiloxane polymers for biomedical applications: a review. Polym Int 50: 1279-1287.
10. Sorory H, Mashak A, Rahimi A (2013) Application of PDMS-based coating in drug delivery systems using PVP as channeling agent. Iran Polym J 22: 791-797.
11. Selvaraj H, Tan B, Venkatakrishnan K (2011) Synthesis of nanofiber-filled polydimethylsiloxane using ultrafast laser irradiation. J Polym Res 18: 1659-1665.
12. Kim JS, Yang S, Bae BS (2010) Thermally Stable Transparent Sol–Gel Based Siloxane Hybrid Material with High Refractive Index for Light Emitting Diode (LED) Encapsulation. Chem Mater 22: 3549-3555.
13. Jung K, Bae JY, Park S, Yoo S, Bae BS (2011) High performance organic-inorganic hybrid barrier coating for encapsulation of OLEDs. J Mater Chem 21: 1977-1983.
14. Yang SC, Kwak SY, Jin JH, Kim JS, Choi Y, et al. (2012) Thermally resistant UV-curable epoxy–siloxane hybrid materials for light emitting diode (LED) encapsulation. J Mater Chem 22: 8874-8880.
15. Gupta S, Ramamurthy PC, Madras G (2011) Synthesis and characterization of flexible epoxy nanocomposites reinforced with amine functionalized alumina nanoparticles: a potential encapsulant for organic devices. Polym Chem 2: 221-228.
16. Gupta S, Ramamurthy PC, Madras G (2011) Covalent Grafting of Polydimethylsiloxane over Surface-Modified Alumina Nanoparticles. Ind Eng Chem Res 50: 6585-6593.
17. Gupta S, Ramamurthy PC, Madras G (2011) Mechanistic overview of the curing behavior of hydride terminated polydimethylsiloxane with allyl functionalized alumina by calorimetry and rheometry. Thermochimica Acta 524: 74-79.
18. Gupta S, Ramamurthy PC, Madras G (2011) Synthesis and characterization of silicone polymer/functionalized mesostructured silica composites. Polym Chem 2: 2843-2850.
19. Moradi O, Yari M, Zare K, Mirza B, Najafi F (2012) Carbon Nanotubes: A Review of Chemistry Principles and Reactions. Fullerene, Nanotubes and Carbon Nanostuctures 20: 138–151.
20. Yoo BM, Shin JH, Yoon HW, Park HB (2014) Graphene and graphene oxide and their uses in barrier polymers. J Appl Polym Sci 131: 39628.
21. Peng R, Wang Y, Tang W, Yang Y, Xie X (2013) Progress in Imidazolium Ionic Liquids Assisted Fabrication of Carbon Nanotube and Graphene Polymer Composites. Polymers 5: 847-872.
22. Moorthy MS, Park SS, Fuping D, Hong SH, Selvaraj M, et al. (2012) Step-up synthesis of amidoxime-functionalised periodic mesoporous organosilicas with an amphoteric ligand in the framework for drug delivery. J Mater Chem 22: 9100-9108.
23. Park C, Kim H, Kim S, Kim C (2009) Enzyme Responsive Nanocontainers with Cyclodextrin Gatekeepers and Synergistic Effects in Release of Guests. J Am Chem Soc 131: 16614-16615.
24. Slowing II, Trewy BG, Giri S, Lin VSY (2007) Mesoporous Silica Nanoparticles for Drug Delivery and Biosensing Applications. Adv Funct Mater 17: 1225-1236.
25. Park I, Peng HG, Gidley DW, Xue SQ, Pinnavaia TJ (2006) epoxy–Silica Mesocomposites with Enhanced Tensile Properties and Oxygen Permeability. Chem Mater 18: 650-656.
26. Zhang FA, Lee DK, Pinnavaia TJ (2010) PMMA/mesoporous silica nanocomposites: effect of framework structure and pore size on thermomechanical properties. Polym Chem 1: 107–113.
27. Ji X, Hampsey JE, Hu Q, He J, Yang Z, et al. (2003) Mesoporous Silica Reinforced Polymer Nanocomposites. Chem Mater 15: 3656-3662.
28. Bershtein VA, Egorova LM, Yakushev PN, Pissis P, Sysel P, et al. (2002) Molecular dynamics in nanostructured polymide–silica hybrid materials and their thermal stability. J Polym Sci Part B: Polym Phys 40: 1056-1069.
29. Burrows PE, Graff GL, Gross ME, Martin PM, Hall M, et al. (2001) Gas Permeation and Lifetime Tests on Polymer-Based Barrier Coatings. Proc SPIE 4105: 75-83.
30. Gupta S, Sindhu S, Varman KA, Ramamurthy PC, Madras G (2012) Hybrid nanocomposite films of polyvinyl alcohol and ZnO as interactive gas barrier layers for electronics device passivation. RSC Advances 2: 11536-11543.
31. Gupta S, Seethamraju S, Ramamurthy PC, Madras G (2013) Polyvinylbutyral based hybrid organic/inorganic films as a moisture barrier material. Ind Eng Chem Res 52: 4383-4394.
32. Seethamraju S, Ramamurthy PC, Madras G (2013) Flexible polyvinyl alcohol-co-ethylene)modified MMT moisture barrier composite for encapsulating organic devices. RSC Adv 3:12831-12838.
33. Jiao J, Sun X, Pinnavaia TJ (2008) Reinforcement of a Rubbery Epoxy Polymer by Mesostructured Silica and Organosilica with Wormhole Framework Structures. Adv Funct Mater 18: 1067-1074.

34. Cheng CF, Cheng HH, Cheng PW, Lee YJ (2006) Effect of Reactive Channel Functional Groups and Nanoporosity of Nanoscale Mesoporous Silica on Properties of Polyimide Composite. Macromolecules 39: 7583-7590.

35. He J, Shen Y, Yang J, Evans DG, Duan X (2003) Nanocomposite Structure Based on Silylated MCM-48 and Poly(vinyl acetate). Chem Mater 15: 3694-3902.

36. Saravanan S, Gupta S, Ramamurthy PC, Madras G (2014) Effect of silane functionalized alumina on poly(vinyl butyral) nanocomposite films: Thermal, mechanical, and moisture barrier studies. Polymer Composites 35: 1426-1435.