

# **THERMAL CONDUCTION OF NANO-DIAMOND DISPERSED POLYURETHANE NANO-COMPOSITES**

Andrew P Limmack and Dr H-X Peng  
ACCIS, University of Bristol Department of Aerospace Engineering  
Queens Building, University Walk, Bristol. BS8 1TR  
Andy.Limmack@bristol.ac.uk

## **SUMMARY**

Nano-composite materials consisting of nano-diamond in a polyurethane matrix developed for erosion resistant coatings were tested for changes in thermal conductivity over the unmodified resin. A modest increase of 30% was observed but the materials exhibit greater potential when sprayed as coatings due to the elimination of thick casting defects.

*Keywords: Nano-composite, polyurethane, diamond, thermal conduction, nano-particle*

## **INTRODUCTION**

As part of a larger initiative on the development of erosion resistant nano-composite coatings for aerospace applications, the possibility of improving the thermal conduction of these coatings over the base matrix polymer has been looked into. Traditional solutions consisted of a metallic leading edge, typically formed from nickel or titanium, which perform poorly when subjected to solid particle erosion and there has been an increasing trend to use complete polymeric coatings on aircraft and hovercraft propellers and self adhesive tape or thermoformed boot on rotor blades or other aircraft components, such as fuselage components, subject to solid particle erosion in operation. Polyurethane, or a blend containing polyurethane, is normally used due to its outstanding solid particle erosion resistance.

The rapid elastic deformations caused by sustained high speed particle impacts leads to significant localised heating the coating which results in material softening and thermal degradation effects [1-3] which highlights a desire to conduct heat away from the initial impact site as quickly as possible. A separate, but no less important consideration, is that of the effect of polymer coatings on the effectiveness of heater based de-icing systems fitted to aircraft. Insulating coatings and tapes reduce the efficiency of heating elements embedded into the leading edges of blades meaning more energy must be used and the composite materials are subjected to unnecessary levels of heating.

Common methods of obtaining increased thermal conduction in polymers is to include metallic particles such as aluminum, silver and carbon nano-tubes [4, 5] however an electrically conductive filler and hence an electrically conducting coating is not desirable for many applications and this requirement for an easy to obtain a thermally conductive but

electrically insulating filler that had the potential to improve erosion and cutting resistance led to the selection of commercially produced nano-diamond.

## **EXPERIMENTAL**

### **Materials**

The selection of polyurethane resin and thinning solvent was restricted due to the larger scheme of spray able coatings and industrial collaboration and requirements and was thus not entirely suitable for the production of samples needed for this section of the research. The resin used is a low isocyanate TDI (toluene diisocyanate) polyurethane resin and was obtained from Baxenden Chemicals Ltd. Ethacure 300 chain extender was supplied by Albermarle Ltd. Solsperse 34750 Hyperdispersant was supplied by Noveon (UK) Ltd. 100nm detonation nano-diamond was obtained from Shandong Beifang Jidian Zongchang, Shandong, PR China.. This form of diamond is very low cost and is well known to have the possibility of various functional groups [6] which have the potential to be exploited for improved mechanical performance for erosion purposes and they may also offer a small benefit in thermal conduction [7, 8] however no effort to remove or deliberately exploit these functional groups were made for this work and the diamond was used as received.

### **Sample Preparation**

Due to the loading limits imposed by the massive surface area of nano-particles It was decided to limit the weight fraction of nano-diamond to 5% for the sprayed coatings however an additional 8% weight fraction was introduced for this investigation into thermal conduction. Weight loadings are based on the final weight of the nano-composite after chain extender has been added and all solvents have evaporated.

The pure polyurethane sample was produced by mixing the viscous pre-polymer with a pre-determined amount of solvent using a high speed saw tooth mixer prior to the manual mixing of the chain extender and pouring into an open glass 120x40x2mm mould. The ratio of solvent to resin was carefully selected to give adequately low viscosity for thorough chain extender mixing and rapid degassing while not giving rise to large shrinkages through solvent evaporation during cure which could lead to cracking during the fragile gel phase.

Due to significant viscosity increases from the addition of the nano-diamond into the ratio of resin to solvent needed to be adjusted for each loading to maintain possibility. Rheological analysis of the 1, 3 and 5% weight loadings was performed to enable formulations to be calculated. The pure resin to solvent ratio was used as a starting value and the behavior and viscosity of the resin was compared to that of the pure material as more solvent was added to the solution.

The first stage of sample production was to produce a highly loaded nano-particle slurry with the nano-diamond dispersed at high loading in ethyl acetate which was pre-mixed with Solsperse 34750 to help disperse and stabilise the nano-diamond. Solsperse 34750 was supplied as a 50% by weight solution with ethyl acetate and was used in the ratio of 0.4g

active polymeric dispersant to every 1g of nano-diamond which was selected through initial surface area approximation and sedimentation analysis. Electron microscopy and size distribution analysis was then used to verify dispersion. Dispersion was performed using a high powered Sonics and Materials Inc. Vibra-Cell 750 fitted with a 13mm diameter half wave extender due to the low surface tension solvent. The ultrasound unit was used at 60% amplitude for one minute following the addition of each 0.5g of diamond into the solution and then a further 30 minutes at 25% amplitude utilising the pulse feature and a cooled oil bath to reduce heating solvent evaporation.

The nano-particle slurry was then combined with the pre-polymer resin using a saw tooth high speed dispersing blade in the ratios required to make the desired final nano-composite loadings.

The normal production technique for this resin is through spraying the heavily thinned resin in a two component spray system with component mixing occurring at the gun due to the rapid onset of cure of the pre-polymer with the chain extender. This method was not suitable due to the thickness of samples required so an open glass mould was used with samples produced in layers to mimic the spray process, all be it with thicker coats, approximately of approximately 0.15mm thick. This technique was employed to prevent trapping solvent during the cure which would cause highly destructive internal stresses and lead to the samples cracking. Mixing of the chain extender was performed by hand using a sample of each solution immediately prior to pouring and samples were left for 2 hours between the application of each layer to allow solvent to evaporate. The samples were then left for 24hrs before post curing at 95°C for 6 hours.

## **TESTING APPARATUS**

Rheometry was performed on a Malvern Gemini Rheometer, courtesy of the EPSRC.

Particle sizing was performed on a Malvern HPPS, also courtesy of the EPSRC.

Thermal conduction analysis was conducted by Dr Z Y Zhang at the University of Plymouth using a Kyoto QTM-500 Thermal Conductivity Meter using a hot wire method at 23°C.

SEM analysis was performed on a JEOL JSM 6330F electron microscope.

## **RESULTS AND DISCUSSION**

Two sets of nano diamond samples, A and B, were produced and a single pure polyurethane sample. The production of the pure sample was much easier and could be performed with a single layer and bubble content and surface quality was the best of all the samples. As the diamond loading increased as did the bubble content and defects of the surface as the sample viscosity increased making it more difficult to mix and pour without creating bubbles and this increasing level of defect must be considered when analysing the results.

## Rheometry

Rheological testing was performed on a Malvern Gemini rheometer using 40mm diameter 4° steel cone and plate geometry at 25°C to mimic the room temperature processing conditions. A solvent trap was utilised due to reduce evaporation of the volatile solvent. Figure 1 shows the shear rate ramp results for the 1, 3 and 5% nano-diamond solutions at the same ratio of resin to solvent as the 0% solution. The 1 and 3% weight solutions exhibited very similar viscosities however it can be seen that the increase to 5% weight massively increases the viscosity, especially at low shear rates.

For the 1 and 3% samples it was possible to reduce the viscosity of the solutions to those near that of the unmodified resin and solvent solution with approximately 20% more solvent. However the 5%, and 8%, solutions required over double the amount but this would create massive levels of shrinkage during cure so a trade-off had to be made between ease of preparation and sample quality.

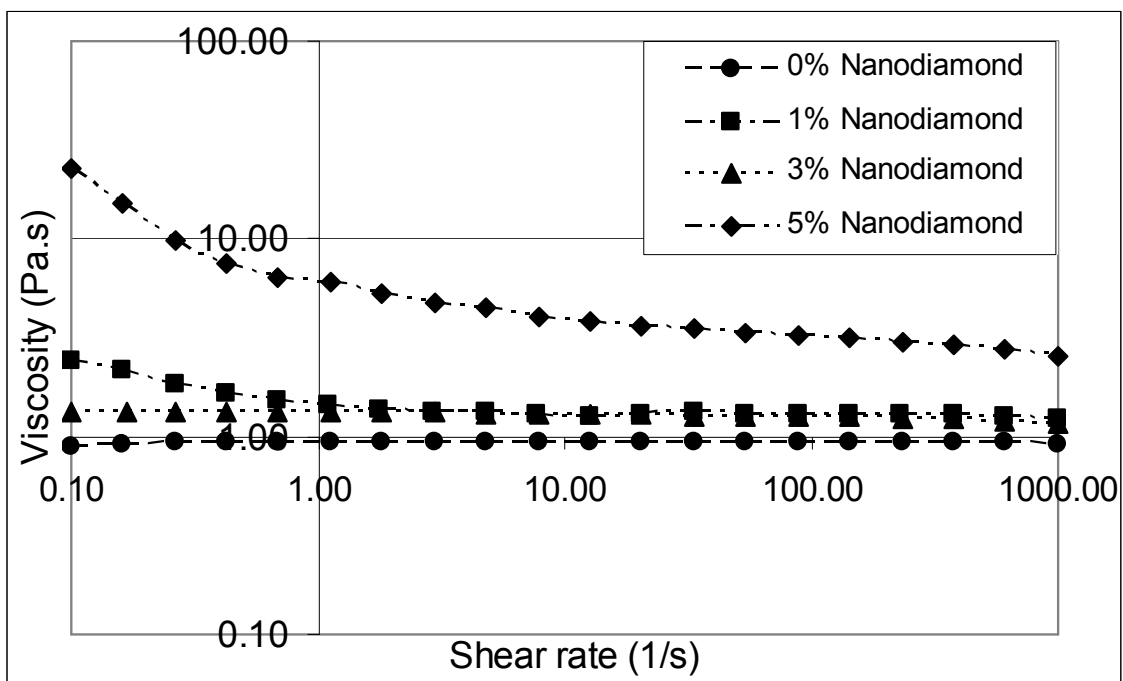


Figure 1: Shear rate ramp results for nano-composite formulations at normal solvent level

## SEM Analysis

The edges of the samples trimmed prior to sending for thermal analysis were examined with an SEM. In low magnification the images show the fracture planes and bubble content

and in high magnification allows us to examine the dispersion. Samples were prepared by freezing in liquid nitrogen; however the higher nano-composite samples would self fracture during the rapid cooling with an increasing speed and ferocity with increasing loading.

Low magnification images of the fracture planes for each of the samples are shown in figures 2. It can be clearly seen that the internal defects inside the samples increases with nano-particle loading and this is also apparent on the surface finish of the samples with a greater amount of bubbles on the surface.

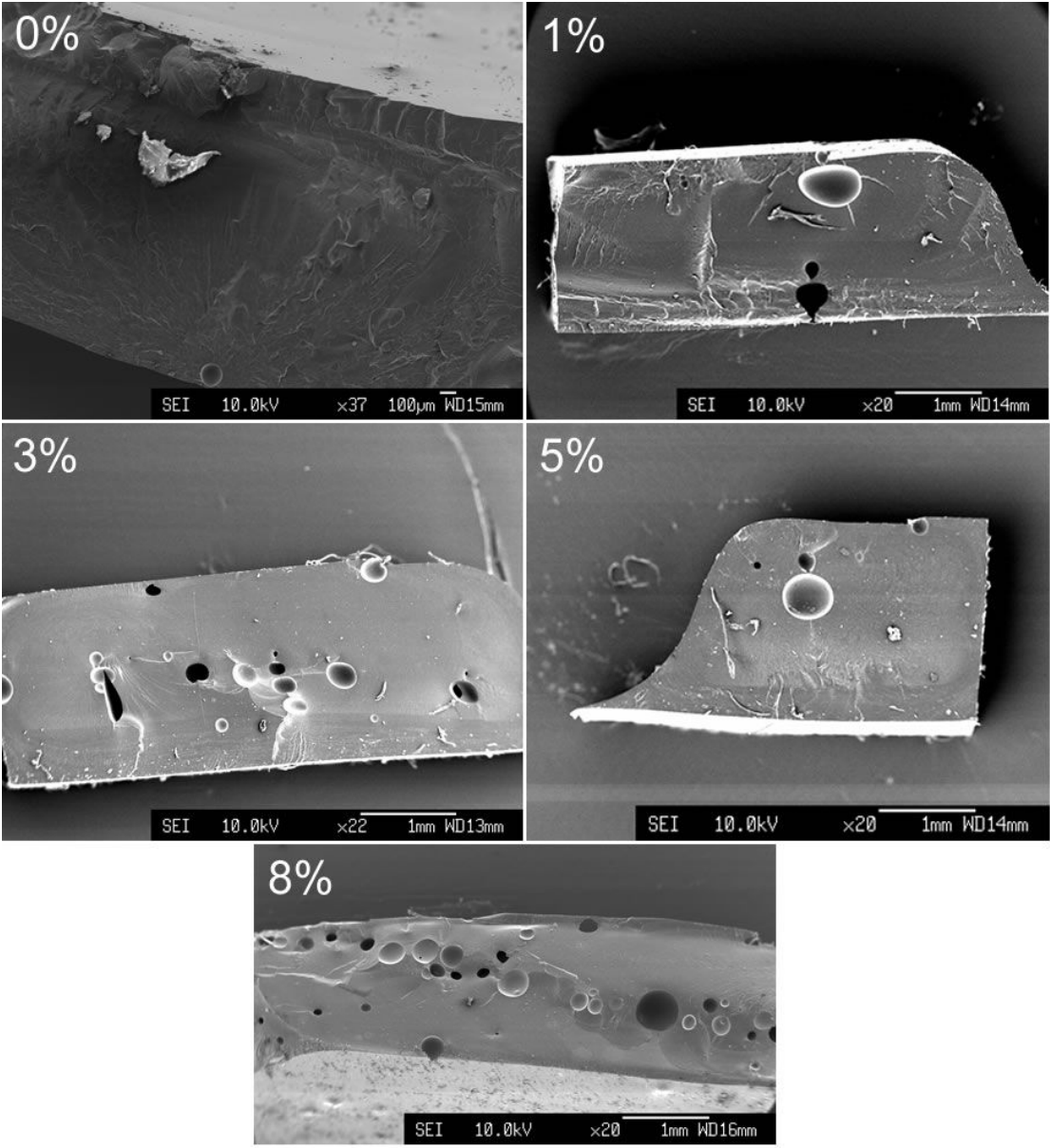


Fig. 2: Polyurethane nano-composite fracture planes

Higher magnification images, shown in figure 3, show the presence of nano-particles on the fracture planes. The 1% sample shows both what appears to be a single particle, labeled A, and a pull out crater, labeled B. The particle seems to be well embedded in the resin and of the order of 100nm as expected. The 3% sample shows two distinct particles on the fracture plane, again the size is in the order of 100nm and the dispersion is good and particle density what we expect in a 3% (by weight) nano-composite. The 5% sample shows a noticeable increase in the number of visible entities which we can regard as nano-diamond particles. Again these particles are in the 100nm range and well dispersed with spacing coherent with a 5% nano-composite. The 8% sample is much less magnified to show the particle density. While it is clear that there are a large number of visible particles the size and elongated shapes would suggest there is some agglomeration of particles in the 8% nano-composite samples. On further magnification in figure 4 we can indeed see that while there is evidence of particles in the 100nm range there is also evidence of clustering which could lead to a less than proportional improvement in thermal conduction from lower loaded samples.

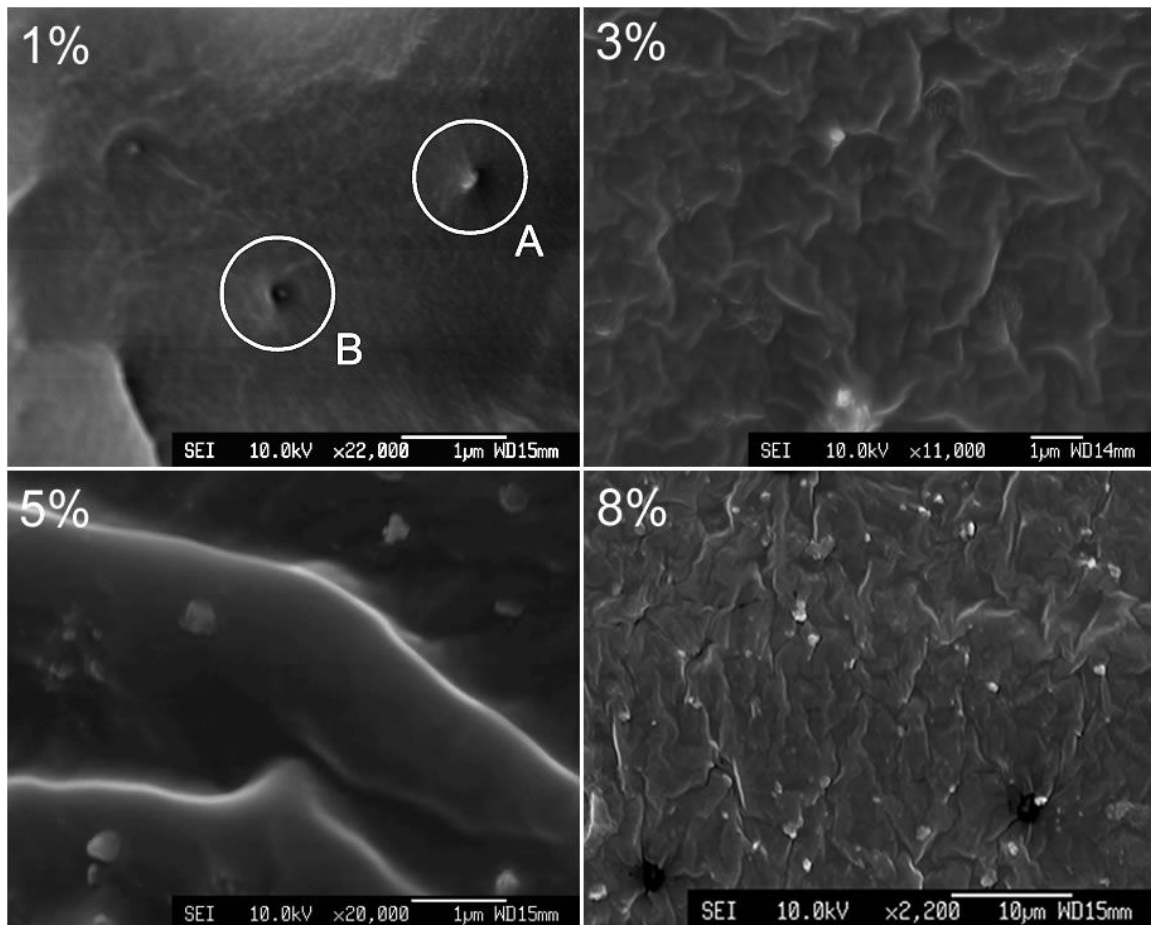


Fig. 3: 1, 3, 5 and 8% nano-diamond dispersion in polyurethane

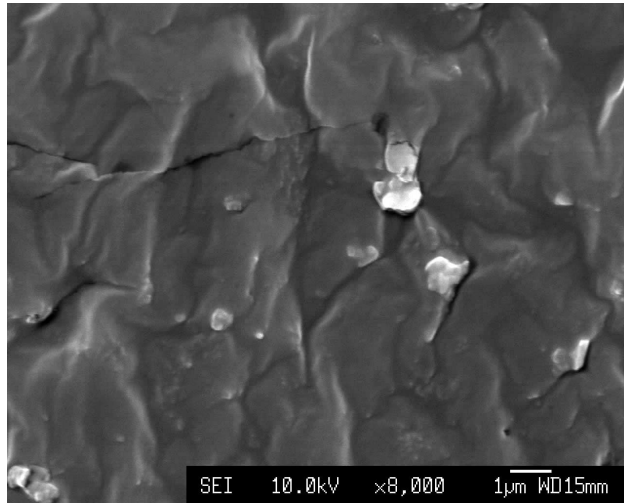


Fig. 4: Higher magnification of 8% nano-composite

### Thermal Conduction

The results for the pure polyurethane sample came to an average of 0.1692W/mK which is a typical and as expected value for pure polyurethane. The results of all of the samples are shown in table 1. It should be noted that the 1% sample ‘1A’ had particularly poor surface quality for a significant proportion of one contact side and this has resulted in the significant drop in conduction for this sample.

Table1: Hot wire thermal conduction results

Sample	Test conductance (W/mK)					Average (W/mK)	Standard Deviation
	1	2	3	4	5		
<b>Pure (0%)</b>	0.1729	0.1767	0.1691	0.1619	0.1655	<b>0.1692</b>	0.0052
<b>A1 (1%)</b>	0.1461	0.1615	0.1510	0.1488	0.1501	<b>0.1515</b>	0.0053
<b>B1 (1%)</b>	0.2067	0.2001	0.2051	0.2046	0.2078	<b>0.2049</b>	0.0026
<b>A3 (3%)</b>	0.2101	0.2108	0.2113	0.2056	0.2062	<b>0.2088</b>	0.0024
<b>B3 (3%)</b>	0.2150	0.2084	0.2173	0.2174	0.2088	<b>0.2134</b>	0.0040
<b>A5 (5%)</b>	0.2028	0.2065	0.2077	0.2007	0.2038	<b>0.2043</b>	0.0025
<b>B5 (5%)</b>	0.2172	0.2185	0.2226	0.2176	0.2202	<b>0.2192</b>	0.0020
<b>A8 (8%)</b>	0.2070	0.2089	0.2082	0.2100	0.2102	<b>0.2089</b>	0.0012
<b>B8 (8%)</b>	0.2139	0.2218	0.2177	0.2232	0.2186	<b>0.2190</b>	0.0033

Figure 5 shows the relative thermal conduction of the nano-diamond filled polyurethane when compared to the pure polyurethane value of 1692W/mK. Batch A had a much greater number of surface defects, particularly the 1% sample as mentioned previously which actually shows a reduction in conduction due to the large uneven region and this shows the extent to which the surface defects affect the results of this testing method. Batch B samples were much improved and show a conduction increase of over 20% with just 1% weight, a then modest rise through 3 and 5% up to 30% were it plateaus.

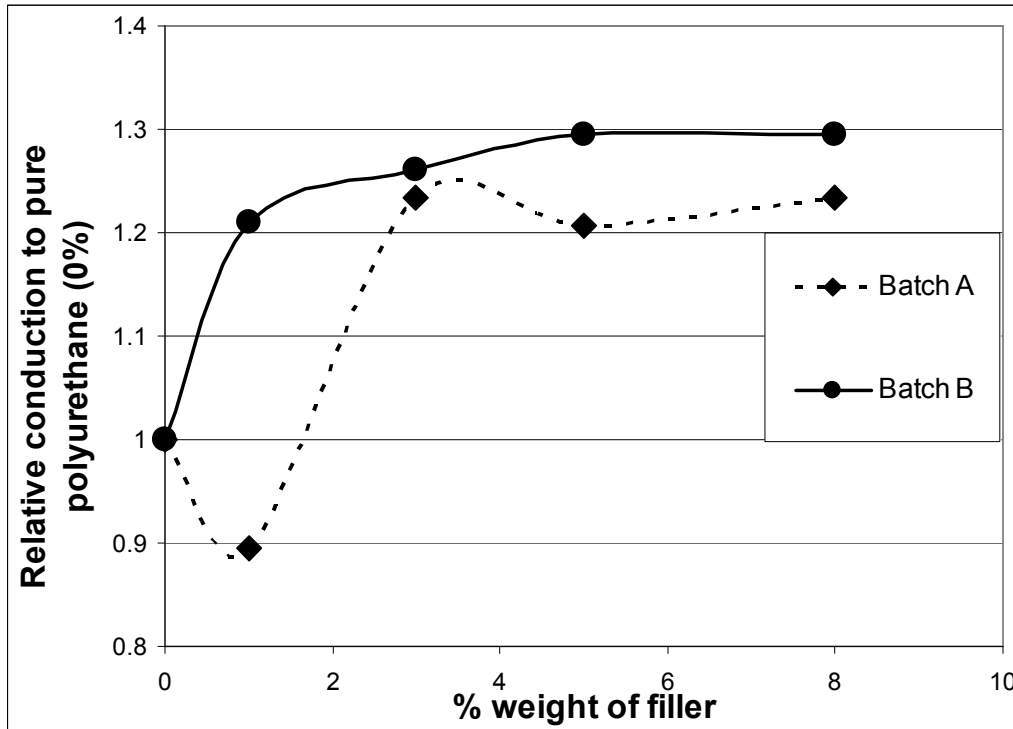


Fig. 3: Relative thermal conduction of nano-composites compared to pure polyurethane

### CONCLUSION

Preparation of thick, over 1mm, samples with loadings of 5% and above by weight was very difficult with this resin system as it is designed as a thin sprayed coating but good dispersion of 100nm nano-diamond using a suitable chemical dispersant and high powered ultrasound was demonstrated.

The improvement in thermal conduction plateaus at 30% is modest but reasonable at nano-diamond loadings as low as 5%, however analysis of both of internal defects and external surface defects it is not unfeasible that this figure can be significantly improved. These defects increased greatly between the 5% and 8% samples and there would also appear to be a degree of nano-particle agglomeration in the high magnification SEM pictures of the 8% which were not seen in the lower loaded samples. This agglomeration can always be



expected in nano-composite polymers but further optimization of the processing conditions should remedy the agglomeration in these samples and maximise the effectiveness of the nano-diamond inclusion.

The SEM results also suggest that the sample were no-where near the percolation density and with further processing and when coupled with the spray production methods it may be possible to further increase the nano-diamond loading. Further testing work will also be focused on evaluating performance for the real life application of thin sprayed coatings bonded to substrates for de-icing applications.

### ACKNOWLEDGEMENTS

The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC) and industrial partners for their support and funding for this CASE project. Particular thanks should go to the EPSRC Engineering Instrument Pool for the loan of equipment as well as Noveon UK and Albermarle ltd for the supply of chemicals.

### REFERENCES

1. S. W. Zhang , Wang Deguo, and Yin Weihua, *Investigation of abrasive erosion of polymers*. Journal of Materials Science, 1995. 30(18): p. 4561-4566.
2. Zhang, S.W., et al., *Abrasive erosion of polyurethane*. Journal of Materials Science, 2001. 36(20): p. 5037-5043.
3. Molinari, J.F. and M. Ortiz, *A study of solid-particle erosion of metallic targets*. International Journal of Impact Engineering, 2002. 27(4): p. 347-358.
4. Zhang, J., M. Tanaka, and T. Matsumoto, *A simplified approach for heat conduction analysis of CNT-based nano-composites*. Computer Methods in Applied Mechanics and Engineering, 2004. 193(52): p. 5597-5609.
5. Ju, S. and Z.Y. Li, *Theory of thermal conductance in carbon nanotube composites*. Physics Letters A, 2006. 353(2-3): p. 194-197.
6. Liu, Y., et al., *Functionalization of Nanoscale Diamond Powder: Fluoro-, Alkyl-, Amino-, and Amino Acid-Nanodiamond Derivatives*. Chemistry of Materials, 2004. 16(20): p. 3924-3930.
7. Singh, I.V., M. Tanaka, and M. Endo, *Effect of interface on the thermal conductivity of carbon nanotube composites*. International Journal of Thermal Sciences, 2007. 46(9): p. 842-847.
8. Shenogin, S., et al., *Effect of chemical functionalization on thermal transport of carbon nanotube composites*. Applied Physics Letters, 2004. 85(12): p. 2229-2231.