Enhancing Thermal Transport in Nanocomposites by Polymer-Graft Modification of Particle Fillers

Clare Mahoney^{a1}, Ching Ming Hui^b, Shubhaditya Majumdar^c, Zongyu Wang^b, Jonathan A. Malen^c, Maxim N. Tchoul^d, Krzysztof Matyjaszewski^b, Michael R. Bockstaller^{a}*

- a. Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213
- b. Chemistry Department, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, PA 15213
- c. Department of Mechanical Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213
- d. OSRAM Sylvania, 71 Cherry Hill Dr., Beverly, MA 01915

1) current address: Materials and Manufacturing Directorate, Air Force Research Laboratory, 2941 Hobson Way, B654/R331 Wright Pattern AFB, OH 45433-7750

corresponding author: Phone: ++1 412 268 2709; Fax: ++1 412 268 7247;

Email: bockstaller@cmu.edu

ABSTRACT

The role of polymeric tethers on the effective thermal conductivity of polymer nanocomposites is evaluated for the particular case of silica particle fillers dispersed within poly(methyl methacrylate) (PMMA). The effective thermal conductivity of both thin film and bulk composites is found to sensitively depend on the interaction between tethered and matrix chains. In particular, tethering of polymeric chains exhibiting favorable interactions with the matrix (such as poly(styrene-*r*-acrylonitrile), PSAN with molar composition S:AN = 3:1) is shown to raise the effective thermal conductivity. The results point to the relevance of the ‘ligand phase’ (constituted of the tethered chains) as well as the *tether/matrix* interface in determining the thermal transport in polymer nanocomposites and suggest opportunities to raise the thermal conductivity of nanocomposite materials by the deliberate design of polymeric tethers to facilitate attractive ligand/matrix interactions.

1. INTRODUCTION

The dissipation of heat in high power density devices presents a major challenge across a range of technologies such as solid-state lighting, energy storage as well as electronics. Contributing to the challenge of devising economic solutions to thermal management is the low thermal conductivity of polymer materials that are widely used as packaging materials or as components in devices.¹ In device applications the low thermal conductivity of polymer components often requires the engineering of auxiliary ‘heat conduction channels’ that raise fabrication costs, reduce design flexibility and limit the marketability of technologies. There is hence a significant technological need for polymer materials with enhanced thermal conductivity.

The thermal conductivity of polymers is typically found to be within the range $k \sim 0.10 - 0.25 \text{ W m}^{-1}\text{K}^{-1}$ (where the thermal conductivity k relates the heat flux density Q across a unit area and unit time to the temperature gradient ∇T via Fourier’s law, $Q = -k\nabla T$).¹ The low thermal conductivity of polymers has been rationalized as a consequence of weak intermolecular bonding and inefficient packing that are characteristics of common polymeric solids.¹⁻³ Strategies to increase the thermal conductivity of polymer materials encompass the orientation of polymer chains (for example, by mechanical stretching or the fabrication of fibrillar crystal morphologies) as well as the design of molecular architectures in which directional interactions give rise to the formation of ‘thermal network structures’ that promote heat flow within the material.^{2, 3} However, while these strategies have shown the potential to significantly raise thermal conductivity, the required processing conditions (to achieve chain orientation) or chemistries (to achieve hydrogen bond formation) limit the applicability of either approach. The addition of high- k inorganic fillers to polymer matrices thus remains the most widely used strategy to raise the thermal conductivity of polymer materials while (in the ideal case) retaining their favorable

combination of economic formability as well as mechanical, optical and electrical (insulating) properties.⁴⁻⁶ Understanding of the parameters that govern thermal transport in heterogeneous materials and developing methodologies to enhance thermal transport in polymer nanocomposites therefore presents an important objective.

In general, the thermal conductivity of nanocomposites depends on morphological characteristics such as the shape or dispersion state of filler particles as well as the physical properties of constituents.⁷ In the case of uniform filler dispersions (that are preferable when optical transparency or high electric breakdown strength are required) the thermal transport properties depend on both the thermal conductivity k of the constituent materials as well as the interface thermal resistance G^{-1} that arises due to thermal scattering at the organic/inorganic interface (G is the interfacial thermal conductance that relates the heat flux through an interface to the resulting temperature discontinuity ΔT , $G = Q/\Delta T$).⁸⁻¹⁰ Due to the strong increase of the surface-to-volume ratio with decreasing size of particle fillers ($S/V \sim 1/r_0$, with r_0 denoting the radius of a filler particle), thermal transport in polymer nanocomposites strongly depends on G . The Kapitza length $r_K = k/G$ corresponds to the distance within a material of thermal conductivity k that provides a thermal resistance equivalent to the interface.⁹ It is a measure for the effect of interface resistance on the thermal conductivity of nanocomposite materials. In particular, an enhancement of the thermal conductivity of the composite requires the particle radius to exceed the Kapitza length, *i.e.* $r_0 > r_K$. This minimum particle size (typically in the range of tens of nanometers for polymer nanocomposites) renders the enhancement of thermal conductivity a difficult problem as it should be balanced against other physical properties (such as optical transparency) that generally require small filler dimensions.

The relevance of the thermal resistance of inorganic/organic interfaces to the attainable

thermal conductivity in heterogeneous systems has fueled research to understand the governing parameters that determine boundary resistance. In a seminal experimental study Putnam *et al.* evaluated the interface thermal conductance of nanoparticle/polymer (γ -Al₂O₃/poly(methyl methacrylate), γ -Al₂O₃/PMMA) composites and reported values of $G \approx 30 \pm 10 \text{ MW m}^{-2} \text{ K}^{-1}$ for temperatures between 40 and 280 K, suggesting a minimum critical particle radius of $r_K \approx 7.5 \text{ nm}$ for particles to enhance the thermal conductivity of the composite (assuming $k_{\text{PMMA}} = 0.2 \text{ W m}^{-1} \text{ K}^{-1}$).¹¹ More recent research has focused on the role of surface modification on boundary conductance and suggested intriguing opportunities to enhance thermal interface conductance by the application of ‘surfactant interlayers’ to reduce thermal scattering across material interfaces. For example, O’Brien *et al.* demonstrated the tenfold increase of thermal conductance across planar copper/quartz interfaces by silane coating of the quartz interface.¹² Systematic evaluation of the effect of end-group chemistries on the thermal transport across planar gold/surfactant interfaces by Losego *et al.* revealed the pronounced relevance of the bonding strength between the surfactant and the respective inorganic on G . For the particular case of aliphatic surfactants sandwiched between gold and quartz substrates the thermal interface conductance was found to increase from 36 to 68 $\text{MW m}^{-2} \text{ K}^{-1}$ when dispersion interactions were exchanged by strong covalent bonding of surfactants.¹³ These results are supported by more recent work by Ong *et al.* who reported the effective thermal conductivity of surfactant-coated semiconductor nanocrystals to sensitively depend on the bonding strength of ligands.^{14, 15} In conclusion, these previous results highlight the role of ‘surfactant interlayers’ in modulating (and possibly enhancing) thermal conductance across inorganic/organic interfaces. Building on this previous work it is the purpose of the present contribution to evaluate the role of *polymeric* tethers on the effective thermal conductivity of polymer nanocomposites. For the particular case of SiO₂ particle fillers

embedded in PMMA we found that the effectiveness of particle fillers to raise the thermal conductivity of the polymer matrix (as measured by the relative change in thermal conductivity $(k_{\text{eff}} - k_{\text{m}})/k_{\text{m}}$, where k_{eff} and k_{m} refer to the effective and matrix thermal conductivity) is significantly increased if polymeric tethers were designed to exhibit favorable interactions with the matrix chains, *i.e.* if the Flory Huggins interaction parameter between tethered and matrix chains was negative ($\chi_{\text{matrix/tether}} < 0$). This result suggests that *tether/matrix* interactions assume an important role in determining k_{eff} . In support of previous reports on the thermal conductivity of planar polymer brushes our results further reveal that the grafting density and conformation of tethered chains is of subordinate relevance (as compared to the tether/matrix interactions) in determining the ultimate thermal conductivity of polymer nanocomposites materials.

2. EXPERIMENTAL SECTION

Materials. Silica nanoparticles were donated by Nissan Chemicals (MIBK-ST) and functionalized with the alkyl halide initiator 1-chlorodimethylsilylpropyl 2-bromoisobutyrate according to a procedure described in.¹⁶⁻²⁰ PMMA (atactic, M_{N} : 120,000 by GPC, CAS: 9011-14-7) was purchased from Sigma-Aldrich. The physical properties of PMMA (needed for the interpretation of FDTR measurements) were assumed as follows: density $\rho = 1.18 \text{ g cm}^{-3}$; heat capacity $c_v = 1466 \text{ J kg}^{-1} \text{ K}^{-1}$; the glass transition temperature was determined to be $T_g = 104 \pm 2$ °C.

The silicon wafer substrates used for FDTR studies were purchased from Siltronic Wafers ([100] orientation, N-doped (SB dopant, $1.5\text{E}18$), $525 \text{ }\mu\text{m}$). The thermal conductivity, κ , of silicon was estimated to be $120\text{-}130 \text{ W m}^{-1}\text{K}^{-1}$. Removal of native oxide layer was performed by

immersion of substrates in 3:1 H₂O:HF solution followed by spin casting of samples within the hour.

The gold used for thermal evaporation was purchased from Kurt J. Lesker (99.999% purity). The thermal conductivity of gold was determined through Wiedemann-Franz measurements. For SI-ATRP, the styrene, acrylonitrile and methyl methacrylate (Aldrich, 99%) were purified by passing through a basic alumina column. Copper(I) bromide (Aldrich, 98+%) and copper(I) chloride (Aldrich, 99.999%) were purified by washing sequentially with acetic acid and diethyl ether, and then filtered, dried, and stored under vacuum until use. The density and heat capacity of PSAN were estimated to be 1 g cm⁻³ and 1250 J kg⁻¹ K⁻¹. All other chemicals and solvents, such as tetrahydrofuran (THF) dichloromethane (DCM) and toluene were obtained from Sigma-Aldrich and Acros Organics, and used as received. Molecular weight distribution and molecular weight dispersity of tethered chains were measured by gel permeation chromatography (GPC) using a Waters 515 pump and Waters 2414 differential refractometer using PSS columns (Styrogel 10⁵, 10³, and 10² Å) in THF as an eluent (35⁰C, flow rate of 1 mL/min) with toluene and diphenyl ether used as internal references. A linear polystyrene (PS) standard was used for calibration. To perform GPC, chains were cleaved from particles by etching of particles in hydrofluoric acid (HF) in a polypropylene vial for 20 h and subsequent neutralization with ammonium hydroxide and drying with magnesium sulfate before performing GPC. Hydrofluoric acid (50 vol% HF) was purchased from Acros Organics and used as received (caution: Hydrofluoric acid is highly corrosive, please consult materials safety data sheet prior to handling HF). THF was purchased from Aldrich and used as received.

Film Preparation. Bulk films of 1 mm thickness were fabricated by blending of appropriate amounts of particle brush and PMMA solutions (10 wt%) in DCM or toluene and subsequent

solvent evaporation of the solution followed by depositing the solution in a 1.3 inch diameter Teflon mold for 4 days. Thermal annealing under vacuum (505 mBar for toluene, 844 mBar for DCM) for 10 days up to $T = 150\text{ }^{\circ}\text{C}$ was performed to ensure removal of all residual solvent. Thin films were prepared by spin coating of particle/PMMA solutions (3-5 wt% in toluene) to create films of thickness around 100-200 nm. The film thickness was determined by using a Dektak surface profilometer and confirmed with ellipsometry. Prior to FDTR a gold film of 80-100 nm thickness was evaporated onto the surface.

Heat Flux Measurements. The thermal conductivity of the bulk films was performed at OSRAM Sylvania (Beverly, MA) in accordance with ASTM E1530 using a guarded heat flow meter.

Frequency Domain Thermal Reflectance (FDTR). The FDTR measurements use two lasers – an intensity modulated pump laser with a wavelength of 488 nm, and an initially un-modulated 532 nm probe laser. The pump laser creates a periodic heat flux at the sample surface (coated with an Au transducer layer), which in turn leads to a periodically modulated surface temperature. The modulation of the surface temperature in turn creates a modulation of the reflectivity of the Au layer, which is detected by the probe laser. A phase lag exists between the probe and pump signals and is related to the phase lag of the surface temperature with respect to the heat flux. An analytical solution to the heat diffusion equation for a radially Gaussian-shaped, periodic heat flux on the surface of a layered structure is fit to experimental data of phase lag between the pump and probe beams for a range of modulation frequencies.^{21, 22} The thermal conductivity of the nanocomposite film is the lone fitting parameter and its value is determined by least squares optimization of the fit. The specific experimental details are as follows: The Au transducer layer is 95 ± 5 nm thick with a thermal conductivity of 190 ± 10 W/m K, which is independently

measured using a four-point probe measurement of its electrical resistivity and the Weidemann-Franz law. Several input parameters to theoretically model the layered structure are needed to generate the fits. Material density and specific heat capacity of the composites were calculated using a rule of mixtures based on the following values of pure components: $\rho_{\text{PMMA}} = 1.18 \text{ g/cm}^3$, $\rho_{\text{PSAN}} = 1.00 \text{ g/cm}^3$, $\rho_{\text{silica}} = 1.90 \text{ g/cm}^3$, $c_{\text{PMMA}} = 1466 \text{ J/kg K}$, $c_{\text{PSAN}} = 1250 \text{ J/kg K}$ and $c_{\text{silica}} = 740 \text{ J/kg K}$. Error bars are defined as the larger of two values: (1) the experimental error obtained by averaging over (at least) five distinct sample areas for each respective film sample and (2) an uncertainty estimate, as derived by propagating uncertainty in the input parameters to the fitting model, to the predicted value of the nanocomposite thermal conductivity.²² A variation of the material parameters within a range of about 10% (corresponding to the spread of values of material parameters found in the literature) was found to have no significant effect on the resulting thermal conductivity.

Transmission Electron Microscopy (TEM). Electron imaging was performed using a JEOL 2000 FX electron microscope operated at 200 kV. Imaging was based on the amplitude and phase contrast, and images were recorded by a Gatan Orius SC600 high resolution camera.

Differential Scanning Calorimetry (DSC). The glass temperatures (T_g) of nanocomposite films were determined using a TA Instruments DSC-Q-20. Each sample was heated from $T = 40\text{--}160$ °C at a rate of 10 °C/min. T_g was determined as the temperature corresponding to half the complete change in heat capacity, calculated as the peak maximum in the first derivative of heat flow.

Thermogravimetric Analysis (TGA). The polymer weight fraction in particle brush was measured using a TA Instruments Q50 thermal analyzer operating in the temperature range of T

= 20–800 °C, under nitrogen, with a heating rate of 10 °C/min. Chain grafting densities were calculated based on the polymer weight fraction and M_n measured by GPC.

3. RESULTS AND DISCUSSION

To evaluate the role of tether/matrix interactions as well as particle brush architecture on the thermal transport properties of nanocomposites, four particle brush systems were synthesized using surface-initiated atom transfer radical polymerization (SI-ATRP, see section ‘Materials and Methods’): (1) silica particles densely tethered with short-chain poly(methyl methacrylate) ($\sigma = 0.6 \text{ nm}^{-2}$, $N = 28$, sample ID: SiO₂-MMA28); (2) silica particles sparsely tethered with poly(methyl methacrylate) ($\sigma = 0.1 \text{ nm}^{-2}$, $N = 200$ sample ID: SiO₂-MMA200); and (3) silica particles tethered with poly(styrene-*r*-acrylonitrile) random copolymer with molar ratio S:AN = 3:1 ($\sigma = 0.6 \text{ nm}^{-2}$, $N = 24$, sample ID: SiO₂-SAN24; and $\sigma = 0.55 \text{ nm}^{-2}$, $N = 14$, sample ID: SiO₂-SAN14). Here, σ denotes the grafting density and N the degree of polymerization of surface-tethered chains. It is noted that the coupling chemistry of polymeric tethers (via ‘Si-O’ bonds) is identical for all particle systems. All silica particle systems were of equal particle radius $r_0 = 7.7 \pm 2 \text{ nm}$. The characteristics of all particle systems are summarized in Table 1.

Table 1. Summary of molecular characteristics of polymer and particle brush systems.

Sample ID	σ/nm^{-2}	M_n	$\mathcal{D}$	ϕ_{SiO_2}
PMMA	–	120,000	1.3	–
PSAN	–	2,550	2.2	–
SiO ₂ -SAN24	0.6	2,099	1.2	0.48 ± 0.015
SiO ₂ -SAN14	0.5	1,288	1.2	0.72 ± 0.02
SiO ₂ -MMA28	0.6	2,805	1.3	0.37 ± 0.013
SiO ₂ -MMA200	0.1	20,036	1.2	0.42 ± 0.013

σ denotes the grafting density of polymer tethers, M_n the number-averaged GPC molecular weight, $\mathcal{D}$ is the molecular weight dispersity index and ϕ_{SiO_2} denotes the volume fraction of silica. The particle radius for all samples is ($r_0 = 7.7 \pm 2$ nm).

Table 1 reveals that particle brush systems SiO₂-MMA200 and SiO₂-MMA28 exhibit near identical volume fraction of inorganic component ($\phi_{\text{SiO}_2} \sim 0.4$) and hence selectively illustrate the role of grafting density on thermal transport. In contrast, SiO₂-MMA28 and SiO₂-SAN24 are (approximately) isostructural and thus allow the selective evaluation of the effect of tether/matrix interactions on thermal conductivity. Poly(styrene-*r*-acrylonitrile) with molar ratio S:AN = 3:1 was chosen as polymer tether because of its weakly negative Flory-Huggins interaction parameter ($\chi_{\text{MMA/SAN}} = -0.003$ at $T = 298\text{K}$) with the PMMA matrix polymer.²³

Nanocomposite films were prepared by dissolution of appropriate amounts of filler in matrix PMMA ($N \sim 1200$) solution in toluene (10 wt%) and subsequent casting of films. Bulk films (with a thickness of approximately 1 mm) were vacuum annealed for 14 days at $T = 150$ °C to remove residual solvent prior to testing while thin films (prepared by spin casting of 3-5 wt% solutions in toluene) were annealed for 30 minutes at $T = 120$ °C. The microstructure of composites was evaluated by electron imaging. Figure 1 depicts representative micrographs for

the case of composite systems with about equal inorganic loading of $\phi_{\text{SiO}_2} \sim 0.03$ (the ‘apparent’ variation of particle densities between the different samples is attributed to thickness variation of sectioned films and its effect on the apparent particle density in projection images). The figure reveals the uniform dispersion of particle fillers in case of PSAN grafted fillers (Fig. 1a and 1b) while the formation of small ‘particle associate structures’ in case of PMMA tethered particle brushes (Fig. 1c and 1d) suggests an ‘approximately dispersed state’ by kinetic trapping of a weakly phase separating polymer/particle blend system (apparent variation of particle size is due to differences in the magnification during imaging, see the associated scale bars for reference). This is consistent with the expectation that autophobic dewetting of the brush/matrix interface should drive phase separation in athermal binary blends of densely tethered particles embedded in polymeric media in the limit of $N_{\text{matrix}} \gg N_{\text{tether}}$ (where the term ‘athermal’ indicates that tether and matrix polymer exhibit equal chemical composition and thus the contribution of enthalpy to the free enthalpy of mixing can be neglected). For more information on the role of polymeric tethers on the miscibility of particle brush/polymer blends we refer the reader to a recent work by Ojha *et al.* who investigated the effect of polymer graft architecture and interactions on the miscibility of SiO_2 -SAN/PMMA and SiO_2 -MMA/PMMA blends.²⁴⁻²⁹

To evaluate the uniformity of particle-in-polymer dispersions the average particle distance $\langle d \rangle$ was determined after image thresholding using the image processing software ImageJ. For all particle brush/polymer thin film systems the average nearest neighbor distance between particles (determined from micrographs such as those shown in Figs. 1b-1d) is within approximately 80% of the theoretical value $\langle d \rangle = (V/N_p)^{1/3}$ (with N_p/V denoting the particle number density). The proximity of experimental and theoretical values confirm that while mixing is not thermodynamically favored in the case of PMMA-tethered systems, the rapid

vitriification of the films during spin coating effectively traps an particles during the early phase separation state thus resulting in an approximately uniform morphology. The latter is a critical prerequisite for the application of effective medium theory to interpret the thermal conductivity of the polymer/particle blends systems in the following discussion.

Figure 1. Bright field transmission electron micrographs of particle/PMMA ($N = 1200$) blends. Panels correspond to: (a) SiO₂-SAN24 ($\phi = 0.03$), (b) SiO₂-SAN14 ($\phi = 0.04$), (c) SiO₂-MMA28 ($\phi = 0.02$), and (d) SiO₂-MMA200 ($\phi = 0.03$). PSAN-tethered particle systems exhibit uniform dispersion while the formation of associate structures is indicative of early-state phase separation in case of PMMA-tethered systems. Sample shown in panel (a) was prepared by microsectioning from a bulk film whereas samples shown in panels b-d were prepared by spin casting on poly(acrylic acid) substrates and subsequent lift-off. Apparent differences in particle loading are attributed to variation of section thickness, apparent differences of particle size are caused by distinct image magnifications; line-type contrast variations seen in panel (a) are caused by knife marks. Colored symbols represent the respective sample identifier used in subsequent figures. Scale bars are 100 nm.

To assess the effect of polymer graft composition on tether/matrix interactions, the glass transition temperatures of (bulk) composite systems were determined by differential scanning calorimetry. Figure 2 depicts the trend of glass transition temperatures for both PMMA and PSAN-grafted particle brush systems dispersed in PMMA. The figure reveals a pronounced increase of T_g with addition of PSAN-tethered particles consistent with stronger ‘cohesive interactions’ that are expected in mixed systems of polymers with negative interaction parameter.²⁴ The change in T_g is approximately equal for PSAN tethers with $N = 14$ and 24 thus suggesting that interactions are dominated by the tether/matrix interface rather than the interpenetration of brush with matrix chains (since in the latter case a more pronounced increase for the PMMA/SiO₂-SAN24 system would be expected due to the increased number of SAN/MMA contacts). In contrast, the T_g of SiO₂-MMA28/PMMA systems are approximately constant and equal to the glass temperature of the pristine PMMA matrix – this is consistent with previous reports on enthalpy neutral (non-interacting) systems.

Figure 2. Dependence of the glass transition temperature T_g on the filler content for SiO₂-MMA28/PMMA (blue triangles) and SiO₂-SAN14/PMMA (red squares) composites. The open red square at ($\phi \sim 0.35$) corresponds to the SiO₂-SAN24/PMMA system – the agreement with the respective value of the SiO₂-SAN24/PMMA system confirms that the increase of T_g is independent of the degree of polymerization of PSAN-tethers. Dashed black line corresponds to T_g of quiescent PMMA. All measurements were performed at a cooling rate of 10 °C/min. The pronounced increase of T_g in case of PSAN-tethered fillers confirms favorable interactions consistent with the negative interaction parameter (see text for more details). Inset shows DSC traces for the PMMA reference (blue) as well as the SiO₂-SAN14/PMMA ($\phi = 0.35$, red).

Thermal conductivity of nanocomposites systems was determined by frequency-domain thermal reflectance (FDTR) – a versatile non-contact laser based method that deduces the thermal conductivity of layered thin film materials through measurement of thermorefectance that arises from the periodically modulated frequency of the laser incident the film surface, as further explained in the literature.^{21, 22} In addition, heat flow measurements were performed on bulk films for SiO₂-SAN24/PMMA blends to validate thin film experiments – results from both techniques were found to agree within the experimental uncertainty. For FDTR analysis, data for at least five distinct film areas per sample were averaged to determine experimental uncertainty. Figure 3a depicts representative FDTR phase lag data for samples SiO₂-MMA200/PMMA with

$\phi_{\text{SiO}_2} = 0.05$ and 0.39 , respectively, Figure 3b summarizes the thermal conductivity of all particle-brush/PMMA blends.

Figure 3. Thermal conductivity of nanocomposite systems. Panel a: Phase lag vs. modulation frequency from FDTR measurement 40% (blue circles) and 5% (red squares) by volume inorganic content (SiO_2) for the SiO_2 -MMA200/PMMA system. Panel b: Thermal conductivity of PMMA-based composite materials. Symbols represent SiO_2 -SAN24/PMMA (filled red squares) and SiO_2 -SAN14/PMMA (open red squares), SiO_2 -MMA28/PMMA (blue triangle) and SiO_2 -MMA200/PMMA (open blue diamond), respectively. Lines represent effective medium predictions based on the Nan effective medium model (eq.1) assuming infinite interface thermal conductance ($G = \infty$, black dashed line) and $G = 420 \text{ MW m}^{-2} \text{K}^{-1}$ (black solid line) as well as PMMA (blue dashed line) and PSAN (red dashed line.)

The data shown in Figure 3b displays several pertinent features: First, the thermal conductivity of PSAN-tethered particle systems consistently exceeds (in the limit of high particle concentrations by as much as 50%) the thermal conductivity of the respective non-interacting analogs. Second, the thermal conductivity of the SiO₂-MMA28/PMMA dense brush system consistently exceeds the respective values for the SiO₂-MMA200/PMMA sparse brush system, albeit the difference remains somewhat ambiguous due to the experimental uncertainty. It should be noted, however, that the reported uncertainties are conservative estimates (see ‘Materials and Methods’ section) and that the true experimental error is likely smaller than the indicated error bars. We hypothesize that two factors could contribute to the increase of k_{eff} in the case of dense PMMA-brush systems as compared to their sparse analogues, *i.e.* the increase of silica/tether interface thermal conductance due to the higher density of covalently bound tethers (in analogy to observations reported previously by Ong *et al.*, see reference 14) as well as the potential increase of the intrinsic thermal conductivity of the tethered polymer due to the stretched chain conformations in dense brush architectures.¹⁴ However, it should be noted that previous work by Cahill and coworkers – demonstrating the thermal conductivity of PMMA brushes to be similar to those of regular solution-cast PMMA thin films – suggests that the latter contribution is of lesser significance.³⁰

To gain further insight into the origin of the pronounced increase of k_{eff} in the case of PSAN-tethered particle brush systems, Figure 3 compares the experimental data with effective medium calculations based on the Nan effective medium model that predicts the effective thermal conductivity of nanocomposites with spherical particle fillers (in the limit of small concentration) to be

$$k_{eff} = k_m \frac{k_p(1+2g) + 2k_m + 2f(k_p(1-g) - k_m)}{k_p(1+2g) + 2k_m - f(k_p(1-g) - k_m)} \quad (1)$$

where $k_m = 0.2 \text{ W m}^{-1}\text{K}^{-1}$ and $k_p = 1.38 \text{ W m}^{-1}\text{K}^{-1}$ denote the thermal conductivity of the matrix and particle core, respectively, and $\gamma = k_m r_0^{-1} G^{-1}$.³¹ The prediction for k_{eff} on the basis of Eq.1 assuming a perfectly conducting interface ($G = \infty$) as well as $G = 420 \text{ MWm}^{-2}\text{K}^{-1}$ (corresponding to a value determined for (spun cast) PMMA/silica interfaces in reference 30) are shown in Figure 3 as dashed and solid black lines, respectively.³⁰ The comparison between experimental and predicted values reveals that PMMA-brush composites approximately follow the predicted trend for realistic values of G (with k_{eff} of dense brushes somewhat exceeding those of sparsely grafted systems as explained above) while SAN-tethered particle composites significantly exceed effective medium predictions even for the assumption of $G = \infty$ (both in the thin film as well as the bulk state). We attribute the increase of k_{eff} in the case of SiO_2 -SAN14/24/PMMA blends to attractive tether/matrix interactions that could promote thermal transport, for example, by the reduction of the materials' free volume (as indicated by the increase of T_g , see Fig. 2) or by increasing the thermal conductance across the tether/matrix interface. The increase of k_{eff} beyond the effective medium prediction even for the (unphysical) assumption of infinite interface conductance suggests that two-phase homogenization models cannot capture the relevant physical processes giving rise to the increase of thermal conductivity in SiO_2 -SAN14/24/PMMA blends. Here it should be mentioned that the applicability of effective medium models is limited to small filler concentrations even under otherwise 'ideal' conditions.³² Our interpretation is hence preliminary and further research is needed to better understand the role of particle brush architecture, nature and disposition of chain end groups as well as interactions on thermal transport in brush particle composites.

4. CONCLUSIONS

In conclusion, our results highlight the role of ‘polymer-surface modification’ (and perhaps more generally ‘surface chemistry’) on the thermal transport in nanocomposites materials. In particular, the results suggest that the deliberate design of polymeric tethers to facilitate attractive interactions between brush and matrix chains can provide an effective means to raise the thermal conductivity in nanocomposites materials. Given the wide range of accessible brush chemistries we expect that this finding could benefit the development of composite materials in which adequate levels of the thermal conductivity are realized at moderate particle loading levels that maintain favorable attributes such as transparency and processibility.

ACKNOWLEDGEMENT

This work was primarily supported by the National Science Foundation via grant DMR-1410845, DMR 1501324 and the Department of Energy via grant DE-EE0006702 as well as by OSRAM Sylvania. JM acknowledges support by the American Chemical Society (ACS) PRF DNI Award (Award No. PRF51423DN10). CM further acknowledges support by the Bertucci Graduate Fellowship program.

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