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Investigation of various graphene fillers for improving properties of thermoplastic polymers

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Abstract
The application of graphene in polymers and polymer-based composites was investigated in an application-oriented research project. The aim was the improvement of mechanical, electrical and thermal properties by using graphene as nanofiller in the polymer matrix. Research concentrated on developing appropriate formulations of graphene-based plastics for functionally integrated components, which can be processed in an industrial environment. Since most of recent studies have been done in lab environment, guaranteeing ideal processing conditions not relevant in industrial production, the approach of this project was hallmarked by using industrial equipment for compounding and further processing.

Keywords: graphene, plastics, polymer filler, compounding, hot embossing, nanoparticles

1. Introduction

Many industries are looking for plastics with very good mechanical, electrical or thermal properties at low densities. Fillers are used to adjust the desired properties. However, the potential of typical micrometre-sized fillers (e.g., glass fibres, carbon black) is limited. Therefore, nanofillers are increasingly being used, which, owing to their large specific surface area and the resulting large filler-polymer interaction area, allow for significant property improvements with low filler contents.

Graphene is a young nanofiller which is highly promising as a result of the excellent physical properties as well as the cheaper production costs compared to carbon nanotubes. It offers potentially an economically interesting way for improving mechanical [1] or barrier [2] properties of plastic components as well as the integration of functions such as electrical and thermal conductivity [3].

Although the potential of graphene-based plastics has already been demonstrated in laboratory scale studies, there are no scalable methods for the preparation and further processing of these materials [4]. However, these are indispensable for the industrial use of graphene, especially by SMEs.

Since the novel material places high demands on process technology, industrially relevant processes for the production and further processing of the graphene-based plastics have been investigated and optimized. Therefore, the entire process chain is considered from material development through preparation to processing. The economic and technical feasibility of the developed processes and the material are validated on the basis of applications from industrial practice.

2. Sample Applications

The study of sample applications is to evaluate the relevance from an economic and technical point of view. Only in this way the path to the industrial use of graphene-based polymer composites can be levelled. The basis was the fact that graphene as a filler in polymer composites can potentially improve the mechanical, electrical and thermal properties.

In the field of mechanical improvements, the expectations aim at increasing the strength, in order to replace existing metal-plastic composites, or to significantly improve the wear and abrasion properties of components. New light-weight solutions would also be possible (consumer goods, sports goods, etc.).

The electrical properties of plastics could, on the one hand, be directed towards conductive plastics and thus enable new solutions for sensor components. On the other hand, graphene in the plastic should also be used to improve the barrier properties against electrostatic and electromagnetic fields.

The thermal property improvement is relevant for household components, but also for embedded heating elements in sensors or optimized heat exchanger components. Optimized thermal properties can also improve the weldability of plastics.

Specific examples for the qualification and evaluation of the test results are:

- Barrier effect of graphene for stabilizing bioplastics
- Improvement of the tribological properties of POM
- Plastic material with a thermal conductivity > 5 W/mK

3. Experimental

Different commercially available graphene powders as well as reduced graphene oxide and exfoliated graphite were compounded using an Extrusiograph® - 19/25 D with measuring mixer from the company Brabender. The matrix was a polypropylene (PP), with the tradename SABIC PP 515A. The filler content was 0.2 %, 2 %, 5 % and 10 %. After the compounding, the graphene filled polymers were pressed into test specimens with a dimension of 90 x 90 x 3 mm³.

The characterization of the mechanical properties was done with a tensile testing machine from Hegewald & Peschke (Inspect 10) with a 10 kN load cell. The crosshead speed was 10 mm/min.

The characterization of the surface energy of the compounds were done with a contact angle measuring instrument Easy Drop from KRÜSS. The measurements were done at ten different locations at the test specimen.

3.1. Mechanical properties

Figure 1 summarizes the results for yield stress and strain of the compounds. The yield stress of the polymer decreases with increasing graphene content. It can been seen that the nanofiller graphene cannot increase the mechanical properties of the PP matrix. Caused by the high surface energy, graphene seems to agglomerate. The agglomerates are potential trouble spots.

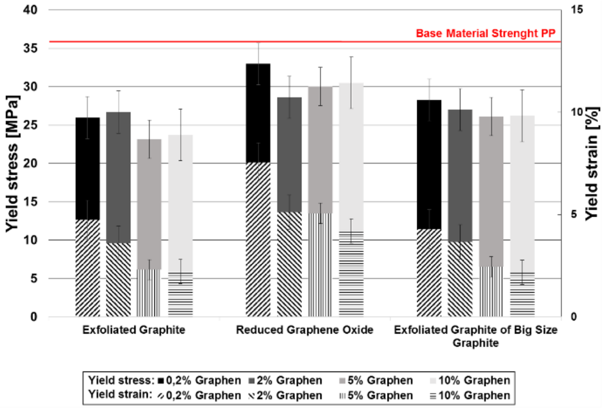

Figure 1. Yield stress and strain of the graphene compounds

3.2. Surface energy

Figure 2 shows the surface energy of the graphene compounds. It can been seen that the surface energy can be reduced by adding graphene. It also shows that with increasing of the filler content, the surface energy decreases. The type of the graphene also influences the surface energy. By using the reduced graphene oxide it is possible to decrease the surface energy with a filler content of only 0.2 %. So it is possible, to adjust the surface energy for a particular point. This is important for microfluidics, because there it needs hydrophilic and hydrophobic areas.

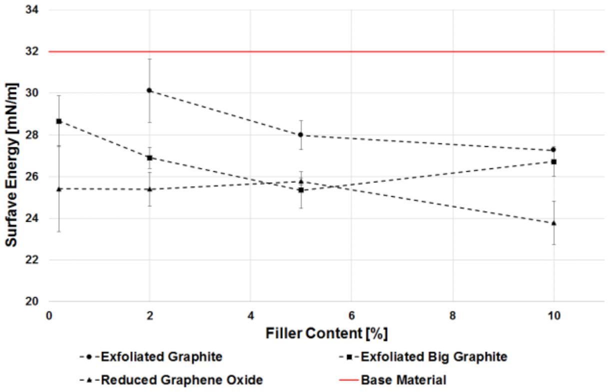

Figure 2. Surface energy of the graphene compounds

4. Processing by hot embossing

The aim of the further processing by hot embossing was the production of structural cavities of different geometries and dimensions in the millimetre and micron range in graphene-based polymer composites. In the field of microfluidics, films in the thickness range between 0.25 and 1 mm are generally used for this purpose. As base material extruded films of polyethylene (Lupolen 2420 D) having a foil thickness of 250 micrometres and the pressed PP (SABIC PP 515A), primarily thinned to 0.5 mm were used. The graphene content of the films was 0%, 0.5% and 5% of the mass. The experiments were carried out on hot embossing equipment at Fraunhofer IWU.

The first experiments were used to characterize the flow behaviour in terms of temperature and to derive the process parameters (temperature, speed, and atmosphere). This was realized with a channel tool with different geometries (channel width to depth, steepness). Based on this, a complex microfluidic demo structure was hot embossed with the same parameters in the various samples. The films were not quite uniformly thick and the thickness variability also varied, but no measurable difference in the flow behaviour between the pure PE film and the graphene-filled polymer film could be detected. Typical microfluidic structures were achieved without restrictions, which are shown in the following figure. The typical parameters were 100 °C embossing temperature at a process force of 2000 N which corresponds to an approximate compression of 8 MPa.

Figure 3. Microfluidic test structure, tool left, PE film middle, graphene-filled polymer film right

5. Summary/Conclusion

In summary, graphene as filler material cannot improve the mechanical properties in the described way of material processing. The reason is suspected in the agglomeration of the graphene. The agglomeration takes place during transportation and it is hard to resolve the agglomerates by the compounding process. However, graphene can affect the surface energy of the tested polymer. Hence it is interesting for microfluidic systems. The graphene shows no influence on the hot embossing process. The flow behaviour and the tool surface reproduction of the graphene-filled polymers were as good as unfilled polymers. Therefore, it is possible to manufacture microfluidic systems from graphene-filled polymers and adjust the surface energy by using different filler contents.

In future works one of the main challenges is the compounding process in industrial grade. Our experiences indicate that the graphene agglomerates already during transportation. For that reason it is difficult to break up agglomeration during the compounding process. Nevertheless, a further step is to manufacture different microfluidic structures with graphene modified areas. Following this, the structures are analysed regarding advantages to use graphene-filled polymers for hydrophilic and hydrophobic areas in microfluidic systems.

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