Rheological and Mechanical Properties of TPU Composites Reinforced with Silver-Coated Copper Flakes

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ABSTRACT

The study investigates the preparation of conductive thermoplastic polyurethane (TPU) composites using a twin-screw extrusion, focusing on the effects of silver-coated copper (Cu@Ag) particles as conductive fillers. The rheological, mechanical, and electrical properties of the composites were characterized as a function of filler volume concentration. The rheological analysis enabled the determination of a percolating network formation, which is important both for processing the composites and for mechanical reinforcement in the solid state. With increasing Cu@Ag loading, the composites exhibited pronounced changes in viscoelastic behaviour. The results of the mechanical tests show that increasing filler concentration of the Cu@Ag filler in the TPU polymer affects the mechanical properties, i.e., an increase in the storage moduli (E') and loss moduli (E'') was observed, resulting in a more brittle structure of the composite. Furthermore, the electrical conductivity increased sharply to 46.7 S/m at the highest filler concentration. The results showed that geometrical and electrical percolation thresholds were similar, occurring at ~15 vol.%. These results highlight the crucial role of filler loading in tailoring the conductive and viscoelastic properties of functional TPU composites.

INTRODUCTION

Composite materials have several advantages over metals, especially in applications where customized properties and shapes are of great importance. Therefore, much attention is given to the study of polymer-based composites where the effect of the pigment filler loadings has been varied[1,2]. This is particularly important in the production of electrically and thermally conductive polymer composites. Since polymer matrix is usually non-conductive, conductive filler particles or conductive polymers must be added to improve the conductivity. Such conductive filler particles can be metallic, carbon-based, ceramic or metal-coated. Copper (Cu) is a promising metal as a conductive filler as it is inexpensive and abundant. However, Cu particles are prone to oxidation, which significantly reduces the electrical conductivity, therefore, the surface of these particles must be protected from oxidation. To reduce surface oxidation and consequently improve the conductivity of Cu particles, their surface can be protected with silver (Ag), creating a core-shell (Cu@Ag)[3] structure. To improve conductivity of a non-conductive material, a network of conductive particles must be established. This

network forms at certain volume fraction, known as the "percolation threshold", which depends on various factors (type, shape, size of the filler, etc.). However, higher filler concentration can have a negative impact on the properties of the polymer matrix. In our previous study[2], where unmodified and modified Cu-based flakes were used as fillers in a polyethylene matrix, increased concentration of the flakes increased the hardness but drastically reduced the toughness, leading to the brittleness of the final composite.

The presented research is focus on the influence of different filler volume concentrations (0 – 40 vol.%.) of conductive silver-coated copper particles (Cu@Ag) incorporated into TPU polymer, where the rheological, morphological and electrical properties were investigated in order to determine the geometrical and electrical percolation thresholds.

EXPERIMENTAL

The composites were made of polyether-based thermoplastic polyurethane - TPU (Elastollan 1195A, BASF, Germany) with a density of ρ_{TPU} = 1.15 g/cm^3 and silver-coated copper flakes - Cu@Ag (eConduct Cu 340500, Eckart, Germany). The Cu@Ag flake-shaped particle size was d_{50} = 42 µm. The mass concentration, Φ_m, of Ag coating material on Cu particle was Φ_m = 5%. The TPU-based composites with different volume concentrations Cu@Ag filler, i.e., Φ_{vol} = 0 – 40 vol.%, were prepared by melt processing at 215 °C in a twin-screw extruder (Xplore Micro compounder MC 15 HT, The Netherlands), using a counter-rotating mode. For each composition, the dosing time was 5 min at a screw speed of 50 rpm and a mixing time of 5 min at a screw speed of 75 rpm. During mixing, the melt was purged with N_2 gas to prevent oxidation of the surface of the Cu@Ag particles. The TPU polymer was pre-dried at 90°C for 3 hours before the extrusion process. Subsequently, the melt was transferred into the injection molding piston, heated at 210 °C and then molded into a final shape with an injection pressure of 5-6 MPa for 10 s and holding pressure of 7-8 MPa (depending on the filler concentration) for an additional 10 s. Two different sample geometries were prepared for the characterization, i.e., disk-shaped samples for the rheological characterization with a diameter of 25 mm and a thickness of 1.5 mm, while DMA test bars with a length of 60 mm, a width of 10 mm and a thickness of 1 mm were produced for mechanical and electrical characterization.

The rheological analysis of the TPU-based composites was performed with a rheometer (MCR302, Anton Paar, Graz, Austria) at a constant temperature of 210 °C with a plate-plate sensor geometry (25 mm diameter) and a gap of 1 mm. Rotational tests under destructive shear conditions were performed using the triangular method. The viscoelastic properties of the investigated composites were determined by frequency sweep tests in the range of 100 Hz to 0.01 Hz. The measurements were performed in the linear viscoelastic range, using a strain excitation of 0.01-0.04%, depending on the particle concentration, while a strain excitation of 10% was used for pure TPU polymer. The results are presented as the average value of 3 replicates for each composite tested.

The dynamic mechanical analysis (DMA) was used to determine the mechanical reinforcement of the TPU-based composites filled with Cu@Ag particles. The tests were performed in bending mode using a 3-point bending sensor geometry in the temperature range of -10 °C to 70 °C with a heating rate of 3 °C/min under an inert nitrogen atmosphere by using a MCR702 rheometer (Anton Paar, Graz, Austria). Before measurements, all samples were annealed at 60 °C for 9 hours and cooled to room temperature at 0.1 °C/min in a nitrogen atmosphere. In addition, the measurements were carried out in the linear viscoelastic range with a strain excitation of 0.1%. The results of the DMA tests are presented as the average value of 3 repetitions for each composite tested.

The conductive performance of composites was determined at room temperature using a custom-built 4-wire DC measuring rig coupled with a Keithley 237 measure unit (Keithley Instruments, Solon, OH, USA). Conductivity (σ) through the sample was determined by measuring current at excitation voltages ranging from -120 V to 120 V. Conductivity results represent an average of 3 repetitions for each material.

RESULTS

Optical microscopy

The surface microstructure of the injection molded TPU/Cu@Ag composites at volume concentrations (Φ_{vol} = 0 – 40 vol.%) was investigated using optical microscopy (AxioScope 2, Carl Zeiss, Germany). Figure 1 shows that the amount of irregular, flaky Cu@Ag particles on the surface increases with increasing volume concentration of the filler, which also increased the roughness of the moulded sample. It was also found that the surfaces of the flakes were not uniformly covered with Ag coating material as the Cu uncoated particles have a copper-like colour, the Cu@Ag flakes appear grey.

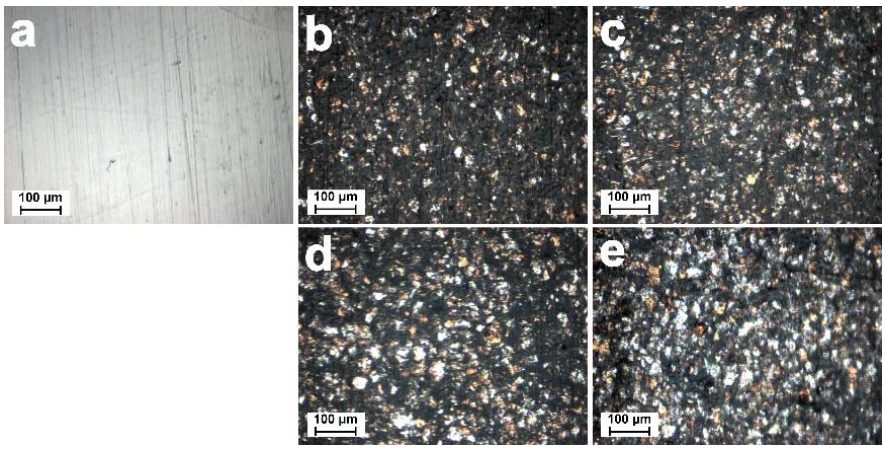

FIGURE 1: TPU-based composites with different volume concentrations of the Cu@Ag fillers.

Oscillatory tests: frequency sweep

The particle interactions in polymer composites and its network formation was observed with rheological characterization. Viscoelastic behaviour, i.e., storage modulus (G′), loss modulus (G″) and complex viscosity (η^*) were determined as a function of frequency in the linear viscoelastic range at a constant temperature of 210 °C.

The frequency-dependent viscoelastic response of TPU/Cu@Ag filled composites are presented in Fig. 2A. The results show that in the entire frequency range investigated the TPU exhibits a flow-like behavior (G″ > G′), while all composites exhibit a solid-like behavior (G′ > G″). The transition from liquid- (G″ > G′) to solid-like (G′ > G″) behaviour was only observed with the addition of 10 vol.% of Cu@Ag particles to TPU polymer, where the cross-over frequency ω_{co} (G′ = G″) was 11.4 Hz. The dynamic moduli of the composites were significantly higher than those of pure TPU and increased with the increasing concentration of Cu@Ag particles, indicating a significant influence of particles in the TPU polymer. The high increase in G′ indicates the geometrical entanglement of particles and the formation of a network in the polymer matrix. Moreover, the viscous response of the composite was hindered and an increase in G″ by five orders of magnitude at the highest concentration of Cu@Ag particles was observed. Figure 2B shows that at low frequencies, the highly filled Cu@Ag/TPU composites

exhibited significantly higher complex viscosity (six orders of magnitude) than pure TPU polymer. This is consistent with the established understanding that particle-particle interactions and network formation dominate the viscoelastic properties of polymer composites at low frequencies[4].

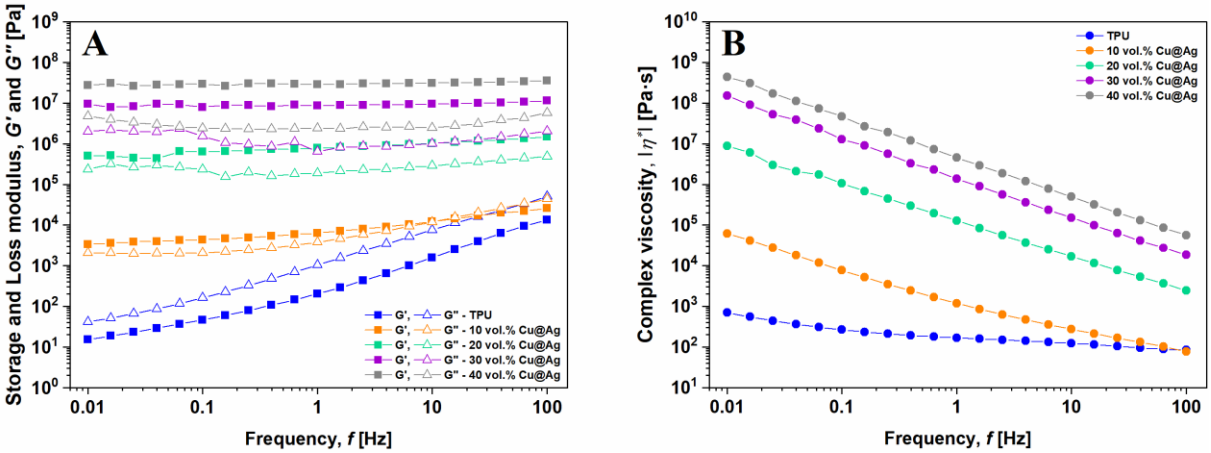

FIGURE 2: Viscoelastic behaviour of TPU-based composites with different volume concentrations of the Cu@Ag fillers.

Network formation in the investigated composites was evaluated by analyzing the low-frequency region, i.e., complex viscosity (η^*) at 0.01 Hz, as a function of Cu@Ag volume concentration Φ_{vol} (Fig 3). The results show that the critical volume concentration (geometrical percolation point) at which the particles become geometrically entangled in the polymer matrix was $\Phi_{v,crit}$ ~15 vol.%. This value is twice as high as for the LDPE polymer matrix filled with Cu@Ag flakes ($\Phi_{vol,crit}$ ~ 7.5 vol.%) and the same as for LDPE/Cu composite[2]. After the network was established (above $\Phi_{vol,crit}$), the long-range interactions between the particles predominate, which significantly influence the viscoelastic response and functionality of the material.

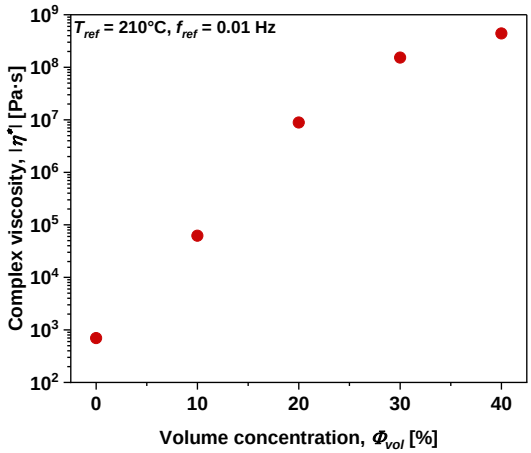

FIGURE 3: Viscoelastic behaviour of TPU-based composites with different volume concentrations of the Cu@Ag filler.

Mechanical behaviour

Dynamic Mechanical Analysis (DMA) is a powerful tool for characterizing the mechanical properties of TPU-based polymer composites. In the temperature range between -10°C and 70°C, the influence of the addition of Cu@Ag filler on the mechanical properties was determined using the 3-point bending mode. The measurements were performed under low load

(linear viscoelastic region), which resulted in small deformations that did not damage the sample.

The temperature dependence of the extensional storage (E') and extensional loss (E'') modulus of Cu@Ag filled composites at different filler concentrations is presented in Fig. 4A. For all composites, E' was approximately one decade higher than E'' over the whole temperature range investigated. The increase in modulus is related to the presence of particles that contribute to the reinforcement of the TPU polymer matrix by forming a network. It was also observed that E' decreased with increasing temperature for all samples, reflecting a transition from a rigid to a more flexible state. The difference in E' and E'' ratio with increasing temperatures suggests that TPU polymer has more soft segments. The glass transition point of soft segments ($T_{g,soft}$) for TPU was at -36.2°C (determined from differential scanning calorimetry (DSC) - not shown here). Below T_g the polymer behaves like a rigid material with high stiffness. Above T_g, polymer becomes more flexible and exhibits viscoelastic behaviour, with the hard segments in the TPU contributing to maintaining structural integrity at higher temperatures.

The values of E' *and* E'' moduli increased with the increase in the filler content at the same temperature (Fig. 4B). Increasing the filler content enhances the interfacial adhesion between the filler and matrix, leading to higher matrix stiffness and improved stress transfer at the interfaces.

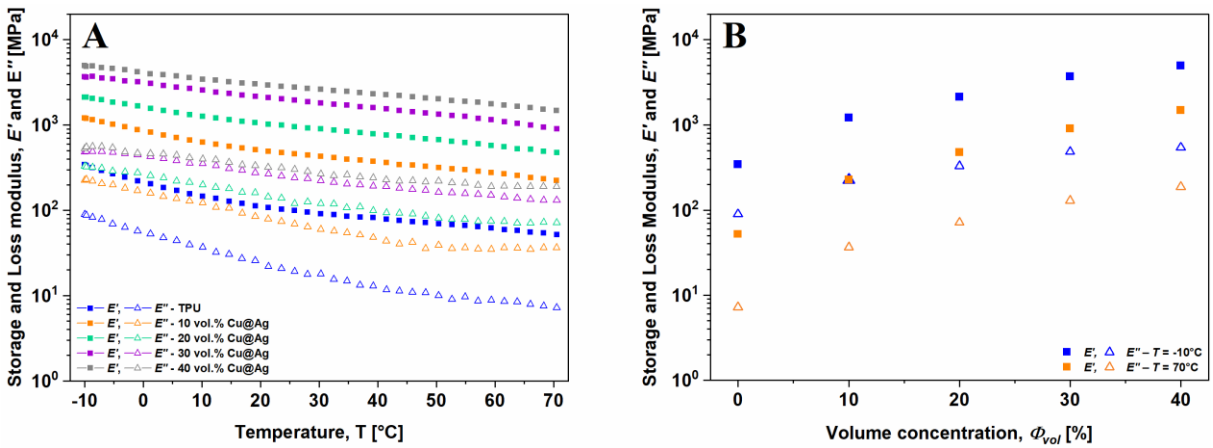

FIGURE 4: Viscoelastic properties of TPU-based composites (A) and E', E'' values at -10°C and 70°C (B) at different volume concentrations of the Cu@Ag filler.

Electrical conductivity

The electrical conductivity of TPU-based composites filled with different volume concentrations of Cu@Ag particles is shown in Fig. 5. The results indicate that the pure TPU polymer is non-conductive, while the addition of conductive particles to the polymer matrix increases the conductivity of the composite. The conductive network starts to develop at 10 vol.%, while a higher increase was observed at 20 vol.% Cu@Ag loading. The maximum conductivity (46.7 S/m) was reached at 40 vol.% Cu@Ag loading.

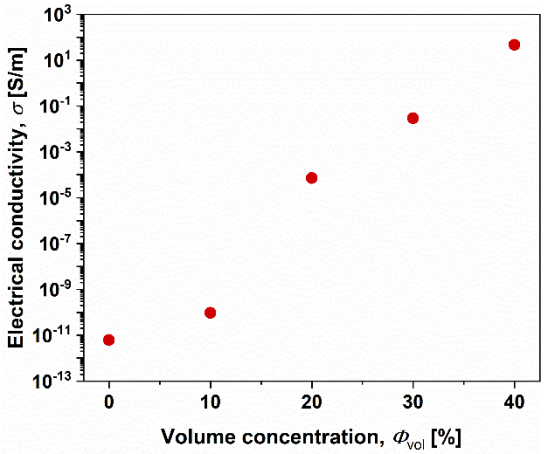

FIGURE 5: Electrical conductivity of TPU-based composites with different volume concentrations of the Cu@Ag filler.

According to the percolation theory, the transition from insulator to conductor in the polymer or polymer composite is determined by the percolation threshold, i.e., the critical volume concentration at which the conductive pathways are formed in the polymer composite. For the TPU polymer matrix filled with Cu@Ag particles, the percolation threshold was observed at pigment loading of ~15 vol.%. Similar values for electrical conductivity have already been observed when copper particles were added to semi-crystalline low-density polyethylene (LDPE) polymer[2,5,6] and to amorphous PMMA[7], where it was reported that the percolation threshold begins to establish between 10 and 20 vol.% copper. Kim et al. investigated the addition of copper particles to CNT/TPU composite material used as a conductive filament for 3D printing. The addition of copper particles further reduced the resistivity at lower CNT concentrations, but this effect decreased at higher concentrations. The volume resistivity (ρ) of the polymer composite TPU/CNT (19.2 wt.%)/Cu (23 wt.%) was 0.12 Ω/cm. However, at high concentrations of CNT and Cu fillers, the composites become more brittle[8].

Several factors influence the concentration of filler particles required to achieve conductive pathways within the composite material (percolation threshold), including particle size and shape, the presence of surface coatings on the copper particles, and the type of polymer used. Furthermore, the higher concentration (i.e., 10 wt.%) of the silver coating on the copper flakes improves the electrical percolation threshold, which decreased to 7.5 vol.%[2]. This means that a better oxidation protection of the copper pigment particles has formed, thus enhancing the formation of electrical pathways through the polymer composite.

CONCLUSION

This study investigated the influence of silver-coated copper (Cu@Ag) filler particles on the rheological behavior, mechanical properties, and electrical conductivity of thermoplastic polyurethane (TPU) composites. The composites were prepared with different concentrations of Cu@Ag filler, ranging from 0 to 40 vol.%, by twin-screw extrusion. The samples were afterwards injection molded into suitable shapes for further characterization.

The incorporation of Cu@Ag filler into TPU polymers significantly improves their viscoelastic properties, as observed by increased storage (G') and loss (G") moduli as well as complex viscosity compared to neat TPU. This improvement is due to the fact that the filler reduces the free volume of the polymer and thus restricts chain mobility while promoting

macromolecular adsorption on the filler surface, further hindering chain movement and thus increasing viscoelasticity. The DMA analysis has shown that the mechanical properties of TPU/Cu@Ag composites were significantly affected by increasing filler concentration and temperature. The non-conductive TPU polymer becomes electrically conductive as the volume concentration of the Cu@Ag filler increases, reaching a maximum value of $\sigma = 46.7$ S/m at the highest volume concentration of filler. The electrical percolation threshold of TPU/Cu@Ag composites was determined to be at ~15 vol.% filler concentration. These results highlight the crucial role of filler concentration in tailoring TPU composites for applications requiring balanced mechanical and electrical performance, used for flexible electronics and EMI shielding.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Slovenian Research Agency (research core funding No. P2-0264).

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