On Nanoparticles Release from Polymer Nanocomposites for Applications in Lightweight Automotive Components

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Abstract. Nano and micro reinforced glass fibre-polymer composites have been manufactured to investigate different effect such as filler type, filler size and matrix materials on the particle emission during low velocity impact test. Nano and micro-silica, as well as nanoclay reinforced crash cones were prepared with a two step extrusion process and final injection moulding of the structures. The addition of secondary filler into the glass-fibre reinforced polymer composites had significant influence on the mechanical behaviour of the material as well as on the particle emission. In general, nano and ultrafine airborne particles were emitted from all investigated materials. However, composite filled with nanoclay emitted higher amounts of particles than those filled with nano and microsilica. One reason for the increase of particle emission of the nanoclay filled composites was the change of the failure behaviour of the matrix. However, similar results of particle emission were obtained for both nano and microsilica fillers, which in general did not vary significantly from the results obtained from traditionally reinforced glass fibres polymer composites.

1. Introduction

Material used for crashworthy structural application, traditionally have been metals, due to their plastic deformation characteristics, which enable them to absorb impact energy in a controlled manner. Polymer composite materials, contrasting metals, do not typically exhibit plastic deformation. However their stress-strain relationships may show signs of other types of nonlinearities, but they are superior to metals for specific energy absorption. Nanoreinforced polymers have focused the attention, because of their potential to exhibit impressive enhancements of material properties compared to the pure polymers [8]. Therefore, polymer nanocomposites are manufactured commercially for diverse engineering applications and are used in many economic sectors.

However, the increasing research, production and utilisation of nanomaterials nurture questions on their fate and behaviour. It is likely that, once nanocomposites undergo mechanical and thermal stress situations nanoparticles will be detached as free nanofillers or hybrids particles into the air. Therefore, the understanding of the exposure mechanism is crucial for the assessment of the potential environmental and health risks.

A present various research groups have investigated the release of nanoparticles during different mechanical stress situations such as shredding [9], drilling [10, 11, 2], sanding [7, 4], impact [12] and abrasion [1,18, 16, 13, 5, 6] of nanocoating and nanocomposites. In general, only very low amounts of nanoparticle were measured and no free pristine nanoparticles were detected. These findings raise the question on the release-ability of nanomaterials and the compatibility of the applied methods.

In order to release pristine nanofillers from a matrix, huge accelerations are necessary to generate forces able to compete with van der Waals forces, for example through instantaneous shocks [15]. However, larger nano-objects including carbon nanotubes (CNT) or nanofibres are expected to be removed under lower acceleration from the matrix surfaces. Hence, the aim of this study is to simulate mechanical shocks, through low velocity impact on nanocomposite cones and to evaluate the particle released from the structures.
2. Experiments

2.1. Material selection and preparation of test samples
Polyamide 6 (Tarnamid T30, Azoty Tarnow, Poland) and polypropylene (Moplen HP500J, Basell Polyolefins) were used as matrix material for all composites. As fillers the following materials were utilised (5mass%); surface modified montmorillonite (DELLITE® 43B and 72T, Laviosa) and fumed nanosilica particles (AEROSIL® R 974 and 200, Degussa, Evonik Industries). Nanofillers and polymer materials were compounded via extrusion to a master batch (Granulate 1 in Figure 1). Additionally, polyamide with 30% glass fibres and 30% glass spheres (MM-PA I 1F30 & MM-PA I 1K30, MacroMass Verkaufs AG, Germany) and polypropylene 30% glass fibres and 25% glass spheres (MM-PP BI 24 and MM-PP HE25, MacroMass Verkaufs AG, Germany) were used as secondary filler. Further, glass fibres for PP and PA6 (Thermoflow 636/672, Johns Manville Fibres) compounding were integrated. This approach of melt blending was chosen to maximise nano and micro particle distribution throughout the polymeric matrix, as well as the ease of granulates handling. The composition of the manufactured crash cone was as follows: glass fibre content was kept at 30 mass% for all composites, while nanofiller loading accounted 1.6 mass% and microfiller loading varied between 9 mass% for the PP matrix and 10.7 mass% for the PA6 matrix.

[Figure 1: Manufacturing of test specimen]

Exploiting this recipe, fibre reinforced nanocomposites granulate were obtained and then utilised for injection moulding of crash cones and tensile bars for mechanical testing. Figure 2 shows the dimensions of the manufactured crash cones.

[Figure 2: Crash cone dimensions (left) and injected moulded crash cones (right)]
2.2. Measurement of airborne particle number, concentration and size distribution
Crash cones were impacted utilising a high energy capacity drop tower rig. This machine permits impact
testing at up to 8 m/s velocity and maximum falling weight of 300 kg. External devices for measuring of
load and displacement were used for external acquisition system. The low velocity impact tests were
conducted at three different velocities 4.4, 6.2 and 7.7 m/s corresponding to 1, 2 and 3 m drop heights.
The tests were performed by direct impact of the falling beam. The impactor mass of 54 kg was constant
in all tests, giving the overall impact energies of 520 J, 1050 J and 1580 J. The load was measured using
a 200 kN load cell which was located underneath the cones.

To characterize the physical properties of particles generated during these impact tests, crash cones were
placed into a crash chamber, as illustrated in Figure 3. The particle emissions were measured using a
Condensation Particle Counter "CPC" 5.403 with Classifier "Vienna"-DMA 5.5-U (SMPS+C, Grimm
Aerosol, Germany). SMPS+C measured sub-micrometer particles generated during impact process over a
particle size range of 5.6-1083 nm and a particle size resolution of 32 channels in total. Prior to the
measurements, the chamber was purged with laboratory air for about 20 min. Each sampling cycle
comprised a 60 min background air monitoring in the chamber, and a 60 min post-impact period. The
experiment was repeated 2 times for each material composition.

Figure 3: Experimental set up (left) and chamber set up (right)

3. Results and Discussion

3.1. Effect of matrix type on particle emission
For low velocity impact test, the matrix material was found as an important parameter on the particle
emission. In general PA6 generated 4-8 times more airborne particles than PP based composites. A
pronounced difference in energy absorption between the composites made of PP and PA matrices was
observed as shown in Figure 4. All PP composites absorbed more impact energy compared to the PA6
composites. It was discovered that all PP composites fail in a progressive and stable manner, whereas the
PA6 composite in a brittle and unstable condition. This behaviour can be directly associated with the
mechanical properties of the matrix/fibre interaction. In general, PP is a ductile material with relatively
low strength, whereas PA6 is a brittle material which possessed a high strength.

The brittleness of the material causes larger cracks and fragmentation, reducing the energy absorption
capabilities of the material. In case of PP nanocomposites the matrix cracks and failure were localised in
a close proximity of the impact point and they were no crack propagation along the structure. Delamination and debonding of the fibres increase the effectiveness of the energy absorption, and at the
same time avoiding the weakening of the non-crashed section of the structure. As impact on PP based
composite only caused localised failure and not complete failure of the composite, it can be assumed that
the emission rate of particles during impacting can be influenced, through the matrix materials.
3.2. Effect of nanofiller type on particle emission

A significant influence of the nanofiller type used on the particle emission was noted for the low velocity impact test. Nanoclay filled PP and PA6 composite generated the most particles throughout all impact tests. The cause of this behaviour can be explained by the fracture behaviour of the composite cones during impact test. The incorporation of nanosilica particles did not increase the impact strength of the material, however changed the fracture mechanism. The brittleness of the material was significantly reduced, which was observed as an increase in elongation to brake, determined in the tensile tests. However, the opposite behaviour was observed for the nanoclay nanocomposites. In this case the impact strength of the material was increased but at the cost of reduced ductility. Hence, the strain reached the maximum allowable limit and the crack propagated along the structure, leading to a complete failure of the structure. As a result the energy absorption capability of the material remained on the same level, in spite of the increase in quasi-static strength and stiffness.

Damages due to low-velocity impact events weaken the structure of composite materials, due to a continuous service load. In every material, energy is absorbed in two ways (i) deformation of material and (ii) fracture of material. As material deformation is limited to the material properties, the fracture of the material in smaller pieces is the direction towards higher energy absorption capacities. In recent studies, it has been reported that the impact behaviour and related properties (energy absorption capacity) of polymer matrices can be engineered by adding nano-scale fillers. For example, rigid nano-sized particles, carbon nanotubes and clay nanoplatelets have been used [14]. Figure 5 shows the basic principle behind the increase in fracture pieces due to nanofiller and hence a higher degree of energy absorption capacity. In a micro and macro filled composite cracks will propagate from one filler particle to the other. The same principle is valid for nanocomposites, however the distance between particles is reduced and therefore the material breaks in smaller pieces.
3.3. Effect of filler size on particle emission

As shown in the literature [17, 3] and by the results obtained by this study, the utilisation of nanofiller over microfiller in an identical matrix material will lead higher degree of property enhancement. The tensile modulus differed by 0.31 GPa by using nanosilica instead of microsilica particles in PP matrix. Additionally, the specific energy absorbed during impact test increased from 20.7 kJ to 22.6 kJ by using nanosilica alternative to microsilica particles. Hence, it can be assumed that these changes in properties will directly affect the quantity and properties of the release particles.

However, comparing the quantity and geometric mean size of particles release during different impact test (Figure 6) it was observed that there was a clear pattern. While there was a maximum peak of particles concentration for the impact at 1050J energy level, the particles geometric mean size was at a minimum peak. It was further observed that the quantity of particles release was significantly lower for the 530J and 1560J impact, however, particle size increased significantly depending on the impact energy. The geometric particle size increased from approx. 25 nm for the 530 J to approx. 60 nm for the 1560 J impact. Nevertheless, this behaviour was observed for all PP and PA6 reinforced with conventional glass fibre, and the composites having nanosilica or microsilica as a secondary reinforcement Therefore, it can be concluded that the particle size of the secondary reinforcement is not necessarily affecting the particle emission during impact testing, even though it influences the mechanical properties of the composite material, notably.
4. Conclusions
Nano and micro reinforced crash cones have been manufactured through a two step extrusion process and final injection moulding of the nanoreinforced granulates. Quasi-static mechanical properties and crushing behaviour of the various polymer composites were studied. It was shown that addition of secondary filler into the glass-fibre reinforced polymer composites had significant influence on the mechanical behaviour of the material. It could be shown that by varying of the secondary fillers it is possible to change the micro-mechanism of a crash and therefore control the energy absorption characteristics of the composite.
Particulate emissions were evaluated based on size-resolved from various silica based composites during impacting process. Physical characterization of the number concentration and size distribution of sub-micron particles from 5.6 to 512 nm was carried out, for the different composites. In general, nano and ultrafine airborne particles were emitted from all investigated materials. However, composite filled with nanoclay emitted higher amounts of particles than those filled with nano and microsilica. One reason for the increase of particle emission of the nanoclay filled composites was the change of the failure behaviour of the matrix. Nanoclay induced a transition from ductile to brittle fracture. Brittle material behaviour results in fracture of material in many pieces and a low deformation, and hence more particles were generated.
However similar results, of particle emission where obtained for both nano and microsilica fillers, which in general did not vary significantly from the results obtained from traditionally reinforced glass fibres polymer composites.

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