Synthesis and Characterization of Vinylester /Surface Treated ZnO Nano Composites

K. Rajeswari, G. Ramesh, and S. Guhanathan

1,3PG and Research Department of Chemistry, Muthurangam Govt. Arts College, Vellore – 632 002, India.
2PG and Research Department of Chemistry, Dr. Ambedkar Govt. Arts College, Chennai – 600 039, India.

Email: saigugan@yahoo.com

Abstract : A composite material is made by combining two or more materials to get a unique combination of properties. Composites based on a polymer matrix have become more common and are widely used in many industries due to the advantageous properties offered by the polymers. Filling polymers with mineral dispersion has long been a practice in the plastic industry as a way to reduce overall production costs and enhance certain properties. Polymer Matrix Composites were prepared by blending vinyl ester resin with silane surface treated ZnO nanoparticles of various weight percentages. They were characterized by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, and TGA-DTA. Measurement of mechanical properties like tensile strength, impact strength, flexural strength, hardness and physical properties like water absorption, density, specific gravity, etc. have been carried out. The effects of particle size, particle distribution on mechanical properties, thermal properties and physical properties have also been studied. The changes in the properties of the composites with and without coupling agent have been compared. The results of the studies reveal that surface treated composites found to have more significant improvement in overall properties than the untreated one.

Keywords: Nano composites, vinylester, silane, coupling agent, Mechanical properties

I. INTRODUCTION

Nanotechnology is an interdisciplinary field of research which involves production, device design, size and shape control of particle at nanometre scale1. Nanotechnology produces materials with novel functionality and properties2-3. One of such good outcome of nanotechnology is polymer nanocomposite. Polymer nanocomposites have been paid much attention by researchers for more than a decade due to their unique properties like good mechanical strength, light weight, good thermal stability and superior electrical properties4-7. Such properties have made the composites to extend to a wide range of their applications viz. medicine, aerospace, construction, automobile, electronics, communication, etc. So, polymer nanocomposites represent a new alternative to conventionally filled polymers.

Polymer nano composites are materials in which nanoscopic inorganic particles, typically 1-100 nm in at least one dimension are reinforced in an organic polymer matrix. Because of their nanometre sizes, when functional filler of nano scale size is dispersed in polymer matrix, the resultant composite exhibits markedly improved native properties and functional properties when compared to the pure polymers or their traditional composites8-13. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability. In this work, vinyl ester resin was used as polymer matrix and Zinc Oxide nanoparticles were used as reinforcement. Vinyl ester resins are the most commonly used thermosetting resins in the world. More than 1 million tonnes of vinyl ester resins are utilised globally for the manufacture of a wide assortment of products, including sanitary-ware, pipes, tanks, gratings and high performance components for the marine and automotive industry.

Vinyl ester resins are epoxy-based, thermosetting resins that are cured similar to the curing mechanism of conventional polyester resins. Vinyl ester based composites possess good mechanical strength14, shear strength15, corrosion resistance and thermal stability. There are numerous types of reactants that make up the vinyl esters so that each resin has its own characteristic properties. This vinyl ester is the reaction product of a Bisphenol-A epoxy and methacrylic acid. The terminal carbon-carbon double bonds cross-link in a free-radical initiated polymerization. In effect, this structure allows an epoxy to react like a polyester. This by itself is very important as the epoxy reactions in general are very sluggish compared to the polyester free-radical reactions. Another important feature of this ester is that it is styrene soluble; the styrene also enters the free-radical reactions. Since styrene solutions of vinyl ester resins have low viscosity, the resultant resin solution is easily workable in the reinforced plastic processes. Epoxy resins, on the other hand, are high viscosity materials and require more difficult and expensive processing methods. Methyl Ethyl Ketone Peroxide (MEKP) is used as a hardener and Cobalt Naphthenate is an accelerator.
In this work, nano Zinc oxide has been used as a functional filler. Nano zinc oxide has excellent mechanical, thermal, electrical, optical and antimicrobial properties due to which its application in nanotechnology is increasing tremendously16-18. When nano zinc oxide is reinforced with vinyl ester, it reduces the interfacial adhesion between the matrix and filler. This is because if the % by weight of filler exceeds certain limit it results in agglomeration of particles due to which interfacial stress is developed between the matrix phase and the filler. Hence, the properties of the finished product may deteriorate. But when the surface treated zinc oxide is reinforced with vinyl ester resin, it enhances the properties of the finished product. Generally, organic silanes are used as coupling agent, which bridges nanoparticles and the polymer matrix by means of chemical bond as shown below:

![Coupling Mechanism of Nanoparticles by organic silane](image)

### II. EXPERIMENTAL

#### 2.1 Materials

Bisphenol – A vinylester resin, Methyllylelyketonperoxide initiator and Cobalt naphthenate accelerator were received from M/s. Vasavibala Resins, Chennai, India and used as received without any further purification. Nano Zinc oxide of average particle size <90 nm(Sigma Aldrich, India) and \( \gamma \)-Aminopropyltrimethoxysilane (APTMS) also were used as such without any further purification.

#### 2.2 Surface treatment of nano particles

95% Ethanol-5% Water solution was adjusted to pH 5 with acetic acid. APTMS was added to yield 1%, 2% and 3% solutions and allowed undisturbed for 5 minutes for hydrolysis to occur. Nano zinc oxide particles of required weight were added to these solutions and stirred for about 5 minutes. The supernatant solution was decanted from each and the particles were rinsed twice with ethanol. Then, the particles were cured at room temperature for 24 hours.

#### 2.3 Fabrication of nanocomposites

Nanocomposites, in the form of sheets, were prepared by blending various % by weight ratios of nano zincoxide (0.0%-1.5%) with vinylester resin (VE). To these mixtures, 2 % by weight of Methyllylelyketonperoxide (MEKP) and 1% by weight of cobaltnaphthenate were added. The mixtures were casted into sheets by resin transfer moulding in a glass mould with 3.6 mm separator and the mould was degassed using vacuum pump and allowed to cure at room temperature for 72 hours. Another set composite were prepared by following the same procedure but with surface functionalized zincoxide treated with \( \gamma \)-Aminopropyltrimethoxysilane. The composites were cut into required dimensions as per ASTM standards and were characterized.

#### 2.4 Characterization

The physicochemical interactions between the matrix, filler and coupling agent in the composites were characterized by Fourier Transform Infrared Spectroscopy (Shimadzu, IR Affinity – I), morphology of the tensile fractured surfaces by Scanning Electron Microscopy (SEM Jeol JSM-6390 LV, Resolution: 3 nm) and to determine the mechanical properties like tensile strength, flexural strength, impact strength, and hardness, Instron 3382 UT Machine (Capacity: 250 KN, 50 mm/ min), Izod impact Tester and Shore Durometer were used.

### III. RESULTS AND DISCUSSION

#### 3.1 Fourier Transform Infrared Spectroscopy

Figure 3.1.1 and 3.1.2 are the FTIR spectra of ZnO (untreated) and ZnO (surface treated) respectively. Silane coupling of nanoparticles with polymer matrix involves formation of Si-O-Si bond which is here attributed by a strong absorption band at 1010 cm\(^{-1}\) in fig.3.1.2. The incorporation of nano zinc oxide is represented by a strong absorption band at about 500 cm\(^{-1}\).
3.1.2 FTIR spectra of ZnO (Surface treated)

3.2 Surface Morphology – Scanning Electron Microscope (SEM)

The particle size of the filler and its distribution in the polymer matrix are the main key aspects of the mechanical strength of polymer matrix composite. It is obvious, from the SEM images that the tensile fractured surface of vinyl ester /untreated ZnO composite has more crackling when compared to that of the same composite but with surface treated zinc oxide. This is due to the fact that surface treatment of the nano particles improve the uniformity in the particle distribution, reduces particle agglomeration and hence the average particle size. If the average particle size is more, it develops interfacial stress which results in poor strength of the composite.

3.3.1 SEM image of tensile fractured surface of (a) Neat VE (b) VE/0.5 % ZnO (UT) (c) VE/0.5 % ZnO (T)

3.3 Mechanical Properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>VE Resin (% by wt)</th>
<th>Zinc Oxide (% by wt)</th>
<th>Mechanical Properties</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tensile Strength (MPa)</td>
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<tr>
<td>VEZO – 00</td>
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<td>0</td>
<td>46.35</td>
</tr>
<tr>
<td>VEZO – 05</td>
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<tr>
<td>VEZO – 15</td>
<td>98.5</td>
<td>1.5</td>
<td>41.52</td>
</tr>
</tbody>
</table>

Table 3.3.1 Mechanical Properties of VE/ZnO (Untreated) composites

Table 3.3.1 shows the results of characterization of mechanical properties of VE/ZnO (Untreated) composites which are depicted below graphically:

Figure 3.3.1 Variation of Tensile strength of VE/ZnO composite with % by weight of the filler

The trend of tensile strength variation in the above figure shows that the composite having 0.5 % by weight of ZnO has better strength than that of neat composite. But the composites having 1% and 1.5% by weight of ZnO have poor strength. This is attributed by the fact that increasing the amount of filler beyond certain limit causes agglomeration of the particles that reduces in interfacial adhesion19-21. The impact strength and flexural strength also have almost the same kind of trend have occurred as the percentage of nano filler is increased. This is due to the fact that the incorporation of fillers reduces the interfacial adhesion due to agglomeration of the nano particles which enhances the inter boundary stress between the polymer and filler.

Figure 3.3.2 Variation of Impact strength of VE/ZnO composite with % by weight of the filler
Table 3.3.2 shows the results of characterization of mechanical properties of VE/ZnO (Surface treated) composites. The results reveal that there is an appreciable enhancement in the tensile strength, impact strength and flexural strength of surface treated ZnO/VE composites when compared to surface untreated ZnO/VE composites. This is attributed by the fact that the incorporation of surface treated filler enhances the interfacial adhesion by forming chemical bonds with polymeric network and uniform particle distribution which are supported by FTIR and SEM respectively.

3.4 Thermal Studies

Figures 3.4.1 and 3.4.2 are derivative thermograms of VE/ZnO (Untreated) and VE/ZnO (surface treated) composites respectively. It is evident from the thermograms that both the composites undergo one step decomposition and thermal stability of the composites containing surface treated ZnO is slightly better than the composite that contain untreated ZnO.

IV. CONCLUSION

In this work, a set of APTMS coupled ZnO / Vinyl ester resin composites were prepared with various concentrations of coupling agent. The mechanical properties of such composites were compared with that of surface untreated ZnO/VE composites. From the experimental observations, it was found that APTMS coupled ZnO/VE composites have better mechanical strength than the untreated ZnO/VE composites.

V. REFERENCES


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