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Effect of Nano and Micro size of Copper Oxide on the Properties of Thermoplastic Elastomer

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ABSTRACT

The objective of the research was to assess the feasibility of utilizing copper oxide particles as a reinforcing and conductive additive in a thermoplastic elastomer. This study focused on examining the influence of particle size on primary strength characteristics and aging resistance, as well as conducting an impedance measurement to gauge the impact of copper oxide particles on electrical conductivity. The findings of the study revealed that incorporating copper oxide particles at the nanoscale leads to enhanced mechanical and conductive properties in comparison to both the base material and the composite with microparticles. However, it was observed that the addition of microparticles in a 5% by weight ratio failed to provide significant improvements in strength and electrical conductivity. Additionally, the study found that the incorporation of copper oxide nanoparticles improves the aging resistance of the composite.

Keywords: thermoplastic elastomer, copper oxide, mechanical properties, conductive properties, accelerated thermal aging.

INTRODUCTION

Polyvinyl chloride (PVC) is often regarded by the public as one of the most hazardous plastics. Although it has self-extinguishing properties, at a temperature of 120 °C, it releases hydrogen chloride (HCl) and dioxins and furans (PCDD and PCDF), which are among the most detrimental substances. Additionally, stabilizers used in PVC often include harmful heavy metals, such as lead or cadmium. An alternative to flexible PVC is thermoplastic elastomers (TPE), which offer the additional advantage that they can be recycled repeatedly. TPE is the generic term for thermoplastic elastomers, also known as thermoplastic rubbers. These materials exhibit rubber-like properties and can be processed using thermoplastic methods such as molding or extrusion. TPE are composed of hard thermoplastic materials, such as polypropylene, polyamide, or polybutylene terephthalate, combined with soft rubber and often the addition of modifiers and

fillers [1]. The drawbacks associated with thermoplastic elastomers are primarily related to their operating temperature, which must be maintained below that of the hard phase. Despite these limitations, thermoplastic elastomers have found widespread application across a range of industries, including automotive, medical, electronics, construction, and household goods, as well as sporting goods [2, 3]. Thermoplastic elastomers are commonly modified with various fillers and reinforcements to enhance their mechanical and processing properties while simultaneously reducing costs. Common fillers include calcium carbonate, silica, carbon black, kaolin, talc, mica, and nanosilica. The incorporation of these additional fillers not only improves the material's strength properties, but also suspends thermal properties. [4, 5]. Thermoplastic elastomers are increasingly sought after due to their diverse range of applications and versatile properties across various industries. Researchers are exploring novel methods to enhance the properties of these elastomers by incorporating different types of fillers, copolymers, and reinforcing materials. Fang et al. investigated the production of conductive thermoplastic elastomer composites using copolymer-grafted multi-walled carbon nanotubes (MWCNTs) to improve both electrical conductivity and mechanical properties. This study demonstrates the potential of using nanofillers to elevate the overall performance of thermoplastic elastomer composites [6]. In a study conducted by Sreekanth and colleagues, the impact of particle size and fly ash concentration on the properties of polyester-thermoplastic elastomer composites was investigated. This research was conducted with a focus on their potential use in automotive parts, specifically for gears and sprockets. The results of this research highlight the significant influence of filler characteristics on the properties of thermoplastic elastomer composites and their suitability for specific industrial applications [7]. The research conducted by Jiang et al. focused on examining the impact of additional cross-linking in multi-walled thermoplastic elastomers composed of a copolymer-grafted carbon nanotube composite. Their findings demonstrated the substantial enhancement of mechanical properties in these composites as a result of such connections [8]. Costa et al. explored the use of extruded thermoplastic elastomers and styrene-butadienestyrene/carbon nanotube composites for strain gauge applications, highlighting the promising prospects of employing thermoplastic elastomer composites in advanced technological applications [9]. Tagliabue et al. explored the potential use of styrene-butadiene-based thermoplastic magnetorheological elastomers containing surface-treated iron particles, suggesting their applicability in magnetorheological applications [10]. Wang et al. concentrated on the design and synthesis of thermoplastic elastomers derived from a multigraft copolymer, emphasizing the unique attributes of TPEs that combine high processability and recyclability with elastomeric properties [11]. Ilčíková et al. conducted a comprehensive review of thermoplastic elastomers with photoactive properties, demonstrating the potential to develop intelligent materials that can be activated using TPEs and their composites [12].

Thermoplastic polyolefin elastomers (TPO) composites can benefit from the addition of various substances that enhance their properties. Common additives include fillers such as talc, calcium carbonate, and mica, which reduce

production costs and improve properties such as stiffness, heat distortion temperature, and dimensional stability [13]. Studies have demonstrated that the inclusion of nanofillers such as sodium montmorillonite and Cloisite 20A, using maleic anhydride-grafted polypropylene as a compatibilizer, can enhance the mechanical, thermal, and morphological properties of TPO nanocomposites [14]. Moreover, the addition of multi-walled carbon nanotubes and low-density recycled polyethylene can improve the mechanical properties of TPOs, including modulus, stress/strain, and strength [15]. Natural fibers such as coconut and sisal have been investigated as reinforcements for TPO composites, and the pre-treatment of the surface of these fibers affects the mechanical properties of the composites [16]. The addition of nanoclays increases the stiffness and tensile strength of TPO, which indicates improved mechanical properties [17[. Furthermore, the addition of modified silica and halloysite nanoparticles increases elongation at break and enhances the mechanical properties of TPO-reinforced polypropylene composites [18].

The objective of this investigation was to assess the influence of copper oxide on the characteristics of a polyolefin-based thermoplastic elastomer (TPO). Copper oxide particles of micro and nanometric dimensions were incorporated into the matrix. Copper oxide particles have been widely studied for their potential applications in polymer composites. Studies by Mallick et al. revealed that copper nanoparticles with an average size of 5 nm exhibited excellent dispersion within the polymer matrix, resulting in a significant improvement in mechanical properties [19]. Bazan et al. demonstrated that copper particlereinforced epoxy resin matrix composites exhibit good electrical and thermal conductivity due to percolation effects [20]. Additionally, Bortolussi et al. found that spraying mixtures of copper and polymer particles can lead to the formation of composite coatings with enhanced electrical conductivity [21]. The findings from academic research suggest that incorporating copper oxide into polymers enhances their performance in a range of applications. The primary benefits include an antibacterial effect, heightened thermal conductivity, UV protection, increased mechanical strength, and elevated electrical conductivity. These improvements render the material more suitable for use in healthcare, electronics, textiles, and the packaging industry. Given that polymer materials, such as flexible thermoplastic elastomers utilized in the production of textiles, sporting goods, gaskets, and others, are renowned for their insulation, the integration of copper oxide particles also enables the dissipation of electrical charges that accumulate in the material during use. This feature highlights the significant potential of copper oxide-based composites.

In summary, the investigation of thermoplastic elastomer composites encompasses a broad spectrum of studies aimed at enhancing their characteristics by incorporating a diverse array of fillers, copolymers, and reinforcing materials. Collectively, these studies contribute to the formulation of composite materials with customized properties suited for various industrial applications, thereby underscoring the promising prospects of thermoplastic elastomer composites across numerous fields.

MATERIALS AND METHODS

Materials

Three distinct material compositions were produced for the research endeavor. The matrix material is a thermoplastic elastomer based on polyolefins (TPO) HTC8345/113, manufactured by KRAIBURG TPE (Germany) with a Shore hardness of D50. For reinforcement, copper particles of varying sizes were employed. The copper oxide had a particle size range of 1–10 mm and a range of 40–60 nm (Suzhou Canfuo Nanotechnology Co., Ltd., SuZhou, China). The base material, although it does not absorb water, was subjected to drying at a temperature of 60 degrees Celsius for a period of 6 hours. Prior to the injection process, the copper oxide particles were

weighed from their hermetically sealed packaging. Specimens for strength tests were produced using injection molding, with the injection parameters detailed in Table 1. To guarantee the highest level of uniformity, the mixed base material with the filler was fed into the hopper in small portions. The samples manufactured comprised the materials listed in Table 2.

Methods of testing

The samples for testing were prepared in accordance with standard ISO 3167:2002 ("Plastics – multipurpose test specimens"), for tensile testing these were dog-bone (type A), for bending tests – bar (type B). Samples for density testing were cut from 5 samples type B with a length of 10 mm. The samples were conditioned for a minimum of 24 hours at a temperature of 23 ± 2 °C and relative humidity of approximately $45 \pm 5\%$ prior to testing. The experimental materials were subjected to physicomechanical, accelerated thermal aging, and electrical conductivity tests. The hydrostatic method was used to determine the density of the composites using a RADWAG WAS 22W laboratory balance (Radom, Poland). Basic strength tests, such as nanoindentation and the modulus of the surface layer determined by means of Hysitron TS 77 Select (Bruker, Massachusetts, USA), the static tensile test (PN-EN ISO 527-1:2010) and static bending test (PN-EN ISO 178:2011), were carried out on a Shimadzu AGS-X 10 kN testing machine (Kyoto, Japan) at a speed of testing 50 mm/min. These tests were repeated after the process of accelerated thermal aging. The QUV Accelerated Weathering Tester aging chamber (Q-LAB Corporation, Westlake, Ohio, USA) was used to simulate the damage caused by sunlight and rain that could occur in

Table 1. Injection molding parameters to produce testing specimens

Temperature (°C)							Injection	Compression	Press time (s)
Feed zone	Zone	Zone 2	Zone 3	Zone 4	Nozzle	Mold	pressure (bar)	pressure (bar)	
40	155	165	75	180	195	30	1500	800	

Table 2. Description of manufactured materials

atmospheric conditions over several months or years. Aging tests were carried out in accordance with ASTM G154. The standard covers a repeated cycle of UV radiation, condensation and water spraying. The parameters of one cycle of the aging process are shown in Table 3, and this process is repeated for a period of 1000 hours what is equal 5000 cycles.

The evaluation of the accelerated aging process was conducted by means of a visual assessment. The measurement of color change was carried out using a 3nh colorimeter (ColorCab5 AN-TICORR, Gdansk, Poland) under TL84 (4100K) light conditions, which simulate typical lighting found in shops, offices, supermarkets, and exhibitions. The samples were assessed in the Lab color space, which spans between opposing colors and consists of three dimensions: L (lightness), a (red-green), and b (yellow-blue). The Lab model is beneficial for displaying shades that are intermediate between the primary colors red, yellow, green, and blue. The CIE Lab color difference model was employed to evaluate the color change, and the difference in color was calculated using the formula provided below [22]:

$$
\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}
$$
 (1)

where: *ΔE* – Euclidean distance between two points in three-dimensional space, *L* – lightness, *a* – red-green, *b* – (yellow-blue)

The observer is considered to recognize a color difference based on:

- $0 < \Delta E < 1$ doesn't see the difference.
- $1 < \Delta E < 2$ the experienced observer will see the difference,
- $2 < \Delta E < 3.5$ the inexperienced observer can see the difference,
- $3.5 < \Delta E < 5$ the observer notices a clear difference in colors,
- $5 < \Delta E$ the observer perceives the colors as completely different.

Following the expedited aging procedure, the samples were examined utilizing a Keyence VHX-7000 digital microscope, a product of Keyence International (Belgium) NV/SA. The

electrical conductivity was determined using the IM6 analyzer from ZAHNER-elektrik GmbH & Co (Germany), which measured current at a frequency of up to 8 MHz and a current of up to 3 A, and read impedance values at a frequency of 5 kHz. Electrical conductivities were made on type B specimens, interspersing electrodes at the ends of the specimen. All presented test results are an average of at least 5 measurements.

RESULTS AND DISCUSSION

Physical and mechanical examination

The initial test conducted aimed to assess the density of the materials produced. The tests were conducted using a RADWAG WAS 22W hydrostatic balance manufactured by RADWAG in Radom, Poland. The results of the measurements are depicted in Figure 1. Upon incorporating copper oxide particles at a rate of 5% by weight into the thermoplastic elastomer, the density of the materials increased only marginally, by approximately 0.05–0.07 g/cm³. The discrepancies between the materials modified with copper oxide are relatively small and average at approximately 0.02 g/cm³ , which can be attributed to the uneven distribution of particles in the matrix during the injection process.

The primary objective of the initial phase of the research was to establish the fundamental strength parameters. The findings of the static tensile and bending tests are depicted in Figures 2–3. The deformation at break exceeded 500%, and the static bending test was carried out up to a deflection arrow of 10 mm. However, sample failure was not achieved due to the limited range of the testing machine arm. The outcomes demonstrated the material's strengthening through the utilization of nanoparticles. Although the increase in tensile strength was relatively minor (approximately 6%), Young's modulus experienced a more considerable increase (about 20%). Similarly, in the static bending test, the flexural modulus increased by about 18%, and flexural

Figure 1. Comparison of density values and strength properties of manufactured materials

Figure 2. Comparison of flexural properties

Figure 3. Microscopic images of the particles used: a) microparticles; b) nanoparticles

strength rose by 20% compared to the base material. No substantial changes in strength properties were observed for the material modified with micrometric copper oxide particles. The tensile and flexural strength remained at a comparable level to the properties of the polymer matrix. Additionally, only a slight (approximately 5%) increase in modulus was observed during bending. The incorporation of particles into polymer composites results in a complex interplay of factors that affect the material's mechanical properties. When examining why particles can lead to lower strength but higher stiffness in polymer composites, several key aspects can be distinguished. One of the essential factors is the role of fillers in the stress distribution within the composite. Fillers, like nanoparticles, can function as stress-relieving agents at the interface between polymers and fillers, leading to increased stiffness in polymer composites [23]. The mechanism for reducing stress can enhance the stiffness of the composite material while simultaneously influencing its overall strength. The dispersion and proportion of nanoparticles are also crucial factors in determining the properties of polymer nanocomposites. Nanoparticles, due to their dispersion on a nanoscale and high proportions, can improve the ductility and strength of polymer composites with lower reinforcement loading compared to conventional composites [24]. The increased stiffness is attributable to the unique properties of the nanoparticles and their interaction with the polymer matrix. The interfacial interactions between the nanoparticles and the polymer matrix can alter the stress-strain characteristics of the composite, affecting its mechanical behavior [25]. The nature of these interactions, including surface interactions, concentration, and polymer composition, plays a pivotal role in determining the properties of a nanocomposite [26]. Detachment of particles from the matrix can impact the tensile strength of the composite. If interfacial peeling decreases, this can result in a reduction in the tensile strength of the composite [27]. This phenomenon underscores the significance of the particle-matrix interface in determining the mechanical properties of polymer composites. The research findings suggest that there are no substantial chemical interactions or enhanced adhesion between the components of the composite. Instead, the mechanism that contributes to the increased stiffness is the mechanical obstruction of the elastomeric phase chains stretching

on copper oxide particles. The stiffness of nanocomposites is likely to be influenced by the number of particles themselves, resulting in a larger number of matrix-filler contact points. Studies by Li et al. presented similar conclusions, emphasizing the connection between the particle size of carbon nanotube and the properties of epoxy resin. They highlighted that the aspect ratio and particle size cause the polymer chains to be mechanically locked on the particles, leading to improved stiffness of the composite material [28]. Additionally, Jin and others pointed to the impact of the morphology of block copolymer composites and nanoparticles. They suggested that the properties depend on the copolymer architecture and the properties of the nanoparticles, such as surface energy, geometry, and volume share. In symmetrical lamellar structures, neutral particles decrease the fin thickness, while energy-polarized particles increase it. This effect also depends on the packing density of the particles and their size relative to the thickness of the fins. Hierarchical and block structured polymer nanocomposites like thermoplastic elastomers can achieve significant improvements in material stiffness without compromising elasticity and elasticity [29].

In conclusion, the lower strength and increased stiffness observed in polymer composites that contain particles, particularly nanoparticles, can be ascribed to several factors, including stress relief mechanisms, dispersion characteristics, interfacial interactions, and detachment behaviour. It is essential to comprehend these intricate interactions in order to tailor the properties of polymer composites for particular applications.

Copper oxide nanoparticles and microparticles display distinct mechanical and structural variations that influence their properties and applications. Copper nanoparticles, due to their smaller size, exhibit unique characteristics that differentiate them from larger microparticles [30]. A major challenge when using copper nanoparticles, whether on a nanoscale or microscale, is their susceptibility to oxidation at elevated temperatures, which can impact their conductivity and structure [31]. The dimensions and shape of copper particles have a significant impact on their applications. In particular, incorporating copper nanoparticles that have been synthesized in-situ into a resin can enhance the mechanical properties of materials due to their uniform and spherical nature [32]. On the other hand, copper microparticles have been utilized to prevent the agglomeration of complex-shaped nanoparticles in aluminium matrices, illustrating the critical role that particle size and morphology play in the performance of composite materials [33]. The differences in morphology and size of the applied particles are shown in Figure 3.

The materials were subjected to nanoindentation tests and measurements of their modulus of elasticity for the surface layer. The results of the study are provided in Figures 4–6 and Table 4. The findings revealed that the incorporation

of copper oxide particles led to an increase in the hardness of the microparticle-modified material. However, no change in the hardness of the nanolayer was observed in the nanoparticlemodified material. The research indicated an increase in the stiffness of the modified materials. The highest modulus, which was more than twice that of the base material, was observed for the microparticle material and was related to the particle size. A nanoindentation depth is more likely to be measured in the microparticle area

Figure 4. Hardness results and reduced modulus for TPO

Figure 5. Hardness and reduced modulus results composites with nanoparticles additives

Figure 6. Hardness and reduced modulus results composites with microparticles additives

5 µm CuO 0.08 ± 0.02 0.82 ± 0.12 285.6 ± 30.2

Table 4. Average results of hardness and educed modulus of tested materials

than in the nanoparticle area. The increase in hardness and stiffness was also confirmed by the difference in indenter recess at the same load forces (0-200 μ N). For the base material, the indenter recess was the highest and averaged 525 nm, while for the material characterized by the highest hardness and stiffness, the indenter recess averaged 285 nm.

Accelerated ageing examination

The study included a process of accelerated thermal aging, which was carried out for 1000 hours, resulting in approximately 5000 cycles, followed by endurance tests. The outcomes of the study are summarized in Figure 7. The static tensile test results show a proportional decrease in

Figure 7. Comparison of strength properties before and after accelerated thermal aging

strength properties, such as tensile strength and Young's modulus, for each of the tested compositions. Although plastics contain stabilizers in their structure, they are still susceptible to weakening from exposure to the external environment. The average decrease in tensile strength was 5 MPa for the base material and the material modified with copper oxide microparticles. The smallest decrease was observed in the material with copper oxide nanoparticles. In addition, the study found a positive effect of the introduced particles on the stiffness of the material. When comparing the results, it appears that the decrease in Young's modulus in percentage terms is smaller for composites than for pure TPO elastomer.

The literature on the aging process delineates that multiple factors collaborate simultaneously. The process of aging can be delineated into various classifications. For example, a distinction is made between external and internal aging. Internal aging is characterized by the loss of thermodynamic stability, resulting in recrystallization, relaxation of internal stresses, and plasticization. Conversely, extrinsic aging can exhibit a plethora of phenomena, such as thermo-oxidative degradation, stress and fatigue cracking, and swelling. Another classification includes physical and chemical aging, which is often synergistic and can engender opposing effects. Elevated temperatures can bring about favorable secondary crystallization and chemical breakdown of the chain, which may result in negative consequences. Physical aging typically stems from the migration of volatile components, water absorption and desorption, and swelling. Chemical changes in structure are frequently triggered by increased temperature in conjunction with oxygen or other factors like radiation. However, in the long run, it contributes to the degradation of the material. Four types of chemical degradation can be distinguished: (1) depolymerization, (2) chain breakdown, (3) thermo-oxidative degradation, and (4) radiation degradation [34–36]. The presented results seem to indicate that modifying humidity and temperature cycles led to an augmentation in strength following the accelerated thermal aging process; however, it is crucial to consider the impact of additional factors, such as particle size and shape.

The process of aging copper oxide polymer composites is influenced by a range of factors that impact the material's properties over time. To comprehend the consequences of thermo-oxidative aging on these composites, it is crucial to examine

various aspects based on the pertinent sources. One of the critical factors to consider is the effect of oxidizing environments on inducing morphological changes in polymer composites. The adsorption of oxygen, its diffusion into the interior, and the reaction with component materials all contribute to the progression of aging damage [37]. Comprehending these oxidation processes is vital for evaluating the long-term durability of copper oxide polymer composites [38]. Recognizing the development of copper nanoparticles in various surroundings is crucial for foretelling the behaviour of copper oxide composites during ageing procedures.

The findings of the study demonstrate the superiority of copper nanoparticles over particles on a micrometric scale. The cause for this superiority may be attributed to the size, structure, and reactivity of the nanoparticles themselves. Nanoparticles exhibit a higher reactivity in comparison to microscale particles. The oxidation process of nanoparticles occurs more rapidly and effectively. The process of injecting samples into the mold does not take place in a closed system without oxygen. Furthermore, the increased temperature accelerates the oxidation process. This can ultimately lead to a certain saturation and reduction in the reactivity of the particles during their use and interaction with an external filter. Previous research by Palza et al. has demonstrated that nanoparticles are more effective than microparticles due to their enhanced specific surface area, which leads to a greater release of metal ions [39, 40]. This increased ion release rate is attributed to the high specific surface area of nanoparticles within polymer matrices, resulting in more rapid oxidation processes in comparison to microparticles.

Additional evidence supporting this conclusion is provided by studies which suggest that nanoparticles are more likely to cause significant changes in material characteristics due to their larger specific surface area [39, 41]. Several studies have demonstrated that incorporating copper oxide (CuO) and aluminium oxide (Al_2O_3) into composite materials enhances their performance and stability by means of various mechanisms. Copper oxide, for example, can provoke exothermic reactions on the surface and within the mass, which can lead to cross-linking of the resin and positively impact mechanical properties [42]. Furthermore, the presence of copper oxide and aluminium oxide in composite materials contributes to the formation of stable structures and protective layers [43]. In conclusion, adding copper

oxide and alumina to composite materials enhances their mechanical properties, thermal stability, corrosion resistance, and the formation of protective layers. These oxides provide unique properties that positively affect the overall properties and functionality of composite materials in numerous applications. Additionally, the aging of epoxy resins can result in modifications to their mechanical, thermal, and chemical properties [44]. As stated by Wang et al., an extended service life can result in several adverse consequences, including yellowing, diminished gloss, cracks, and a decline in mechanical and insulating properties [45].

Another important consideration is the formation of particle agglomerates, which can be observed in Figure 10. Bazan and colleagues have demonstrated in their research that the size of the particles plays a crucial role in determining their resistance to aging. The formation of agglomerates introduces additional stresses that weaken the polymer structure, making these sites more susceptible to the breakdown of the polymer structure by disrupting the polymer chains [46]. The samples were subjected to colorimetric testing both before and after the aging process, as outlined in Table 5 and illustrated in Figure 8–10. The research findings demonstrated that the material with microparticles was the most susceptible to accelerated thermal aging. The differences in colour before and after the process were considerable, and the colours were perceived as entirely distinct. While the neat material and composites with nanoparticles also underwent changes in colour after the aging process, the alterations were less noticeable. However, noticeable changes were observed in the outer layer of both the

 $b)$

Figure 8. Color of the manufactured TPO: a) before and b) after the accelerated thermal stabilization

Figure 9. Color of the manufactured 5 nm CuO composite: a) before and b) after the accelerated thermal stabilization process

Figure 10. Color of the manufactured 5 μ m CuO composite: a) before and b) after the accelerated thermal stabilization process

unmodified and microparticles-filled material, including cracking and crushing of the material. The elastomeric phase is typically marked by cracking, crumbling, and whitening, while the appearance of the polyolefin phase can be discerned between the crack areas. Although the material exhibited a noticeable colour change, the extent of cracking and crumbling was significantly reduced in the presence of nanoparticles, corroborating the previously proposed hypothesis regarding the reduced oxidation capacity of the material.

Electrical conductivity

The present study examined the materials' resistance. The conductive mechanism of the tested samples can be understood as the resistive mechanism found in resistors. The impedance value can be considered as the sample's resistance to alternating current. The findings revealed that the incorporation of copper microparticles led to a slight decrease in impedance, approximately 2%, while the addition of copper oxide nanoparticles caused a more significant decrease in impedance, approximately 14%. These results indicate a higher conductivity for the nanoparticles as compared to the microscale particles. The study's outcomes are illustrated in Figure 11. Research findings related to the comparison of copper nano and microparticles reveal similar conclusions. The study by Chung et al. demonstrates that copper/silver hybrid nano-particle ink exhibits high electrical conductivity, which is comparable to the resistivity of bulk copper. This suggests that nanoparticles can achieve excellent electrical conductivity in composite materials [47]. Additionally, the work by Zhang et al. highlights the achievement of optimal electrical resistivity with copper nanoparticles, indicating their potential for high conductivity applications [48]. Furthermore, the study by

Figure 11. Impedance changes depending on the composition of the composite: a) impedance curves, b) impedance value at a frequency of 5 kHz

Fu et al. shows that copper films prepared from nanoparticles synthesized via arc discharge exhibit high electrical conductivity after sintering. This suggests that nanoparticles can contribute to achieving low electrical resistivity in copper films [49]. Furthermore, according to research conducted by Huaman and colleagues, the electrical resistivity of copper nanoparticles synthesized via hydroxyl ion-assisted reduction displays variation based on annealing conditions, highlighting the impact of processing on conductivity [50]. Ultimately, it is concluded, based on the cited literature, that copper nanoparticles possess the potential to attain high electrical conductivity in diverse applications. The studies indicate that the utilization of nanoparticles can enhance the electrical properties of copper-based materials, demonstrating their effectiveness in improving conductivity when compared to microparticles.

CONCLUSIONS

The present research study aimed to examine the consequences of incorporating copper oxide nanoparticles and microparticles into a thermoplastic elastomer (TPO) matrix, focusing on the material's physical, mechanical, and electrical properties, as well as its response to accelerated thermal aging.

The incorporation of copper oxide nanoparticles significantly increased the material's stiffness, resulting in a notable improvement in Young's modulus of approximately 20%. Additionally, the addition of nanoparticles led to a considerable increase in flexural strength by about 20%. Although the increase in tensile strength was relatively small, the use of nanoparticles demonstrated a superior overall performance compared to the use of microparticles. This improvement in overall performance was attributed to the nanoparticles' efficient stress distribution and mechanical interactions with the polymer matrix. In contrast, the introduction of microparticles resulted in only minimal improvements in strength and stiffness, highlighting the exceptional effectiveness of copper oxide nanoparticles.

Thermal aging tests revealed that copper oxide nanoparticles were more effective at mitigating the negative effects of aging, such as reduced tensile strength and Young's modulus, as compared to microparticles. The nanoparticlemodified material demonstrated lower decreases

in these properties and less visible degradation, such as cracking and colour changes, than its microparticle counterpart. This suggests that nanoparticles offer superior protection against environmental factors that contribute to aging. Electrical conductivity tests indicated that the introduction of nanoparticles significantly reduced impedance by 14% compared to only 2% for microparticles, suggesting excellent electrical performance. The higher conductivity of the nanoparticles is attributed to their larger surface area and increased interaction with the polymer matrix. In conclusion, the study found that copper oxide nanoparticles significantly enhance the mechanical and electrical properties of TPO composites, while offering better resistance to thermal ageing than microparticles. These findings emphasize the potential of nanoparticles to enhance the performance and durability of polymer composites in various applications.

REFERENCES

- 1. Shanks R, Kong I. Thermoplastic elastomers. El-Sonbati AZ, editor. Thermoplastic elastomers. 2012; 137–153.
- 2. Sreekanth MS, Bambole VA, Mhaske ST, Mahanwar PA. Effect of concentration of mica on properties of polyester thermoplastic elastomer composites. J Miner Mater Charact Eng. 2009; 8(4): 271–82.
- 3. Veli D, Nursel K, Osman G. Effects of fillers on the properties of thermoplastic elastomers. SPE Plast Res Online, [Internet]. Available from: https://www. yumpu.com/en/document/read/16864270/effects-offillers-on-the-properties-of-thermoplastic-elastomers
- 4. Wongtimnoi K, Guiffard B, Bogner-Van De Moortele A, Seveyrat L, Gauthier C, Cavaille J. Improvement of electrostrictive properties of a polyetherbased polyurethane elastomer filled with conductive carbon black. Compos Sci Technol. 2011; 71(6): 885–8.
- 5. Babu RR, Naskar K. Recent developments on thermoplastic elastomers by dynamic vulcanization. 2010; (July 2010): 219–47.
- 6. Fang C, Zhang Y, Wang W, Wang Z, Jiang F, Wang Z. Fabrication of copolymer-grafted multiwalled carbon nanotube composite thermoplastic elastomers filled with unmodified MWCNTs as additional nanofillers to significantly improve both electrical conductivity and mechanical properties. Ind Eng Chem Res. 2015; 54(50): 12597–606.
- 7. Sreekanth MS, Bambole VA, Mhaske ST, Mahanwar PA. Effect of particle size and concentration

of flyash on properties of polyester thermoplastic elastomer composites. J Miner Mater Charact Eng. 2009; 8(3): 237–48.

- 8. Jiang F, Zhang Y, Fang C, Wang Z, Wang Z. From soft to strong elastomers: The role of additional crosslinkings in copolymer-grafted multiwalled carbon nanotube composite thermoplastic elastomers. RSC Adv [Internet]. 2014; 4(104): 60079–85. Available from: http://dx.doi.org/10.1039/C4RA11626G
- 9. Costa P, Silvia C, Viana JC, Lanceros Mendez S. Extruded thermoplastic elastomers styrene-butadiene-styrene/carbon nanotubes composites for strain sensor applications. Compos Part B Eng [Internet]. 2014; 57: 242–9. Available from: http://dx.doi. org/10.1016/j.compositesb.2013.10.006
- 10. Tagliabue A, Eblagon F, Clemens F. Analysis of styrene-butadiene based thermoplastic magnetorheological elastomers with surface-treated iron particles. Polymers (Basel). 2021; 13(10).
- 11. Wang H, Lu W, Wang W, Shah PN, Misichronis K, Kang NG, Mays J. Design and synthesis of multigraft copolymer thermoplastic elastomers: Superelastomers. Macromol Chem Phys. 2018; 219(1): 1–11.
- 12. Ilčíková M, Mrlík M, Mosnáček J. Thermoplastic elastomers with photo-actuating properties. In: Das CK, editor. Thermoplastic Elastomers. IntechOpen; 2015; 115–43.
- 13. Austin J, Kontopoulou M. Effect of organoclay content on the rheology, morphology, and physical properties of polyolefin elastomers and their blends with polypropylene. Polym Eng Sci. 2006; 46(11): 1491–501.
- 14. Nalini R, Nagarajan S, Reddy BSR. Thermoplastic polyolefin nanocomposites: effect of mechanical, thermal, and morphological properties. J Reinf Plast Compos. 2011; 30(4): 319–24.
- 15. Ahmed MA, El-Shafie M, Kandil UF, Taha MMR. Improving the mechanical properties of thermoplastic polyolefins using recycled low-density polyethylene and multi-walled carbon nanotubes. Egypt J Chem. 2021; 64(5): 2517–23.
- 16. Pereira JF, Ferreira DP, Bessa J, Matos J, Cunha F, Araújo I, Luís F. Silva, Pinho E, Fangueiro R. Mechanical performance of thermoplastic olefin composites reinforced with coir and sisal natural fibers: Influence of surface pretreatment. Polym Compos. 2019; 40(9): 3472–81.
- 17. Tjong S., Ruan Y. Fracture Behavior of Thermoplastic Polyolefin/Clay Nanocomposites. J Appl Polym Sci. 2008; 110: 864–71.
- 18. Rajaee P, Ghasemi FA, Fasuhi M, Sadeghi A, Kakeh B. Effect of fumed silica and halloysite nanoparticles on the microstructure, mechanical, and fracture properties of thermoplastic polyolefin elastomer toughened polypropylene. Polym Compos. 2022; 43(7): 4495.
- 19. Mallick K, Witcomb MJ, Scurrell MS. Optical and micro-analytical study of a copper-conjugated polymer composite. Phys Status Solidi Appl Mater Sci. 2007; 204(7): 2263–9.
- 20. Bazan P, Gajda M, Nosal P, Bąk A, Setlak K, Łach M. The influence of copper oxide particle size on the properties of epoxy resin. Appl Sci. 2024; 14(6).
- 21. Bortolussi V, Figliuzzi B, Willot F, Faessel M, Jeandin M. Electrical conductivity of metal–polymer cold spray composite coatings onto carbon fiberreinforced polymer. J Therm Spray Technol. 2020; 29(4): 642–56.
- 22. Tor-Świątek A, Garbacz T. Effect of abiotic degradation on the colorimetric analysis, mechanical properties and morphology of PLA composites with linen fibers. Adv. Sci. Technol. Res. J. 2021; 15(1): 99–109.
- 23. Suhailath K, Thomas M, Ramesan MT. Studies on mechanical properties, dielectric behavior and DC conductivity of neodymium oxide/poly (butyl methacrylate) nanocomposites. Polym Polym Compos. 2021; 29(8): 1200–11.
- 24. Zhou G, Movva S, Lee J. Preparation and properties of nanoparticle and long-fiber-reinforced unsaturated polyester composites. Polym Compos. 2009; 30(7): 861–5.
- 25. Petrova VA, Nud'Ga LA, Bochek AM, Yudin VE, Gofman IV., Elokhovskii VY, Dobrovol'skaya IP. Specific features of chitosan-montmorillonite interaction in an aqueous acid solution and properties of related composite films. Polym Sci - Ser A. 2012; 54(3): 224–30.
- 26. Pazmiño Betancourt BA, Douglas JF, Starr FW. Fragility and cooperative motion in a glass-forming polymer-nanoparticle composite. Soft Matter. 2013; 9(1): 241–54.
- 27. Kareem S, Al-Ansari LS, Gömze LA. Modeling of modulus of elasticity of nano-composite materials: review and evaluation. J Phys Conf Ser. 2022; 2315(1).
- 28. Li J, Ma PC, Chow W.S, To CK, Tang BZ, Kim JK. Correlations between percolation threshold, dispersion state, and aspect ratio of carbon nanotubes. Adv. Funct. Mater. 2007; 17(16): 3207–3215.
- 29.Jin J, Wu J, Frischknecht AL. Modeling microscopic morphology and mechanical properties of block copolymer/nanoparticle composites, Macromolecules. 2009; 42(19):7537–7544.
- 30. Chiu PH, Cheng WH, Lee MT, Yasuda K, Song JM. Low-thermal-budget photonic sintering of hybrid pastes containing submicron/nano cuo/cu2o particles. Nanomaterials. 2021; 11(7).
- 31. Abbas B. Processing of nano-micro copper materials for the production of conductive circuits Bahaa Hanou Abbas [Internet]. 2021. Available from: file:///C:/Users/Bahaa Abbas/OneDrive - Swansea University/Bahaa pc/PhD/Thesis final submission/

Submitted final/Thesis FINAL (Bahaa Abbas).pdf

- 32. Li F, Ye C, Huang Y, Liu X, Fei B. Incorporation of in situ synthesized nano-copper modified phenolformaldehyde resin to improve the mechanical properties of Chinese fir: A preliminary study. Polymers (Basel). 2021; 13(6).
- 33. Sharifi MJ, Azadi M, Azadi M. Fabrication of heattreated nano-clay-composite for improving highcycle fatigue properties of AlSiCu aluminum alloy under stress-controlled fully-reversed bending loads. Proc Inst Mech Eng Part C J Mech Eng Sci. 2021; 235(19): 4143–60.
- 34. Abenojar J, Pantoja M, Martínez MA, Carlos del Real J. Aging by moisture and/or temperature of epoxy/SiC composites: Thermal and mechanical properties. J Compos Mater. 2014; 49(24).
- 35. Azizan A, Johar M, Karam Singh SS, Abdullah S, Koloor SSR, Petrů M, et al. An extended thicknessdependent moisture absorption model for unidirectional carbon/epoxy composites. Polymers (Basel). 2021 Feb 1; 13(3): 1–13.
- 36. Frigione M. Assessment of the Ageing and Durability of Polymers. Polymers (Basel). 2022; 14: 1934.
- 37. Liang J, Pochiraju K V. Oxidation-induced damage evolution in a unidirectional polymer matrix composite. J Compos Mater. 2015; 49(11): 1393–406.
- 38. Goncharova DA, Kharlamova TS, Lapin IN, Svetlichnyi VA. Chemical and Morphological Evolution of Copper Nanoparticles Obtained by Pulsed Laser Ablation in Liquid. J Phys Chem C. 2019; 123(35): 21731–42.
- 39. Palza H, Delgado K, Moraga N, Molina S-HW. Polypropylene in the Melt State as a Medium for In Situ Synthesis of Copper Nanoparticles. AIChE J. 2014; 60(10): 3406–11.
- 40. Palza H, Delgado K, Pinochet I. Improving the metal ion release from nanoparticles embedded in a polypropylene matrix for antimicrobial applications. J Appl Polym Sci. 2014; 132(1): 1–8.
- 41. Marani D, D'Epifanio A, Traversa E, Miyayama M, Licoccia S. Titania nanosheets (TNS)/Sulfonated poly ether ether ketone (SPEEK) nanocomposite proton exchange membranes for fuel cells. Chem Mater. 2010; 22(3): 1126–33.
- 42. Li AP, Müller F, Bimer A, Nielsch K, Gösele U. Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina. J Appl Phys. 1998; 84(11): 6023–6.
- 43. Xu N, Sarkar DK, Grant Chen X, Zhang H, Tong W. Superhydrophobic copper stearate/copper oxide thin films by a simple one-step electrochemical process and their corrosion resistance properties. RSC Adv. 2016; 6(42): 35466–78.
- 44. Wang B, Ci S, Zhou M, Di C, Yu J, Zhu B, Qiao K. Effects of hygrothermal and salt mist ageing on the properties of epoxy resins and their composites. Polymers (Basel). 2023; 15(3).
- 45. Wang J, Wang Z, Yan N, Han Z, Chang Y, Wang J, Li Q. Clarifying the chemical reactions of the weakening of adhesion between epoxy resin and aluminum by molecular dynamic simulation and experiment. Front Mater. 2022; 9(August): 1–10.
- 46.Chung WH, Hwang YT, Lee SH, Kim HS. Electrical wire explosion process of copper/ silver hybrid nano-particle ink and its sintering via flash white light to achieve high electrical conductivity. Nanotechnology [Internet]. 2016; $27(20)$: 1-13. Available from: http://dx.doi. org/10.1088/0957-4484/27/20/205704
- 47. Bazan P, Mazur KE, Rybicka K, Kuciel S. The influence of organic and inorganic antibacterial additives on the strength and biocidal properties of thermoplastic elastomers (TPO). Ind. Crop. Prod. 2023; 198, (March): 116682
- 48. Zhang Y, Zhu P, Li G, Zhao T, Fu X, Sun R, Zhou F, Wong C-P. Facile preparation of monodisperse, impurity-free, and antioxidation copper nanoparticles on a large scale for application in conductive ink. ACS Appl Mater Interfaces. 2014; 6(1): 560–7.
- 49. Fu Q, Li W, Kruis FE. Highly conductive copper films prepared by multilayer sintering of nanoparticles synthesized via arc discharge. Nanotechnology [Internet]. 2023; 34(22): 225601. Available from: http://dx.doi.org/10.1088/1361-6528/acbd1f
- 50. Cuya Huaman JL, Sato K, Kurita S, Matsumoto T, Jeyadevan B. Copper nanoparticles synthesized by hydroxyl ion assisted alcohol reduction for conducting ink. J Mater Chem. 2011; 21(20): 7062–9.