PREPARATION AND CHARACTERISATION OF PP/TiO_2/GRAPHENE HYBRID NANOCOMPOSITES AND THEIR FOAMS FOR EMI SHIELDING APPLICATIONS

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by

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Submitted

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Dedicated to my

Mother “Arti Rani Verma”

&

Father “Mahesh Kumar Prasad”

CERTIFICATE

This is to certify that the thesis entitled, **"Preparation and Characterisation of PP/TiO_2/Graphene Hybrid Nanocomposites and their Foams for EMI Shielding Applications"** submitted by **Mr. Mayank Prakash** to the **Indian Institute of Technology Delhi**, for the fulfilment of award of the degree, **Doctor of Philosophy**, is a record of bonafide research work carried out by him under our supervision and guidance. This thesis has been prepared in conformity with the rules and regulations of the Indian Institute of Technology Delhi, New Delhi.

The thesis in our opinion, is worthy of consideration for award of the degree of **Doctor of Philosophy** in accordance with the regulations of the Institute. To the best of our knowledge, the results embodied in the thesis have not been submitted to any other University or Institute for the award of any other Degree or Diploma.

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Mayank Prakash

Abstract

This study is a comparative research conducted to establish the enhancement of shielding effectiveness of material via foaming using supercritical carbon dioxide. This study focuses on the preparation of PP-TiO_2-Grahene hybrid nanocomposites and their foams using supercritical carbon dioxide as physical blowing agent for EMI shielding applications. Titanium dioxide and graphene have been used as nanofillers explicitly due to their dielectric properties leading to interfacial polarising and high conductivity for energy dissipation respectively. A non-conventional synthesis technique for the formation of titanium dioxide nanoparticles was thoroughly investigated which is a modified form of sol-gel technique and can be successfully used for the formation of anatase phase of titanium dioxide nanoparticles up to the size of around 7 nanometres with the reaction time of merely 3-5 seconds. The synthesis technique was further studied for varying reaction parameters namely catalysts, catalyst concentration, solvent to precursor ratio and temperature, and their effect on particle size and structure were studied using X-ray diffraction spectroscopy and Dynamic Light Scattering analysis. Selected synthesized nanoparticles were also melt-mixed in polypropylene matrix and the prepared nanocomposites were subjected to thermogravimetric analysis to determine the effect of synthesized nanoparticles on the thermal stability of the nanocomposites.

As a precursor to foaming of hybrid nanocomposites, this work also attempts to establish a correlation between rheological properties of nanocomposites and the resultant foam morphology. To achieve this, optimized foams based on temperature, pressure and saturation time of nanocomposites containing 1, 2 and 3 wt.% of titanium dioxide nanoparticles were prepared. Prepared nanocomposite and their foams were characterised for their rheological and morphological properties to study the effect of added nanofillers and resultant rheological

properties on the foamability and foam morphology of the prepared foams. It was observed that foaming mechanism of polymer nanocomposites can be represented by linear Maxwell model depiction of polymer structure, where viscosity and storage modulus of nanocomposites played a key role in determining the foam morphology.

To obtain a deeper understanding of the physical foaming process, the effect of supercritical carbon dioxide treatment on structural and morphological properties of polypropylene and its nanocomposite were also studied by subjecting films of respective materials to supercritical carbon dioxide treatment at different process conditions (pressure, temperature, saturation time). Structural and morphological characterisations were obtained using X-ray diffraction analysis and Electron microscopy of the optimized samples. This supercritical carbon dioxide treatment was found to result in formation of β crystals of polypropylene in small amounts along with change in percentage crystallinity and crystallite size. Use of supercritical carbon dioxide was also found to enhance the distribution/dispersion of nanofillers in the nanocomposite thereby capable of enhancing the resultant properties.

Finally, hybrid nanocomposites of polypropylene incorporated with titanium dioxide (2 and 3 wt.%) and graphene (5 and 8 wt.%) were prepared and characterised for their structural and rheological properties. The correlation established for PP-TiO_2 nanocomposites was also found to be efficiently applicable in case of hybrid nanocomposites. Rheological properties of the nanocomposites were thus found to significantly affect the foam morphology which in turn affected the specific shielding efficiency of these foams which increased significantly than compared to unfoamed nanocomposites.

अमूर्त

यह सुपरक्रिटिकल कार्बन डाइऑक्साइड का उपयोग करके फोमिंग के माध्यम से सामग्री की EMI (विद्युत चुम्बकीय हस्तक्षेप) परिरक्षण प्रभावशीलता के संवर्धन को स्थापित करने के लिए किया गया एक तुलनात्मक शोध है। यह अध्ययन EMI परिरक्षण अनुप्रयोगों के लिए PP-TiO_2- ग्रेफीन हाइब्रिड नैनोकंपोजिट और भौतिक ब्लोइंग एजेंट के रूप में सुपरक्रिटिकल कार्बन डाइऑक्साइड का उपयोग करके उनके फोम के निर्माण पर केंद्रित है। टाइटेनियम डाइऑक्साइड और ग्रेफीन का उपयोग नैनोफिलर्स के रूप में स्पष्ट रूप से क्रमशः उनके परावैद्युत गुणों (इंटरफेसियल ध्रुवीकरण) और ऊर्जा अपव्यय के लिए उच्च चालकता के कारण किया जाता है। टाइटेनियम डाइऑक्साइड नैनोकणों के निर्माण के लिए एक गैर-पारंपरिक संश्लेषण तकनीक की गहन जांच की गई, जो सोल-जेल तकनीक का एक संशोधित रूप है और इसे केवल 3-5 सेकंड के रासायनिक अभिक्रिया समय के साथ लगभग 7 नैनोमीटर के आकार तक टाइटेनियम डाइऑक्साइड नैनोकणों के एनाटेस रूप के निर्माण के लिए सफलतापूर्वक उपयोग किया जा सकता है। संश्लेषण तकनीक का आगे विभिन्न रासायनिक प्रतिक्रिया मापदंडों जैसे उत्प्रेरक, उत्प्रेरक सांद्रता, विलायक से अग्रदूत अनुपात और तापमान के लिए अध्ययन किया गया, और कण आकार और संरचना पर उनके प्रभाव का अध्ययन एक्स-रे विवर्तन स्पेक्ट्रोस्कोपी और गतिशील प्रकाश प्रकीर्णन विश्लेषण का उपयोग करके किया गया। चयनित संश्लेषित नैनोकणों को पिघले हुए पॉलीप्रोपाइलीन में मिश्रित किया गया और तैयार नैनोकंपोजिट की तापीय स्थिरता पर संश्लेषित नैनोकणों के प्रभाव को निर्धारित करने के लिए थर्मोग्रैविमेट्रिक विश्लेषण का उपयोग किया गया।

यह कार्य फोमिंग के पूर्ववर्ती के रूप में नैनोकंपोजिट के रियोलॉजिकल गुणों और परिणामी फोम की सेल आकृति विज्ञान के बीच संबंध स्थापित करने का भी प्रयास करता है। इसे प्राप्त करने के लिए, टाइटेनियम डाइऑक्साइड नैनोकणों के 1, 2 और 3 वजन प्रतिशत वाले नैनोकंपोजिट के तापमान, दबाव और संतृप्ति समय के आधार पर अनुकूलित फोम तैयार किए गए। तैयार नैनोकंपोजिट और उनके फोम को उनके रियोलॉजिकल और मॉर्फोलॉजिकल गुणों के लिए अभिलक्षणित किया गया ताकि तैयार फोम की फोमेबिलिटी और फोम मॉर्फोलॉजी पर मिश्रित नैनोफिलर्स और परिणामी रियोलॉजिकल गुणों के प्रभाव का अध्ययन किया जा सके। यह देखा गया कि बहुलक नैनोकंपोजिट के फोमिंग तंत्र को बहुलक संरचना के रैखिक मैक्सवेल मॉडल चित्रण द्वारा दर्शाया जा सकता है, जहां नैनोकंपोजिट की श्यानता और भंडारण मापांक ने फोम मॉर्फोलॉजी को निर्धारित करने में महत्वपूर्ण भूमिका निभाई।

भौतिक फोमिंग प्रक्रिया की गहन समझ प्राप्त करने के लिए, पॉलीप्रोपाइलीन और इसके नैनोकंपोजिट के संरचनात्मक और रूपात्मक गुणों पर सुपरक्रिटिकल कार्बन डाइऑक्साइड के प्रभाव का भी अध्ययन किया गया, जिसमें उनसे बनी फिल्मों को विभिन्न प्रक्रिया स्थितियों (दबाव, तापमान, संतृप्ति समय) में सुपरक्रिटिकल कार्बन डाइऑक्साइड के अधीन रखा गया। अनुकूलित नमूनों के एक्स-रे विवर्तन विश्लेषण और इलेक्ट्रॉन माइक्रोस्कोपी का उपयोग करके संरचनात्मक और रूपात्मक विशेषताएं प्राप्त किए गए। इस सुपरक्रिटिकल कार्बन डाइऑक्साइड के प्रवाह के परिणामस्वरूप पॉलीप्रोपाइलीन के α के साथ β क्रिस्टल भी कम मात्रा में बनते पाए गए और साथ ही प्रतिशत क्रिस्टलीयता और क्रिस्टलीय आकार में भी परिवर्तन पाया गया। सुपरक्रिटिकल

कार्बन डाइऑक्साइड का उपयोग नैनोकंपोजिट में नैनोफिलर्स के वितरण/फैलाव को बढ़ाने के लिए भी प्रभावी पाया गया, जिससे परिणामी गुणों में भी वृद्धि होगी।

अंत में, टाइटेनियम डाइऑक्साइड (2 और 3 वजन प्रतिशत) और ग्रेफीन (5 और 8 वजन प्रतिशत) मिश्रित पॉलीप्रोपाइलीन के हाइब्रिड नैनोकंपोजिट तैयार किए गए और उनके संरचनात्मक और रियोलॉजिकल गुणों के लिए उनका अध्ययन किया गया। PP-TiO_2 नैनोकंपोजिट के लिए स्थापित सहसंबंध हाइब्रिड नैनोकंपोजिट के मामले में भी कुशलतापूर्वक लागू पाया गया। इस प्रकार नैनोकंपोजिट के रियोलॉजिकल गुणों को बनाये गये फोम की सेल आकृति विज्ञान को महत्वपूर्ण रूप से प्रभावित करता हुआ पाया गया, जिसने बदले में इन फोम की विशिष्ट EMI परिरक्षण दक्षता को प्रभावित किया, जो नैनोकंपोजिट की तुलना में काफी बढ़ गया।

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