Thermal conductivity and tensile properties of tin oxide filled UPR/EPS composites with and without organic nanocrystal

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Abstract: Panel composite for building application made from waste expanded polystyrene (EPS) and unsaturated polyester (UPR) were fabricated and tested in this research for their tensile and thermal characteristics in determining its insulation properties. Research had been carried out to incorporate EPS into UPR with addition of two additives types which are tin oxide (SnO) stand alone, and tin oxide in combination with organic nanocrystals. The weight percentage of SnO had been varied from 0.1 to 2%, and the nanocrystals between 0.1 to 0.5%; both fabricated via casting and compression of the UPR/EPS composite. The testing performed are tensile properties by an Instron Universal Tensile Machine; and thermal conductivity test by using KD2 Pro hand-held thermal probe. It was found that, by using UPE/EPS, the additives affected the composites’ thermal conductivity and tensile capabilities. For tensile strength, the control sample showed the highest tensile strength at 22.2 MPa. For thermal conductivity (k value), the lowest value was recorded by the 1% SnO stand alone at an approximate ~ 0.172 W/m.K. Via organic nanocrystal use fixed at 0.1%, the k value increases up to a certain point with increasing SnO. Addition of more SnO and nanocrystal incorporation had mostly increases its thermal conductivity and heat capacity. Heat capacity was also found to be at the lowest in the 1% SnO stand alone sample at 2.008 MJ/m³.K.

1. Introduction

Composite materials has become one of the highly demanded construction material from industrial and commercial consumer worldwide. These composites are made from two or more constituent materials having different physical or chemical properties, that upon combination, produces a hybridized material with characteristics different from the individual components. Generally, the composite material is widely used in building construction. Besides that, the use of composite materials allows many new design possibilities such as orthopaedic biomaterials [1,2].

UPR is a widely utilized economical thermoset material due to its excellent processing ability and good cross-linking tendency as well as mechanical properties when cured; which lead it to be applied for boat construction and panelling manufacture [3]. EPS is a polymeric foam material that has certain desirable properties because of its structure. EPS is a rigid and tough, closed-cell, and often white in colour foam generated from polystyrene beads. Familiar uses include moulded sheets for building insulation and packing material for cushioning fragile items inside boxes [4].
Investigation regarding using EPS foam as continuous filler within UPR matrices had been investigated by numerous researchers [5–7]. These prior researches had focus on several distinct aspects of the EPS continuous filler filled UPR composites such as its thermal conductivity and its flame retardation ability.

This current research had fabricated EPS filled UPR matrix sheet with aerogel as an insulator and nanocrystals acting as an infrared reflector additive to impart better polymeric product life-cycle via lessening polymeric solar degradation. Kandare et al., (2008) shown similar polymer matrix with zinc oxide (ZnO) and SnO acting as effective flame retardant synergist and smoke suppressants in several polymer systems. [8]

Granqvist, et. al. (2016) explained how the usage of infrared additives also played several functions based on its heat insulation properties. They also noted that SnO also had been used before as an infrared additives. In the production of certain film, SnO was used due to its high electrical conductivity and high in visible and near infrared region of solar radiation. [9,10]

Thermal conductivity measures the effectiveness of a material in conducting heat; and thus, acting reciprocally towards a material's thermal resistance and insulation. Thermal insulation is a material or material combinations, that, when properly applied, retards the rate of heat flow by conduction, convection, and radiation. Thermal insulation helps reduces a building’s energy consumption through properly maintaining a building’s internal environmental temperature, and preventing unnecessary heat flow between the walls of the building and its outside [11,12].

2. Materials and Methods

2.1 Materials

The selected thermo-set matrix material used for fabricating these composite systems is UPR system, Reversol consisting of vinyl ester oligomers having density of 1.12 g/cc, viscosity of 450-600cps with 41-44% styrene content. Methyl Ethyl Ketone Peroxide (MEKP) and Cobalt solution used as initiator and promoter each, were supplied together with the UPE resin by Revertex Sdn Bhd. These ingredients are similar to materials used by previous researches as codified by the research of Rashidan et al., (2009) [13].

The EPS or Styrofoam filler was obtained from waste material; organic nanocrystal (ONC) was synthesised by Green Polymer Research Lab, UiTM Malaysia; and finally, SnO solutions were supplied by Merck KGaA.
2.2 Composite Fabrication and Testing

Recycled EPS, fixed at 10% parts by weight (%wt) of UPR resin, was blended together by utilizing a high speed agitation mixer until complete dissolution was attained. Gaseous contaminants present are eliminated from the mixture with vacuum suction, while solid contaminants are removed from the mixture after gravity settling for 24 h. The ONC utilized was independently synthesized by another researcher of the Green Polymer Research Lab, UiTM Malaysia from cellulose microfibers via proprietary acidolysis process, dried using vacuum drying, and was powderized using a ball mill machine.

The designated additives were then added to the mixture before the samples were prepared. The SnO-only set was varied between 0 to 2.0 wt%: For the second set, SnO content was varied between 0 and 0.5 wt%, while ONC was set constant at 0.1 wt%. The MEKP and cobalt solution usage was set to 2.5%wt and 1 drops respectively for each sample. Compressive moulding process were done onto aluminium mould, where the mixture jellifies in the mould before any pressure was applied. Gelling time was set to be about 20 to 30 min. Once sufficient gel forms, low pressure press were applied for 1 h at 70°C to retain required shape, and complete curing were done by leaving the sample outside the mould for 24 h at room temperature. These steps are similar to the research process codified by Rashidan et al., (2009) [13]

This paper was produced from a study conducted via qualitative analysis of the manufactured samples. The tensile properties of the samples were determined by an Instron Universal Machine (model Testometric MICR0500) which adheres to requirements of the ASTM D5083 standard. The samples were also tested via a thermal probe to determine their thermal conductivity, thermal diffusivity and volumetric heat capacity. The thermal utilized is the KD2 Pro Hand-held Thermal Probe which adheres to ASTM D5334-08 and IEEE Standard 422-03 as set by ASTM and IEEE.

3. Result and Discussion

3.1 Thermal Characteristics

The sample A and 1 are basically the same formulation despite produced as part of two separate set of test samples. This is shown by their collective data which are relatively similar and narrowly deviate from each other.

Thermal conductivity is a material property measuring the ease or difficulty of which heat energy is conducted through a specific type of material. The higher thermal conductivity, (k) value indicates the material is conducting heat faster as compared to more thermal resistant material.
Table 1. Thermal properties comparison of SnO-only and SnO-ONC samples.

| Sample Code | Additives           | Thermal Conductivity (W/m.K) | Volumetric Specific Heat (MJ/m³.K) | Diffusivity (mm²/s) |
|-------------|---------------------|------------------------------|-----------------------------------|---------------------|
| A           | -                   | 0.202                        | 2.186                             | 0.092               |
| B           | 0.5 % SnO           | 0.190                        | 2.030                             | 0.094               |
| C           | 1.0 % SnO           | 0.172                        | 1.921                             | 0.090               |
| D           | 2.0 % SnO           | 0.280                        | 3.134                             | 0.089               |
| 1           | -                   | 0.211                        | 2.371                             | 0.089               |
| 2           | 0.1 % SnO - 0.1 % ONC | 0.245                     | 2.743                             | 0.089               |
| 3           | 0.2 % SnO - 0.1 % ONC | 0.331                     | 3.699                             | 0.089               |
| 4           | 0.3 % SnO - 0.1 % ONC | 0.257                     | 2.870                             | 0.090               |
| 5           | 0.5 % SnO - 0.1 % ONC | 0.258                     | 2.890                             | 0.089               |

The thermal conductivity indicated by Table 1 showed a minimum of 0.172 Wm⁻¹K⁻¹ as recorded by the 1.0wt% SnO sample, while the 0.2wt% SnO-0.1wt% ONC sample recorded the highest at 0.331 Wm⁻¹K⁻¹. Hence, the data in Table 1 can show how increasing the amount of SnO affects thermal conductivity and volumetric specific heat in mixed way.

Sample D representing a probable excessive SnO addition reverses the conductivity decrease trend shown between samples A to C; which may indicate a limit which SnO may be integrated with the polymeric matrix. Adding ONC to the mix reports an opposite trend even at a lower concentration of tin oxide; which may indicates how ONC affecting and overloading the SnO integration capability not unlike of sample D.

As SnO and ONC are powdered materials, their heat transfer through radiation in the relatively porous media are probably affected by different parameters. According to Raed (2013) [14], this heat transference may depended on the optical properties or opacity of the solid material; e.g. carbon black addition will increases the extinction coefficient strongly, and thus decreases the radiative conductivity [15,16]. Other than that, the density/porosity could also influence the radiation absorption rate, and reduces their penetration through the porous medium, which will decrease the radiative thermal conductivity [17]. Existence of pore size within the composite, due to metal oxide and nanocrystal incorporation, will decreases the pore size which in turn reduces the overall radiative conductivity [18,19].

Volumetric specific heat indicates the amount of heat store within its material bulk and molecular bond for a given temperature change. This characteristic is important as it determines how the material reacts to heat exposure; whether it routes much of the heat into increasing its temperature due to its limited heat capacity, or storing said heat energy with little effect on its surface temperature [5,20]. As shown in the Table 1, it neatly follows the trend of the thermal conductivity in regards to the effects of additive integration. Thermal diffusivity, meanwhile, is one compound characteristic that is calculated by the ratio
of thermal conductivity to volumetric specific heat. This particular property measures the materials' thermal inertia; in which determines how fast the material changes temperature due to its thermal conductivity and specific heat, [5] or stated in another way, the speed of heat propagation via conduction during temperature changes with time. The heat propagation is hence faster for materials with higher thermal diffusivity [21].

Certain construction industry markets favours a material with low thermal diffusivity as it could withstand rapid changing environmental temperatures. Table 1 shows that the resulting thermal diffusivity of the samples are relatively low, fairly consistent, and parallels well the trends of both thermal conductivity and volumetric specific heat. These consistent ratios, as seen across these samples, thus may indicates that either additives had little impact on the resulted diffusivity values, and also that the changes present on both thermal conductivity and heat capacity are proportionally impacted by these additives.

Thermal diffusivity is often a quite problematic parameter to estimate than that of thermal conductivity. This is due to its strong correlation with the contact resistance, which in most cases, are relatively unknown. The error of estimation will be smaller when said thermal contact resistance is lower; errors for the probe parameters (i.e. power, heat capacity) are known; errors in timing accuracy as well as in measured temperature. Thermal conductivity is hence, in most cases, the best behaving parameter; whereas diffusivity and contact resistance are very sensitive to variations in heating power, probe heat capacity, and timing errors [21].

All in all, the inclusion of SnO lowers both thermal conductivity and specific heat until a certain threshold. This effect may occurs due to their metallic oxide nature, where the dispersed and trapped metal oxide particles might had created thermal barrier bubbles that acts similar to how air trapped in foams slowing heat conduction. Adding ONC might reduces this potential by replacing the metallic oxide integration.

3.2 Tensile Characteristics

Tensile test was conducted following the ASTM D5083 standard with the speed of crosshead at 5mm/minute. Based on Figure 1, the graphs shows how additives integration reduces the tensile strength of the composite slightly. Based on Figure 1, both SnO-only and ONC included samples shown a slight decreasing trend on the maximum strength; while their reported young's modulus are a mixed reaction to the additive integration. As maximum strength indicates how strong a force tending upon the material are required to break it, the slight decrement between samples A to D and 1 to 5 had inferred that said additives used affects, although slightly, the materials' physical strength.
A possible reason for this observation is that the additives' particles may have agglomerated during the mixing and curing process, along with some molecular bonds dissociation between them and the polymer matrices. These lowers the reported strength by the increased sliding allowances created from this available dissociation.

The changes in their young's modulus were much pronounced than the changes in their material strength. Young's modulus indicates the stiffness of the material or the amount of forces required to deform it; a higher value signifies a greater strength need to change a materials shape, whereas any reduction meant a lesser force can now produce similar effects. The jarring difference between the starting sample A and 1 against their successor sample B and 2 are indicative on how the SnO and ONC additives had probably changed the molecular bond dynamics within the resin matrix material as to allow such gapping modulus reduction. The interaction between the bonds to resist tensile force are being affected by the presence of these metallic and organic additives, which hence resulted in less interaction between polymer matrix and EPS fillers.

Heterogeneous nucleating agents have been used industrially for polymers to reduce the process cycle times; via inducing crystallization at a lower degrees of supercooling (i.e., differences between melting temperature and crystallization temperature); and therefore producing translucent materials with smaller crystallite sizes. According to Wang et al., (2004) [22] additives inclusions in a composite and its processing techniques are crucial basis to its properties. Rapid heating and cooling led to a distribution of particles;
leading to agglomeration of SnO and ZnO particles and resulted in low dispersion and lower tensile strength and modulus. Both ZnO and SnO can form faster nucleation formation, and creating noticeable UPR phase amorphocity difference and causes phase variation of composite; which introduces phase incompatibility.

A reason postulated to this effect was that the sample might have been poorly homogenized with poor resin wettability; thus SnO or ONC additions had disrupted the polymer cross-linking site. Improvement in wettability should enhances proper load transfer between the UPR/EPS matrix and the integrated additives. In addition, the probable presence of minute voids and bubbles may lead to ineffective stress transfer between the contents of the polymer matrix.

4. Conclusion
In conclusion, by utilising SnO and ONC, slight changes to the thermal and tensile properties of the composites were reported. Additional tin oxide alone reduces the studied thermal properties before an overloading of the material reverses the trend. Increasing addition of tin oxide with nanocrystal incorporation had increases both its thermal conductivity and heat capacity up to an upper limit as represented by a stable plateau. These observations could probably be attributed to tin oxide metallic nature and a speculated limit of its integration capability within the polymer matrix. In terms of the studied tensile characteristics, the materials' strength aren't directly affected by the additive integration, while the reported young's modulus were substantially affected. The main cause of these observations were postulated to be the effect of the cross-linking conditions between the matrix and its additive.

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References
[1] Hull D 1981 An introduction to composite materials (London, United Kingdom: Cambridge University Press).
[2] Glodek T et al. 2008 Compos. Sci. Technol. 68 2994–3001.
[3] Smith W and Hashemi J 2009 Foundations of Mater. Sci. and Eng. (McGraw-Hill Education).
[4] Vaidya U et al. 2000 Compos. Part A Appl. Sci. Manuf. 31 761–72.
[5] Mohamed R et al 2013 Adv. Mater. Res. 664 600–4.
[6] Ashari M A 2015 The Properties of Unsaturated Polyester Resin (UPR) – Expanded Polystyrene (EPS) Composite (Shah Alam, Selangor).
[7] Khosim R et al 2009 Physical properties and transmission of thermoset polyester composite filled expanded polystyrene.
[8] Kandare E et al 2008 Polym. Degrad. Stab. 93 1996–2006.
[9] Jain G and Kumar R 2004 Opt. Mater. (Amst.) 26 27–31.
[10] Granqvist C G 2016 Mater. Today Proc. 3 S2–11.
[11] Al-Homoud M S 2005 Build. Environm. 40 353–66.
[12] Mamunya Y P et al 2002 Eur. Polym. J. 38 1887–97.
[13] Khosim R et al 2009 Malaysian Polym. Int. Conf.
[14] Raed K 2013 Investigation of Knudsen and Gas-Atmosphere Effects on Effective Thermal Conductivity of Porous Media (Technische Universität Bergakademie).
[15] Lee D et al 1995 J. Non. Cryst. Solids 186 285–90.
[16] Zeng S Q et al 1995 J. Non. Cryst. Solids 186 271–7.
[17] Lu X et al 1995 J. Non. Cryst. Solids 188 226–34.
[18] Smith D M et al 1998 J. Non. Cryst. Solids 225 254–9.
[19] Glicksman L R 1994 Low Density Cellular Plastics ed N C Hilyarad and A Cunningham (London, United Kingdom: Chapman & Hall)
[20] Idicula M et al 2006 Compos. Sci. Technol. 66 2719–25.
[21] Kukkonen I and Suppala I 1999 Measurement of thermal conductivity and diffusivity in-situ: Literature survey and theoretical modelling of measurements vol 3719.
[22] Wang Y C et al 2004 Mater. Sci. Eng. A 370 41–9.