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# Towards the polymer nanocomposites based on hairy nanoparticles

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Polymer nanocomposites exhibit versatility in their mechanical and structural features predominantly due to the huge surface area provided by nanoparticles. Interaction of the nanoparticles with polymer matrix selectively dictates the applications suitable for a particular polymer nanocomposite system. Novel hybrid polymer-derived materials based on polymer grafted nanoparticles (NPs) can either be mixed with the polymer matrix or self-suspended without matrix polymer. In both cases superior properties are demonstrated compared to the traditional polymer nanocomposites, most notably by 1) incorporation of NPs into polymers without “mixing problems” and 2) a wide range of the transport phenomena (from solids to viscous fluids). Hence, hairy nanoparticle-based nanocomposites are equipped to handle specific and unique challenges in manufacturing and processing methods. It is known that the transport properties can be tuned by altering the molecular design of hairy nanoparticles (i.e., grafted polymer chemistry, NP concentrations, grafting density, and polymer molecular weight) and matrix polymer (e.g., molecular weight). In this article, we review the 1) most common methods of synthesizing hairy nanoparticle, 2) their microscopic dynamics and structural features and 3) some interesting applications of nanocomposite based on hairy nanoparticles. We discuss the effect of various parameters like nanoparticle size, molecular weight of the polymer etc. on the features of nanocomposites and its implications on the properties.

## KEYWORDS

nanocomposites, synthesis, dynamics, structure, properties

## 1 Introduction

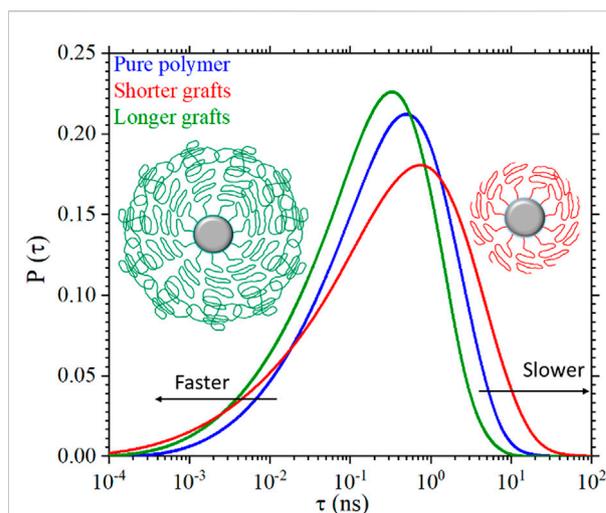
Polymer nanocomposites derived from polymer grafted nanoparticles guarantee uniform dispersion of nanoparticles and immunity from phase separation [1–4]. In the absence of free polymer, they are known as one component nanocomposites (OCNC). Usage of OCNC have been explored in a variety of applications like gas separation, energy storage etc. due to their unique properties [5–10]. The synthesis chemistry of OCNC can control multiple parameters like the diameter, nanoparticle shape, polymer molecular weight (MW), grafting density etc., giving rise to remarkably tunable properties. Application oriented parameter optimization creates opportunity like probing the origin of properties, which is again a multiparametric problem.

The properties of OCNCs are dependent on the dynamics and viscoelasticity of grafted polymer. Dynamical and viscoelastic features of the polymer are governed by the assembly of nanoparticles and confinement effects. The assembly of nanoparticles is also dependent on the conformational entropy of the grafted chains. Therefore, there exists an interdependence of polymer properties, dynamics and particle assembly [4, 11]. Miscellaneous parts of this problem are discussed in literature by several researchers, many times in relevance of an application. Here, we review some of the crucial research in this area. The goal of this short review is to furnish the reader with sufficient knowledge to understand the critical advances in the field.

## 2 Synthesis

Synthesis of OCNC is carried out *via* two approaches: “grafting from” and “grafting to” methods [12–18]. In “grafting from” approach, the monomer is attached to nanoparticle surface and then polymerized, typically by free radical polymerization, such that the polymer grows on the nanoparticle surface [19, 20]. For example, Chevigny et. al. showed the three step polymer grafting process on silica nanoparticles, consisting of silanization of surface with aminopropyltriethoxysilane, followed by grafting of the initiator and polymerization [21]. Similar procedures are used with the other kind of nanoparticles like gold, iron oxide etc., [22–24]. Polymer synthesized from the surface of nanoparticles using reversible addition fragmentation chain transfer polymerization (RAFT) and Atom Transfer Radical Polymerization (ATRP) have been reported widely including the study of polymerization kinetics [25–29]. The advantage of grafting from method is achievement of high grafting densities due to the ease of attaching high number of monomers on surface. However, the grafted polymer suffers from high polydispersity, limiting their suitability for fundamental studies.

In the “grafting to” approach, polymerized chains are attached to the nanoparticles surface [13, 30]. This allows to graft monodisperse polymer on nanoparticle, making these excellent model systems. Polymer chains functionalized with coupling agents like carbonyldiimidazole, disuccinimidyl carbonate etc., are covalently bonded to the silanized particle surface [21, 31]. Due to the bulkiness of chains, the grafting densities are generally lower as compared to the “grafting from” method. However, some newly reported methods claim higher grafting densities even by “grafting to” method. Ligand exchange chemistry produces high grafting density with coordinate bond between the metal nanoparticles and ligand functionalized polymer chains [32, 33]. Shui et. al. reported that using a mixture of good and bad solvent for the polymer, grafting density could be controllably varied [33]. By changing the ratio between solvents, they achieved grafting densities up to



**FIGURE 1**  
Representative distribution of relaxation times for shorter grafted chains and longer grafted chains as compared to the neat polymer.

2.8 chains/nm<sup>2</sup>. In another method, micelles of block copolymers are generated in a solvent followed by the solidification of the micellar core [14, 34]. Different shapes of nanoparticles could be produced such as spheres, plates etc., depending on the ratio of the block lengths and polymer concentrations [35].

We note that there exists a variety of nanoparticle type and polymer combinations e.g., carbon nanotubes grafted with various polymers, polystyrene grafted silica, poly (3-hexylthiophene) grafted ZnO etc., [36–40] However, the discussion for all of these combinations is not the focus of this review. With a brief introduction to the gist of employed synthesis techniques, we now discuss the structure and dynamics of OCNCs.

## 3 Structure and dynamics

Structure and dynamics of OCNCs have been widely studied using techniques such as static and quasielastic light, small angle X-ray and neutron scattering (SAXS and SANS), microscopy, dielectric spectroscopy, rheology etc. Structural and dynamical features of OCNC exist over multiple length as well as time scales with further complexities at each level.

Some of the intriguing and counterintuitive features are present at length scales from few Angstroms to few nanometers of segmental dynamics i.e., from few picoseconds to few nanoseconds. One could assign the relaxation in this region to the monomer mobilities. Kim et al. used dielectric spectroscopy, rheology and SAXS on polyisoprene grafted silica nanoparticles to show that the segmental dynamics of grafted chains is slower and more coupled than that of the ungrafted

chains [41]. They followed the effect of MW and grafting density to conclude that with increase in molecular weight, entanglements and grafting density, the slowing down of dynamics becomes lesser prominent. They attributed their observations to the space filling constraint felt by the grafted chains. On the other hand, Jhalaria et. al. showed using quasielastic neutron scattering (QENS), that for several MW of polymethyl-acrylate grafted silica nanoparticles, the segmental dynamics accelerates as compared to the free polymer [42]. This is attributed to the local increase in the molar volume in nanocomposites. Contrarily, report by Mark et al. showed unchanged segmental dynamics in low MW polyisoprene grafted nanoparticles suggesting MW dependence of the segmental motion in OCNCs [43]. This MW dependence was proven by us for two different MWs of polyisoprene grafted iron-oxide nanoparticles [44]. We analyzed the QENS (backscattering) and dielectric spectroscopy data using relaxation time spectrum analysis and showed a distribution of segmental relaxation times including both faster as well as slower segments for grafted polymer (Figure 1). A difference in the weighted contribution of these appears as the difference in average segmental relaxation times. Mapesa et al. used the distribution of relaxation times extracted from dielectric spectroscopy to study the difference between polymethyl-methacrylate filled with bare silica nanoparticles and corresponding OCNC, for various nanoparticles loadings [45]. The OCNC showed wider distribution of relaxation times especially extended to faster times. They also attributed the increase in segmental dynamics to the increase in molar volume due to increasing interphase between the nanoparticle and polymer. This generates higher packing frustration in OCNC interphase and hence local density fluctuation. The location dependent density of grafted and ungrafted polymers was studied by Power et. al using MD simulations [46]. They found maximum density of polymer segments near the nanoparticle surface, especially for grafted polymers, which gradually decreases to bulk values toward the chain ends. This is in line with the speculations based on QENS [44]. Therefore, the role of interface is crucial in deciding the OCNC properties.

Dukes et. al. discussed the conformational changes of the polymers grafted on spherical nanoparticles obtained by dynamic light scattering (DLS) [47]. At low grafting density, negligible interactions with the adjacent grafts are present. A mushroom like conformation is assumed with brush height ( $h$ ) proportional to the radius of gyration ( $R_g$ ) of the polymer i.e.,  $h \propto 2R_g$ . At moderate grafting densities, the neighboring grafts start to interpenetrate therefore, known as semidilute polymer brushes (SDPB). In this regime,  $h \propto N\sigma^{1/3}l_o^{5/3}$ , where  $N$  is degree of polymerization,  $\sigma$  is the grafting density and  $l_o$  is the monomer length. Polymer chains with much higher grafting densities are known as concentrated polymer brushes (CPB) where,  $h \propto N\sigma^{1/3}l_o^2$ . Simulations have confirmed the transition from mushroom to brush like polymer conformation with

increasing grafting density [10]. However, this transition was not observed for small nanoparticles. Wei et. al. performed SANS and neutron spin echo (NSE) experiments on polymethyl-acrylate grafted silica nanoparticles in solvent with different parts of polymer labelled with hydrogen and deuterium in different samples [48]. They showed that in OCNC, the interfacial region near the particle surface consists of stretched chain segments, hence representing the CPB region. However, the segments away from the particle are SDPB. The impact on the dynamics of different segments is also studied. NSE data showed that the segments near the core are slower than those away from the particle due to strong confinement.

The presence of an interfacial layer exhibiting substantial differences than the bulk polymer has been well reported [42–44, 49]. Holt et. al. compared the dynamics of interfacial layer for the poly (2-vinylpyridine) (P2VP) with different MW in OCNC with the physically adsorbed polymer nanoparticles using SAXS, differential scanning calorimetry and dielectric spectroscopy [50]. For low polymer MW, they found negligible difference in the decelerated dynamics of two nanocomposites. Interfacial model calculations show that the volume of interface includes the entire polymer. Similar dynamics is also observed for the high MW. However, for intermediate MW, the grafted polymer shows slower and more heterogenous dynamics as compared to the composites with ungrafted polymers. Using self-consistent field theory calculations, they showed that these trends could be related to the chain stretching in the interfacial region giving rise to slower dynamics, which is prominent in OCNC at intermediate MW. In a different publication, the same group reported that contrary to segmental motion, the  $\beta$  relaxation in P2VP, which corresponds to rotational relaxation of pyridine side groups, becomes faster in composites than the pure polymer [51]. The fastest dynamics exhibited by the OCNCs is counterintuitively accompanied by an increase in glass transition temperature ( $T_g$ ) and decrease in segmental mobility. This is despite the fact that OCNC have largest free volume available leading to decrease in polymer density. They conclude that while the interfacial chain stretching leads to slower segmental dynamics, the secondary relaxation is controlled by density changes. This also reflects in weaker mechanical properties of OCNC as compared to the pure polymer and polymer adsorbed nanocomposites. Other than the relaxation time scales, the amplitudes of the relaxation are also affected by the presence of interfacial layer [52].

Miller et. al performed core-modified dissipative particle dynamics simulations on OCNC to analyze the effect of grafting on polymer conformation and relaxation [53]. They found an increase in the  $R_g$  of polymers after grafting. The confinement effects induced by grafting were characterized by confinement parameter  $\xi^* = 1/R_{g0} \sqrt{\sigma}$ , where  $\sigma$  is the grafting density,  $R_{g0}$  is the radius of gyration for ungrafted chain.  $\xi^* < 1$  represents highly confined chains. They showed that the relaxation time ( $\tau_1$ ) of grafted chains scales as  $\tau_1 \propto (\xi^*)^{-\beta}$

where  $\beta > 1$  and its values increases from pure composites melt to dispersion in solvent. Importantly, for confinement length  $\xi^* < 1$ , the grafted chains relax following the Rouse mechanism in both melt and solution state. Agarwal et. al. employed dielectric spectroscopy to study the chain end-to-end relaxation in densely grafted polyisoprene-silica OCNC [54]. They reported an entanglement like confinement effect in grafted polymers even below their entanglement MW. These are attributed to the constraints imposed by neighboring grafts. The grafted chains relax by arm retraction and then remain in frustrated state due to long diffusion time of nanoparticles.

At length scales on the order of 100 nm to microns, glass like behavior of the OCNC is observed [1, 55, 56]. Wen et. al. using rheology and time concentration superposition showed that the grafted nanoparticles exhibit soft glass like characteristics where the particles perform in-cage rattling like motion [55]. At longer times, they observed the escape of grafted particles from the cage leading to fluid like response [3, 57–59]. These jamming-unjamming transitions are also observed at time scales on the order of 100 s using X-ray photon correlation spectroscopy (XPCS) [60]. The toughness of nanocomposites is related to this glassy response. Liu et. al. showed that the cage strength increases with equilibration of the nanocomposites systems whereas, decreases with increase in temperature [61]. Using SAXS they showed two types of interaction between the nanoparticles: 1. Repulsive interactions between the grafted particles and 2. Entropic attractions between the particle cores created by the grafted polymer.

Nanocomposites have tendency to assemble in different structural forms, from string to well-developed lattices [16, 62–70]. Other than the regular lattice packing of grafted nanoparticles, it is shown by Akcora et. al. that polymer grafted spherical nanoparticles also exhibit tendency to assemble into anisotropic structures when dispersed in free polymer [71]. This self-assembly is governed by the aggregation forces between the nanoparticle core, competing with the entropy of grafted chains [72]. The self-assembly of polymer grafted nanoparticles in solution has been studied by Bachhar et. al. using theoretical model based on the Daoud and Cotton theory for star polymers [73, 74]. They looked at the effect of polydispersity in the nanoparticle core size and showed that the distribution in the core size controls the self-assembly, overriding the effect of grafted chain dispersity. This led to a conclusion that in order to control the assembly of polymer grafted nanoparticles, tuning the nanoparticle size distribution must be the focus of synthetic efforts.

### 3 Properties

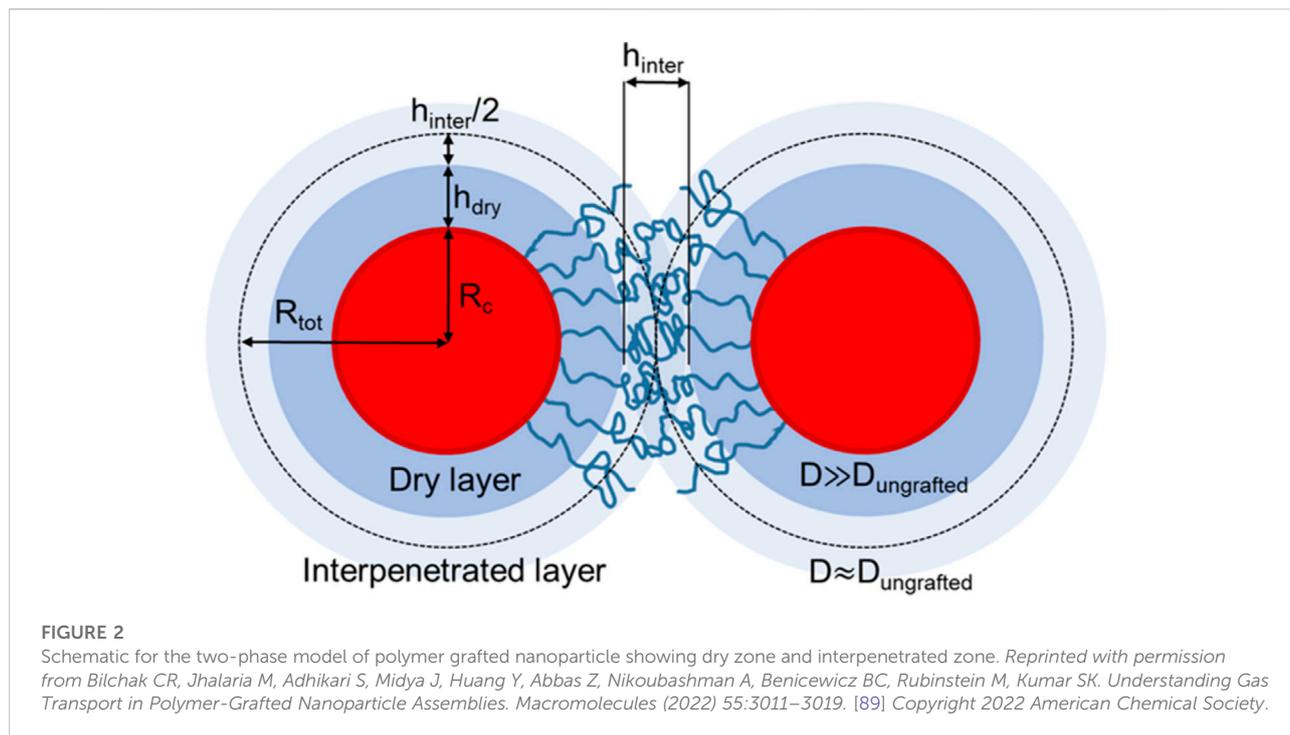
OCNCs exhibit significantly enhanced properties like viscoelasticity, crystallization, gas transport etc. than polymers or nanoparticle reinforced ungrafted polymer. We discuss some of these extensively reported properties here.

### 3.1 Viscoelasticity

OCNC in general exhibit higher viscosity and moduli as compared to the nanoparticle dispersed polymer or neat polymer in the low frequency range [1, 59, 75–78]. Hattemer and Arya used coarse grain MD simulations to probe the origin of higher moduli in OCNC as compared to the particle dispersed nanocomposites [79]. They showed that the existence of grafts introduces additional distortion of the shear field in polymer leading to higher modulus. The low frequency higher modulus is also affected by the slower relaxation of the grafted chains. The higher moduli are captured using a phenomenological model based on the Rouse formulation. Sakib et. al. conducted rheology experiments along with DSC to show the shift of viscoelastic response in OCNC towards lower frequencies as compared to the neat polymer [57]. This is attributed to an increase in  $T_g$  due to the space filling constraint of grafted polymer similar to that reported by Kim et. al. [41, 80]. Whereas, the plateau modulus of grafted chains, which is related to the entanglements decreases for lower MW grafts and increases for high MW grafts. The explanation of this effect has been given as a decrease in the effective entanglement density in shorter chain due to lesser penetration of the nanoparticle core into the polymer of neighboring particles. For larger chains, the nanoparticle core also participates in entanglement, generating higher entanglement density. Chen et. al. investigated the viscoelastic properties of OCNC in terms of the variation in composite toughness with polymer MW [60]. The toughness of polymethylacrylate grafted  $\text{SiO}_2$  nanoparticles exhibits a peak in molecular weights in Laser-induced projectile impact testing. Combination of entanglement and particle jamming controls this behavior [58, 61]. XPCS and QENS are used to relate the toughness of OCNC to the segmental relaxations and the colloidal flow.

### 3.2 Polymer crystallization

Where presence of nanoparticle provides a nucleation site for the polymer, the existence of grafting impedes the formation of folded chain crystals [81, 82]. Kim et. al. showed that the polymer grafted on nanoparticles crystallizes in contrasting manners at different length scales. While at nanometer scale helical structures are abundantly present, at length scales greater than the nanoparticle size, the overall crystallinity is lower than the pure polymer, indicating restricted formation of crystalline domains [83]. They claim that the polymer chains crystallize into extended chain crystals due to crowding and therefore, the spherulites are not formed in the polymer brush on particle surface. However, Zhao et. al. reported the



formation of spherulites even in case of densely grafted nanoparticles [84]. They advocated the formation of extended chain crystals for OCNC with high grafting densities. Employing Avrami analysis, they showed that with increase in the grafting density, the crystallization kinetics becomes faster. They attribute this to the ease of nucleation provided by the presence of nanoparticle surface. Wen et. al. found that for shorter grafted chains of methoxypolyethylene glycol, the confinement effects are stronger than longer chains [85]. For low grafting densities, the crystallinity and crystallization temperature decrease indicating resistance in crystallization. They obtained an Avrami index = 1 for low grafting density OCNC suggesting confined crystallization due to nucleation barrier. This effect is observed because of the enhanced interaction of grafted polymer with nanoparticle surface at low grafting densities.

### 3.3 Other transport properties

Polymer nanocomposites show suitable transport properties for various applications [86]. A series of papers have been published on significant enhancement in  $\text{CO}_2$  vs.  $\text{CH}_4$  separation for polymethacrylate grafted nanoparticles as compared to neat polymer membranes [5, 42, 87–90]. It is shown that by varying the MW and grafting density of the

polymer, selectivity and gas permeability can be tuned. The gas diffusivity increases with increasing MW till a maximum and then decreases. Detailed study of the OCNC membranes is carried out using QENS, SAXS, MD simulations and theoretical models. It is shown that the increase in local free volume (decreased density) of the grafted polymer as compared to the neat polymer gives way for the enhanced gas transport. Midya et. al. presented a two phase model for the grafted polymer chains around the nanoparticles [88]. They showed that there exist two regions of polymer segments; near the particle surface segments are stretched (known as dry layer) and do not interpenetrate with the segments of adjacent particles whereas, away from the surface interpenetration among the polymer segments from different particles takes place (Figure 2). The stretching leads to a decrease in the local friction and hence faster segmental mobility [90]. This creates pathways for the gas transport.

OCNC also show outstanding ion transport in energy storage devices therefore, becoming potential candidates for the solid-state electrolytes [6]. These findings are supported by the tunable mechanical and ion conducting properties of OCNC leading to enhanced device stability. Grabowski et. al. showed that for supercapacitors, while the dispersion and dielectric breakdown remains similar in blended nanoparticle-polymer system and OCNC [91], the charge/discharge efficiency and the energy storage capacity of the hairy nanoparticle systems is substantial greater than the conventional nanocomposites.

Polymer grafted nanocomposite with or without free polymer or solvent present plenty of opportunities in various applications. However, the precise origin of the properties of these materials is still an emerging field. While the fundamental knowledge of OCNC physics is important for optimization and tunability of properties, it is also crucial for understanding the complex behavior of polymers and their derivatives.

## Author contributions

This article is jointly written by AS and MK based on the literature in the field.

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## Conflict of interest

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