

Effective thermal conductivity of condensed polymeric nanofluids (nanosolids) controlled by diffusion and interfacial scattering

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Abstract. Thermal properties of polymeric nanosolids, obtained by condensing the corresponding nanofluids, are investigated using photothermal techniques. The heat transport properties of two sets of polyvinyl alcohol (PVA) based nanosolids, TiO_2/PVA and Cu/PVA , prepared by condensing the respective nanofluids, which are prepared by dispersing nanoparticles of TiO_2 and metallic copper in liquid PVA, are reported. Two photothermal techniques, the photoacoustic and the photopyroelectric techniques, have been employed for measuring thermal diffusivity, thermal conductivity and specific heat capacity of these nanosolids. The experimental results indicate that thermal conduction in these polymer composites is controlled by heat diffusion through the embedded particles and interfacial scattering at matrix–particle boundaries. These two mechanisms are combined to arrive at an expression for their effective thermal conductivity. Analysis of the results reveals the possibility to tune the thermal conductivity of such nanosolids over a wide range using the right types of nanoparticles and right concentration.

Keywords. Polymeric nanosolids; thermal conductivity; photothermal techniques; effective medium theory; interfacial scattering.

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1. Introduction

The polymeric nanosolids presented in this work are uniform dispersions of a single-phase nanomaterial dispersed uniformly in a polymer matrix, which are essentially solid counterparts of the corresponding polymeric nanofluids. A polymeric nanofluid is obtained by uniformly dispersing a known concentration (or volume fraction) of nanoparticles (typically <1% volume fraction) in a polymeric fluid and directly condensing it at room temperature, which results in the formation of the respective nanosolid. The volume

fraction of nanoparticles in such a nanosolid is higher compared to the corresponding nanofluid due to the net decrease in the volume of the base fluid upon condensation. The idea of developing nanosolids with variations in thermal properties has been actually derived from the concept of nanofluids which are known to possess enhanced thermal properties such as high thermal conductivity [1–3]. For the past one and a half decades, these fluid suspensions of nanoparticles have attracted the attention of thermal scientists due to their anomalous thermal conductivity values even at low concentrations of nanoparticles. Moreover, the anomalous enhancements in thermal conductivity in nanofluids made scientists to think about the possibility of designing ultrahigh heat transfer systems based on nanofluid technology. One of the advantages found with nanofluids is the simplicity of their synthesis. The advancements in nanotechnology offer various physical or chemical methods to synthesize and process different types of nanoparticles made of metals, metallic oxides, alloys, carbon nanotubes etc. The corresponding nanofluids are obtained by uniformly dispersing known concentrations of these particles in the desired fluid, resulting in nanoparticle–fluid suspensions of desired concentrations [4,5].

Most of the nanofluids prepared by the above techniques consist of comparatively low molecular weight base fluids like water, oil, ethylene glycol etc. Microstructural characteristics like nanoparticle volume fraction, nanoparticle sizes, particle shapes as well as temperature have been found to influence the effective thermal conductivity of these nanofluids. A number of papers have appeared reporting anomalous enhancements in thermal conductivity for several of these nanofluids [6,7]. Researchers have tried to describe the mechanisms behind the abnormal enhancements in the thermal conductivity of nanofluids using the effective medium theories, originally proposed by Maxwell [8]. However, in many cases the observed enhancements are far beyond the predictions of the effective medium approximation (EMA). So, researchers have tried to renovate the EMA by including other mechanisms like Brownian motion of nanoparticles [9], formation of a semisolid adsorption layer around nanoparticles [10], formation of particle clusters [11], etc. Though inclusion of these mechanisms could partially account for the observed enhancements in many cases, effects like occurrence of semisolid layers with sizes beyond the size of nanoparticles were argued to be unrealistic. Also the wide differences in the results reported by different researchers for the same type or similar nanofluids further increased the complexity of the problem. A few years back, an International Property Bench Mark Exercise (INPBE) involving 34 research groups around the world helped to resolve many of the roadblocks in this subject area and their results have demonstrated that the mechanism of diffusion of thermal waves through nanoparticles (Maxwell's idea) control the effective thermal conduction in nanofluids [12]. According to the findings of INPBE, the percentage enhancement in thermal conductivity of nanofluids with particle loading is in tune with EMA. These and other studies have established that mechanism such as formation of semisolid layer around the particles is not responsible for the anomalous enhancement in thermal conductivity in nanofluids made of low molecular weight base fluids such as water.

Though formation of an adsorption layer does not influence thermal conductivity of a nanofluid made of a low molecular weight base fluid, the situation is different in a nanofluid made of a high molecular weight base fluid such as a polymeric fluid. The high molecular weight and viscosity of polymeric fluids can give rise to adsorption layer around the particles with thickness comparable to particle dimensions. The Langmuir

adsorption isotherm provides an expression to evaluate the strength of adsorption of liquid molecules around a solid surface. According to the Langmuir formula [13], a high molecular weight (more than say 10,000) fluid can form a comparatively thick layer (thickness >25 nm) around a solid particle, which can bring about effects such as thermal wave scattering at the particle–matrix interfaces, which can considerably influence properties such as thermal conductivity. This is in contrast with the situation in a low molecular weight nanofluid where the thickness of the adsorption layer evaluated from Langmuir formula is less than 3 nm, which is far less than the actual particle size.

We have shown earlier that the formation of an adsorption layer significantly influences the thermal conductivity of a polymeric nanofluid [14]. A model has been proposed in the general framework of Maxwell–Garnett effective medium theory, including interfacial thermal resistance due to scattering at liquid–particle interfaces and particle clustering, to account for the experimentally observed dependence of thermal conductivity on particle volume fraction. It has been shown that interfacial scattering can reduce thermal conductivity to values lower than the thermal conductivity of the base fluid. Analysis of experimental data obtained with TiO_2/PVA and Cu/PVA nanofluids have indicated the possibility of tuning thermal conductivity of nanofluids with a proper choice of nanoparticles and concentration.

After evaluating the thermal conduction properties of polymeric nanofluids, we thought that it is interesting to extend these investigations to their solid counterparts. Moreover, such nanosolids, whose thermal properties could possibly be tuned, may lead to the design of special heat transfer systems and accessories. As has been demonstrated by earlier workers, composites have the distinct advantage of having tunability of their properties, which is of great advantage in designing heat transfer systems. Thermal properties of heat transfer materials are relevant in fields such as thermoelectric and thermal management systems [15,16]. The preparation of a uniform nanosolid by the direct condensation of the corresponding nanofluid is easier than the preparation of the same by mixing the components uniformly in the solid state under controlled temperatures. Rayleigh [17] and Maxwell [8] studied effective thermal conductivity of conventional solid composites and derived expressions for the effective thermal conductivity of mixtures of spherical particles in a host medium. Later, Bruggeman [17] introduced a new model to define the effective thermal conductivity of binary mixtures based on mean field theory which considered the interactions among randomly distributed spherical inclusions. Recently, Nan *et al* [18] have described the effective thermal conductivity of a two-phase composite in terms of a general equation, which is applicable to a wide variety of geometries, which includes thermal boundary resistance arising due to the scattering of thermal waves at the interfaces of two phases [18]. These authors and others have discussed the effect of interfacial thermal resistance and aspect ratio of inclusions on the total thermal conductivity of composites consisting of multiphase inclusions [18,19]. The modified EMA developed by them describes the mechanism of thermal conduction in nanosolids in terms of increased interfacial scattering in the light of the fact that in a nanosolid the phonon mean free path, in general, is smaller than the size of the nanoparticles [18].

In the present work, we try to extend investigations on thermal properties of nanocomposites to condensed form of polymeric nanofluids, composing of metallic or nonmetallic nanoparticles embedded in a polymer matrix. Two sets of polymer-based nanosolids consisting of TiO_2 and copper nanoparticles embedded uniformly in PVA were prepared

and their thermal conductivities and specific heat capacities were measured as a function of particle volume fraction following the photopyroelectric (PPE) technique. Their thermal diffusivities have also been measured separately by employing the photoacoustic (PA) technique for confirmation. The experimental results in the case of TiO_2 /PVA system indicate that thermal conductivity as well as thermal diffusivity decrease with increase in particle volume fraction up to a certain value and continue to keep this value. This observation is explained as due to the increased thermal wave scattering at polymer matrix–nanoparticle interfaces. But, in the case of Cu/PVA nanosolids, the effective values of thermal conductivity and diffusivity increase with increase in nanoparticle volume fraction and saturate at high particle volume fractions. To explain the experimental variations of effective thermal conductivity and diffusivity in these samples, we developed a theoretical model by combining interfacial thermal scattering [18] and heat diffusion through the particles as described by the classical EMA [19]. It is found that this model accounts for the observed variations in effective thermal conductivity of these nanosolids with particle volume fractions in terms of the relevant microstructural properties of their components.

2. Experimental methods

We prepared two sets of PVA-based nanosolids by condensing the respective nanofluids, prepared by dispersing metallic copper and TiO_2 nanoparticles in PVA. Their thermal properties were measured by PA and PPE techniques.

2.1 Preparation of PVA-based nanosolids

We prepared the nanosolid samples by the direct condensation of PVA-based nanofluids, dispersed uniformly with copper and TiO_2 nanoparticles at room temperature. Two sets of nanofluid samples, each with different nanoparticle concentrations, were prepared for measurements. These were TiO_2 /PVA nanofluids prepared by uniformly dispersing TiO_2 nanoparticle in PVA and Cu/PVA nanofluids with copper nanoparticles dispersed in PVA. TiO_2 and copper nanoparticle were selected because these have wide differences in their thermal conductivities in their respective bulk forms, and we wanted to bring out the effect of particle thermal conductivity on the interfacial thermal resistance and the consequent thermal conductivity.

TiO_2 nanoparticles of ~ 15 nm average size were prepared by the hydrolysis of TiCl_4 [20]. 99% TiCl_4 was initially digested in concentrated hydrochloric acid and then mixed with water. The pH of the solution was about 1.8. In order to precipitate TiO_2 , 5 M hydrazine hydrate was added drop by drop so as to raise the pH to ~ 8 . The precipitate was then stirred, filtered, washed and dried. The powder was calcined at 200°C for a few hours to obtain TiO_2 nanopowder. The particle size was estimated using powder XRD technique. Copper nanoparticles of ~ 16 nm average size were prepared by chemical reduction of CuSO_4 with hydrazine in ethylene glycol under microwave irradiation in a medium power of 750 W for a few minutes [21]. After cooling to room temperature the mixture was filtered, washed in ethanol and dried to obtain the Cu nanopowder. Initially, the PVA-based fluid was prepared by mixing PVA granules in water under constant stirring for several hours. The degree of hydrolysis of PVA used was about 90%.

Nanoparticles of desired mass fractions were added to the base fluid, thoroughly mixed and sonicated for several hours to obtain highly uniform nanofluid samples. In order to condense the nanofluid, we kept 5 ml of nanofluid in a petridish and allowed it to condense slowly at room temperature. After 2–3 days, condensed forms of nanofluids, or nanosolids, were formed. The volume of the fluid was so chosen that the thickness of the sample after solidification was about 0.5 mm, which was suitable for direct measurements following any of the two photothermal methods. The change in mass fraction as the fluid got condensed to solid was determined by measuring the loss of weight of pure PVA after condensation. The nanosolid prepared by this method was found to be highly uniform.

2.2 Measurement of thermal diffusivity by photoacoustic (PA) technique

Photoacoustic (PA) measurement of thermal diffusivity of a solid is based on the sensitive detection of acoustic waves generated by the absorption of modulated electromagnetic radiation, the most popular radiation source nowadays being lasers. It is now well established that the PA effect [22] involves the production of acoustic waves as a consequence of the generation of thermal waves in the medium. The thermal waves are generated by the non-radiative de-excitation processes in the sample which is a result of the periodic heating by the absorption of modulated light. The PA technique constitutes a comparatively simple and reliable experimental tool [23], which has been extensively used for measuring thermal properties such as thermal diffusivity and conductivity of solid samples [24,25]. The method is based on the analysis of the variations in the amplitude and phase of the PA signal with the light modulation frequency, which is also the frequency of the generated acoustic waves. The sample is kept in an enclosed volume provided with a window to irradiate the sample and a sensitive microphone (electrets microphone in our measurements) picks up the PA signal, which is amplified and processed with a lock-in amplifier. The experiment needs to be carried out in a vibration-free environment so that a sufficiently high signal-to-noise ratio can be achieved. In the present work, we have measured the variations of the PA amplitude with modulation frequency to arrive at the thermal diffusivity values of the samples.

The sample thicknesses chosen are such that at low modulation frequencies (say <50 Hz) the thermal diffusion length of the sample is more than the physical thickness of the sample, in which case the sample is said to be thermally thin. By increasing the modulation frequency to higher values (say >100 Hz), the thermal diffusion length decreases, and at a high enough modulation frequency, it becomes less than the physical thickness of the sample, which takes the sample to a thermally thick regime. The modulation frequency at which the sample changes over from thermally thin to thermally thick regime is called the critical frequency. Critical frequency can be determined by measuring the variation of PA amplitude or phase with modulation frequency, which appears as a distinct change in slope in the PA amplitude plot or as a maximum in the phase plot. Once the critical frequency f_c is determined, thermal diffusivity α can be determined from the relation [24]

$$\alpha = \pi f_c l_s^2, \quad (1)$$

where l_s is the sample thickness.

2.3 Measurement of thermal properties by photopyroelectric (PPE) technique

The thermal characterization of the nanosolid samples was also done by the PPE technique [26]. In this technique, an intensity-modulated beam of light (from a laser) incident on the sample generated a thermal wave, which propagated through the sample generating a corresponding temperature rise on the opposite side of the sample. This temperature rise was picked up with a pyroelectric detector (such as metal-coated PVDF film) thermally attached to the sample. The sample thicknesses used in the present measurements were of the order of 0.5 mm. The amplitude and phase of the pyroelectric signal were recorded as a function of modulation frequency with a lock-in amplifier. From the amplitude and phase values of the thermal wave, thermal properties such as thermal conductivity, thermal diffusivity and specific heat capacity could be evaluated. More details of the experimental technique can be found elsewhere [27].

The PA as well as PPE measurements were carried out on samples prepared with different volume fractions of nanoparticles. The thermal properties of pure PVA, condensed by following the same procedure, were also measured for comparison. From these the thermal properties of each sample, normalized by the corresponding properties of pure condensed PVA, were plotted against the volume fractions of the nanoparticles.

3. Results and discussion

In order to compare the experimental results with theoretical predictions based on diffusion and interfacial scattering of thermal waves in the medium, it is necessary to present the salient features of the mechanisms involved. In the present analysis, we have tried to explain the observed variations in effective thermal conductivity of the nanocomposites under investigation as a combined effect of relevant mechanisms proposed by previous authors. The thermal conductivity of a nanocomposite is a complex function of the geometry of the components, thermal conductivity of the inclusions, aspect ratio of the inclusions, distribution within the medium and the connectivity between particles. The essential mechanisms invoked in this work are: (i) diffusion through the constituents of the medium, which forms the basis of effective medium approximation and (ii) interfacial scattering of thermal waves at matrix–particle interfaces. We have combined these two mechanisms to obtain an expression for the overall thermal conductivity, as outlined in the following sections.

3.1 Effective medium theory under diffusion limit

While discussing the effective properties of solid mixtures such as composites, several theoretical models have been developed, which adequately account for properties such as thermal conductivity. For a two-component mixture, previous researchers have generally tried simple models such as the series and parallel models to describe effective thermal conductivity of composites. These models assume that the components of the composite material are arranged either along series or parallel paths to the direction of heat flow. Applying this model to estimate the effective thermal conductivity of a binary composite

consisting of nanoparticles dispersed in a host matrix, we can write the following expressions for the effective thermal conductivity:

$$k_{\text{eff}} = \phi_v k_p + (1 - \phi_v) k_m \quad (2)$$

$$\frac{1}{k_{\text{eff}}} = \frac{\phi_v}{k_p} + \frac{(1 - \phi_v)}{k_f}, \quad (3)$$

where k_{eff} , k_p and k_m represent the thermal conductivities of the composite, dispersed particle material and the host matrix respectively. ϕ_v stands for the volume fraction of nanoparticles.

Using potential theory, Maxwell obtained an expression for the thermal conductivity of a homogeneous medium with randomly distributed, non-interacting, homogeneous spherical particles. The expression for effective thermal conductivity of such a composite is given by [8]

$$k_{\text{eff}} = k_m \frac{k_p + 2k_m + 2\phi_v(k_p - k_m)}{k_p + 2k_m - \phi_v(k_p - k_m)}. \quad (4)$$

This model also assumes that a composite has a periodic structure. Therefore, k_{eff} can be obtained by considering a representative unit and applying the principles of heat transfer to the entire system.

Another model often used to describe heat transfer in solid composites is the Bruggeman model [17], according to which the thermal conductivity of a composite medium is due to randomly distributed interacting spherical inclusions and the expression for effective thermal conductivity takes the form,

$$k_{\text{eff}} = (3\phi_v - 1)k_p + [3(1 - \phi_v) - 1]k_m + \sqrt{\Delta}, \quad (5)$$

where

$$\Delta = (3\phi_v - 1)^2 k_p^2 + [3(1 - \phi_v) - 1]^2 k_m^2 + 2[2 + 9\phi_v(1 - \phi_v)]k_p k_m.$$

This is an extension of the mean-field theory at higher concentrations of particles.

These two models describe the effective thermal conductivity of binary solid mixtures and do have limitations when applied to composites with particle inclusions of dimensions smaller than the phonon mean free paths for the host matrix. In this case, the properties of materials at particle–matrix interfaces are nearly the same, and so effects like thermal wave scattering at the particle–matrix boundaries cannot be accounted for within the framework of these conventional models, which are essentially diffusion-based. These models consider only the mechanism of diffusion as responsible for the effective thermal conduction in a solid composite. However, while dealing with nanoparticle inclusions in a host matrix, one has to consider effects like interfacial scattering that arises due to thermal impedance mismatch at particle–matrix boundaries.

Cheng and Vachon proposed a model for effective thermal conductivity by following the analogy between heat flow and electric current flow [28]. Based on this model, they have developed a theoretical method to predict the thermal conductivity of heterogeneous solid mixtures. This model assumes a parabolic distribution for the discontinuous phase (nanoparticle inclusions) with the constants of the distribution determined by the analysis and presented as a function of the volume fraction of the discontinuous phase. The

equivalent thermal conductivity of a unit cube of the mixture is derived in terms of the distribution function, and the thermal conductivity of the constituents. The technique was successful in predicting the thermal conductivity of mixtures that agree well with experimental data. Obviously, the Cheng–Vachon model [28] also describes heat transport through the composite as diffusion-controlled process. If a unit cell of the nanocomposite under consideration is sectioned into differential elements which are perpendicular to the direction of the heat flow, the effective thermal conductivity k_{dif} due to diffusion of thermal waves through nanoparticles is given by [28]

$$k_{\text{dif}} = R_e^{-1} = \frac{2}{\sqrt{C(k_m - k_p)}} \arctan \left(\frac{B}{2} \sqrt{\frac{C(k_m - k_p)}{k_p + B(k_m - k_p)} + \frac{1 - B}{k_m}} \right), \quad (6)$$

where k_m and k_p are the thermal conductivities of the polymer matrix and the filler nanoparticles, and other parameters are given by

$$B = \sqrt{\frac{3\phi_v}{2}}, \quad C = -4\sqrt{\frac{2}{3\phi_v}},$$

ϕ_v being the volume fraction of nanoparticle fillers.

Simplifying and rearranging terms in the above expression, the effective thermal conductivity k_{dif} for the mixture can be obtained from the expression

$$\begin{aligned} \frac{1}{k_{\text{dif}}} &= \frac{1}{\sqrt{C(k_m - k_p)}(k_m + B(k_p - k_m))} \\ &\times \ln \frac{\sqrt{k_m + B(k_p - k_m)} + 0.5B\sqrt{C(k_m - k_p)}}{\sqrt{k_m + B(k_p - k_m)} - 0.5B\sqrt{C(k_m - k_p)}} \\ &+ \frac{1 - B}{k_m}. \end{aligned} \quad (7)$$

This model describes the effective thermal conductivity of a nanocomposite as an overall effect of thermal transport through spherical nanoparticles distributed uniformly in a continuous base medium.

3.2 Role of interfacial scattering on thermal conduction in nanocomposites

All physical mechanisms have a critical scale below which the properties of a material change significantly. While downscaling the dimensions of a material to nanoregime, considerable changes in thermo-physical properties have been observed. When nanoparticles are embedded in a host matrix, boundaries are formed between the nanoinclusions and the host matrix, resulting in special effects like thermal wave backscattering at the interfaces. The mismatch in thermal impedance between the particle material and the base matrix, which originate from the differences in phonon spectra of the two media, is the

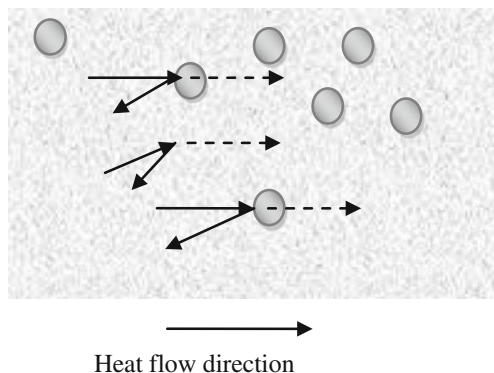


Figure 1. Demonstration of heat flow in a nanosolid, controlled by interfacial scattering at matrix–particle interfaces and diffusion through particles. Heat flow direction is from left to right. Transmission and reflection of thermal waves are shown by arrows.

root cause of these effects. The interfacial thermal wave scattering, demonstrated pictorially in figure 1, causes an interfacial thermal resistance, known as Kapitza resistance R_k , constitutes a barrier to heat flow at the nanoparticle–matrix boundary. The magnitude of the Kapitza resistance at an interface can be estimated using the acoustic mismatch model (AMM) or the diffusion mismatch model (DMM). Even while phonons are backscattered from the interfaces, normal thermal diffusions through the nanoparticles also occur as demonstrated in figure 1. This can be accounted for in terms of the transmission probability of dispersed nanoparticles in the host matrix. The strength of diffusion would be greater at the interface of a nanoparticle with higher mass density and thermal conductivity (higher transmission probability), while backscattering would have a greater influence when the nanoparticles have a lower mass density and thermal conductivity (lower transmission probability). While dealing with a nanocomposite consisting of nanoparticles embedded in a base material like a polymer, a combination of these two mechanisms will control the overall thermal conduction in the material.

3.3 Effective medium approximation including interfacial resistance

As has been outlined earlier, while dealing with nanoparticle inclusions in a continuous base matrix, thermal wave scattering plays a significant role in determining the effective thermal conductivity of nanocomposites. So we have employed the modified effective medium theory (EMT), proposed by Nan *et al* [18], to describe the role of thermal wave scattering at matrix–particle interfaces on the effective thermal conductivity of these nanocomposites.

Nan *et al* have modified Maxwell’s model including the concept of interfacial thermal resistance to describe the thermal conductivity of a two-component composite [18], with the following basic assumptions:

- (i) A composite material consists of different constituent phases; the different mechanical or chemical adherences at the interfaces, as well as the thermal expansion mismatch result in the scattering of thermal waves at the interfaces.

- (ii) Scattering rates at the interfaces vary with the aspect ratio (ratio of the longitudinal to transverse dimensions) of the dispersed particles.
- (iii) The interfacial thermal resistance influences the total thermal conductivity of the composite significantly.

In order to obtain an expression for thermal conductivity, this model considers a composite medium with multiple scatterers in the medium. In such a situation the thermal conductivity inside the composite varies from point to point. The variations in thermal conductivity can be written as

$$k(r) = k^0 + k'(r), \quad (8)$$

where k^0 is the constant part of the thermal conductivity for the homogeneous medium and $k'(r)$ is the arbitrary fluctuating part.

Using Green's function G for a homogeneous medium defined by k^0 and the transition matrix T for the entire composite medium, a rigorous solution for the distribution of the temperature gradient can be obtained. The resulting effective thermal conductivity k^* is given by

$$k^* = k^0 + \langle T \rangle (I + \langle GT \rangle)^{-1}, \quad (9)$$

where I is the unit tensor and $\langle \rangle$ denotes spatial averaging. The matrix T is

$$T = \sum_n T_n + \sum_{n,m \neq n} T_n G T_m + \dots \quad (10)$$

Here the first term is the sum of the T matrices of n particles and the succeeding term represents the interaction between particles. An accurate calculation of T is a formidable problem. For simplicity of calculation we approximate T as

$$T \cong \sum_n T_n = \sum_n K'_n (I - G K'_n)^{-1}, \quad (11)$$

thereby neglecting interparticle multiple scattering. Obviously, this approximation is valid only when the inclusion particles are dispersed uniformly in the base matrix.

Now, let us consider an ellipsoidal particle in the matrix, which is surrounded by a semisolid interface layer of thickness δ and thermal conductivity k_s , as a composite unit cell. Substituting $k^0 = k_s$ we directly obtain the equivalent thermal conductivities k_{ii}^c ($i = 1, 2, 3$) along the X'_i symmetric axis of this ellipsoidal composite unit cell as

$$k_{ii}^c = k_s \frac{k_s + L_{ii}(k_p - k_s)(1 - u) + u(k_p - k_s)}{k_s + L_{ii}(k_p - k_s)(1 - u)}, \quad (12)$$

where

$$u = a_1^2 a_3 / (a_1 + \delta)^2 (a_3 + \delta).$$

Here k_p is the thermal conductivity of the ellipsoidal particle; a_1 and a_3 are respectively, the radii of the ellipsoid along the X'_1 and X'_3 axes; and L_{ii} are the well-known geometrical factors dependent on the particle shape, and are given by [18]

$$\begin{aligned} L_{11} &= L_{22} \\ &= \frac{p^2}{2(p^2 - 1)} - \frac{p^2}{2(p^2 - 1)^{3/2}} \cosh^{-1} p \quad \text{for } p > 1, \end{aligned} \quad (13)$$

and

$$= \frac{p^2}{2(p^2 - 1)} + \frac{p^2}{2(p^2 - 1)^{3/2}} \cosh^{-1} p \quad \text{for } p < 1. \quad (14)$$

Also, $L_{33} = 1 - 2L_{11}$.

In the above expressions, $p = a_3/a_1$ is the aspect ratio of the ellipsoid, and $p > 1$ and $p < 1$ are for a prolate ($a_1 = a_2 < a_3$) and an oblate ($a_1 = a_2 > a_3$) ellipsoidal inclusion, respectively.

By ultimately passing to the limit $\delta \rightarrow 0$, $k_s \rightarrow 0$ (the interfacial thermal resistance is thought of as the limiting case of heat transport across bulk phase by a thin, poorly conducting interface region), we rewrite eq. (12) as

$$k_{ii}^c = \frac{k_p}{(1 + \gamma L_{ii} k_p / k_m)} \quad (15)$$

with

$$\gamma = (2 + 1/p) \alpha, \quad \text{for } p \geq 1$$

or

$$\gamma = (1 + 2p) \alpha, \quad \text{for } p \leq 1. \quad (16)$$

Here a dimensionless parameter, α , is introduced, which is defined by

$$\begin{aligned} \alpha &= \frac{a_k}{a_1}, \quad \text{for } p \geq 1, \\ \alpha &= \frac{a_k}{a_3}, \quad \text{for } p \leq 1, \end{aligned} \quad (17)$$

where a_k is the Kapitza radius defined by $a_k = R_{bd} k_m$, R_{bd} being the interfacial Kapitza resistance and k_m being the thermal conductivity of the host matrix phase.

When the inclusions become spheres, $p = 1$, so that

$$L_{11} = L_{33} = 1/3 \text{ and } \langle \cos^2 \theta \rangle = 1/3,$$

then eq. (15) reduces to

$$K_{11}^c = K_{22}^c = K_{33}^c = \frac{k_p}{(1 + \alpha k_p / k_m)}$$

and thermal conductivity limited by interfacial scattering is then given by

$$k_{\text{sct}} = k_m \frac{k_p(1 + 2\alpha) + 2k_m + 2\phi_v[k_p(1 - \alpha) - k_m]}{k_p(1 + 2\alpha) + 2k_m - \phi_v[k_p(1 - \alpha) - k_m]}. \quad (18)$$

This expression represents thermal conductivity under the effective medium approximation including interfacial thermal resistance. It is evident that a large enough value for α can give rise to a de-enhancement in the effective thermal conductivity for a nanocomposite.

3.4 Combined effect of interfacial scattering and diffusion

We assume that the effective thermal conductivity of the nanocomposite, including diffusion and scattering effects, can be obtained by adopting a series resistance model for conduction at the nanoparticle–matrix interface. Let r_{sct} and r_{dif} represent the resistances corresponding to the scattering and diffusion components of the thermal waves propagating across the interfaces of the two different phases. Then we can write the overall effective thermal resistance r_{nc} as

$$r_{\text{nc}} = r_{\text{sct}} + r_{\text{dif}} \quad (19)$$

or, in terms thermal conductivity we can write

$$\frac{1}{k_{\text{nc}}} = \frac{1}{k_{\text{sct}}} + \frac{1}{k_{\text{dif}}}. \quad (20)$$

The model proposed by Nan *et al* [18] describes the effective thermal conductivity of a nanocomposite as controlled by interfacial effects (k_{sct}), while the Chen–Vachon model [28] discusses the heat transport mechanism in a solid composite in terms of diffusion of thermal waves (k_{dif}). We define the overall conductivity of the nanocomposite under consideration as a combination of these two mechanisms, defined by eqs (7) and (18), so that we can write the effective thermal conductivity of a nanocomposite as

$$k_{\text{nc}} = \frac{k_{\text{sct}} \times k_{\text{dif}}}{k_{\text{sct}} + k_{\text{dif}}}. \quad (21)$$

This expression has been used to calculate the thermal conductivity of the nanocomposites presented in this work and to compare with experimental results.

3.5 Comparison of experimental results with theory

The experimental and theoretical variations of the normalized thermal conductivity of TiO_2/PVA and Cu/PVA nanocomposites with volume fractions of nanoparticles are shown in figures 2 and 3 respectively. The experimental plots shown in these figures are from PPE measurements. It can be seen that the variations of normalized thermal conductivity as a function of particle volume fraction are different for the two sets of samples. From these curves it is clear that the interfacial thermal resistance and thermal conductivity of nanoparticles have strong influence on the effective thermal conductivity of nanocomposites. For TiO_2/PVA , the calculated effective thermal resistance is of the order of 10^{-7} , and the low thermal conductivity of bare TiO_2 nanoparticles gives rise to a decrease in effective thermal conductivity with the increase in nanoparticle volume fraction. Thus, we see that the scattering mechanism is dominant over thermal wave diffusion for TiO_2/PVA samples because of the low transmission probability for thermal waves through TiO_2 nanoparticles. The theoretical curves that we have plotted for

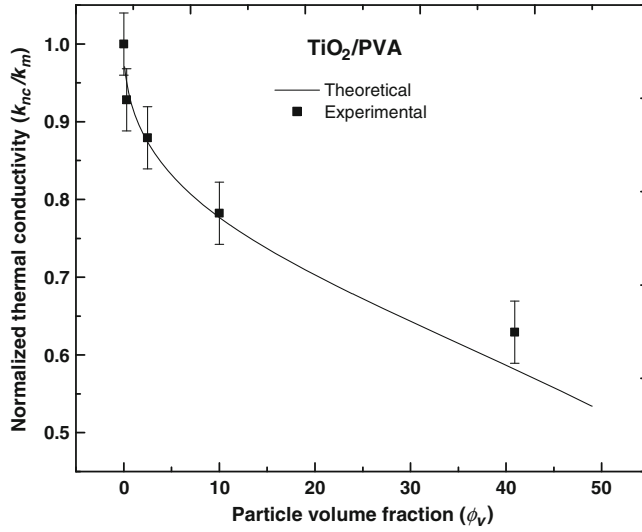


Figure 2. Variations of effective thermal conductivity of TiO₂/PVA nanosolids as a function of volume fraction of TiO₂ nanoparticles. Experimental values are from PPE measurements.

the TiO₂/PVA system is for $\alpha = 0.78$ and the corresponding experimental variation is such that a decrease of about 40% in effective thermal conductivity occurs as the particle volume fraction increases to about 45%. This decrease in thermal conductivity can be interpreted as due to Kapitza scattering of short wavelength phonons from the polymer

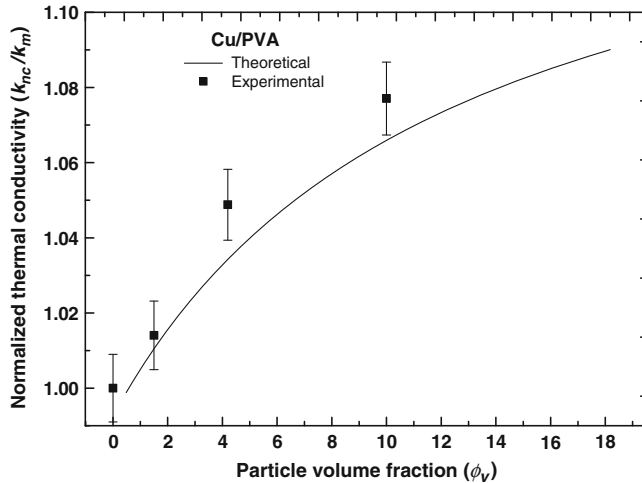


Figure 3. Variations of effective thermal conductivity of Cu/PVA nanosolids as a function of volume fraction of copper nanoparticles. Experimental values are from PPE measurements.

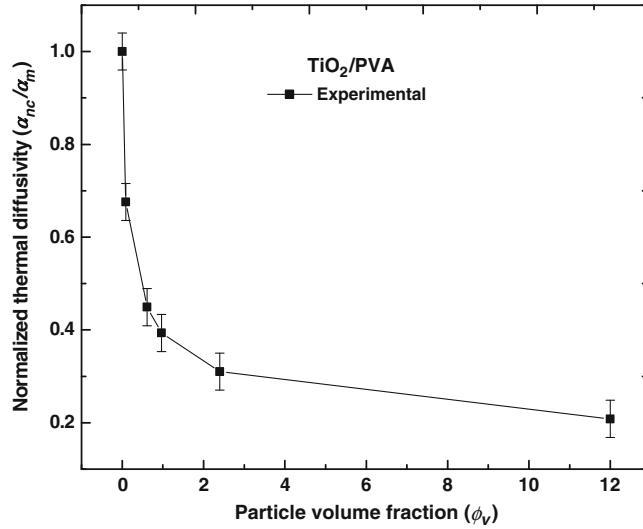


Figure 4. Variation of effective thermal diffusivity of TiO₂/PVA nanosolids with nanoparticle volume fraction. Values are from PA measurements.

matrix–nanoparticle interfaces, with the nanoparticles acting as impurities. The limited diffusion due to low transmission probability as a consequence of low thermal conductivity of bare TiO₂ nanoparticles cannot compensate for the strong decrease due to scattering in the system.

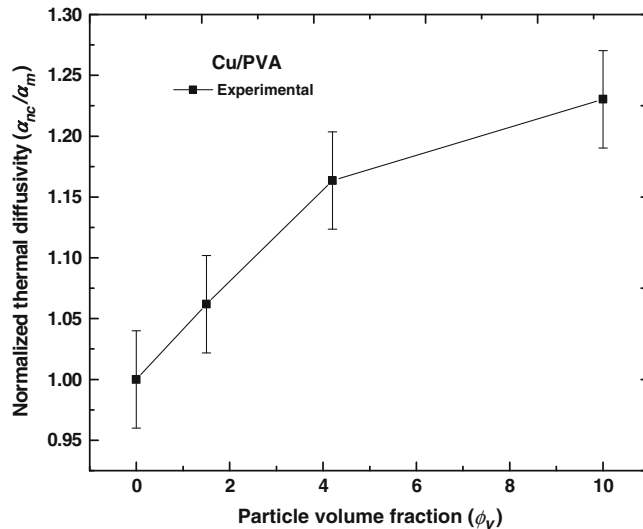


Figure 5. Variation of effective thermal diffusivity of Cu/PVA nanosolids with nanoparticle volume fraction. Values are from PA measurements.

Though the variations of specific heat capacities with particle volume fraction have also been measured using PPE technique, these are not shown here as the results just follow the corresponding effective medium expression and are not of direct relevance to the theme of this paper.

In Cu/PVA samples, the normalized value of effective thermal conductivity increases as the nanoparticle volume fraction increases because of the higher thermal conductivity of the included copper nanoparticles. It is found that for 5% copper nanoparticle concentration, the effective thermal conductivity increases by 7%. Though phonon scattering from the particles acting as impurities is present in this regime also, strong diffusion of thermal waves takes place into the particles, resulting in an effective enhancement. At higher volume fractions, the competing effects of scattering and diffusion mechanisms tend to saturate the thermal conductivity.

The measured variations of thermal diffusivity of these samples using the PA technique are shown in figures 4 and 5. The thermal diffusivity values obtained from PA measurements agree well with the corresponding values obtained from PEF measurements. From these figures it is clear that the effective thermal diffusion in these nanocomposites is also determined by scattering as well as diffusion mechanisms. As expected, variations of thermal diffusivity follow the corresponding variations of thermal conductivity.

4. Conclusions

From the thermal conductivity analysis presented in this work, it is clear that nanocomposites with metallic inclusions exhibit a total reversal in thermal conduction compared to the corresponding materials with nonmetallic inclusions. We see that the effective thermal conductivity of these nanocomposites is essentially determined by particle volume fraction and particle thermal conductivity, and are controlled by the competing mechanisms of scattering and diffusion. Our experimental results as well as theoretical predictions open up the possibility to tune the normalized thermal conductivity of nanocomposites from a low negative to high positive values compared to the thermal conductivity of the base solid. More systematic measurements and analysis of the thermo-physical properties are needed for testing and establishing the applications of these materials.

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