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Nylon 6-Nanocomposite Fibres with Improved Abrasion Resistance

Original Scientific Article

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Abstract
The increase of fibre abrasion properties aims at the lifecycle improvement of technical textiles containing abrasion resistant fibres. Furthermore, the improvement of fibre abrasion properties is – presumably – the key to higher productivity and reduction of energy costs. Especially the fibre composites made of Nylon 6 and two-dimensional particles as organoclays or graphene platelets bear high potentials to achieve increased abrasion properties compared to virgin Nylon 6 fibres. The problems to be solved within this research were the transfer of positive effects known from bulk polymers, the guarantee of stable multifilament spinning and the loss of fibre properties by using additives. The effect of two-dimensional particles was visualised with the analysis of the tribological behaviour and mechanical properties. In order to gain the insight into the relationship among the processing conditions, material composition and resulting material properties, Wide Angle X-ray scattering experiments were performed.
Keywords: Nylon 6, organoclay, nanocomposite fibres, abrasion resistance

1 Introduction

The improvement of fibre abrasion properties is – presumably – the key to higher productivity and reduction of energy costs. The increase of fibre abrasion properties aims at the lifecycle improvement of technical textiles containing abrasion resistant fibres. Especially the fibre composites made of Nylon 6 and two-dimensional particles as organoclays or graphene platelets bear high potentials to achieve increased abrasion properties compared to virgin Nylon 6 fibres [1]. The problems to be solved within this research are the transfer of positive effects known from bulk polymers, the guarantee of stable multifilament spinning and the loss of fibre properties by using additives.
The use of additives, also nanoscaled additives as organoclays or graphene platelets, is well known in the bulk polymer processing [2, 3]. At least the use of nanoscaled TiO_2 in Anatas configuration as a dulling agent is very common in man-made fibre processing [4]. The addition of TiO_2 is carried out either during the polymerisation or by using a masterbatch containing up to 40% of TiO_2. Masterbatches are added via dry blending or a side-stream extrusion device and infused into the melt. Especially in terms of using nanoparticles, the agglomeration of particles is a severe issue caused by their high surface energy. A proper dispersion is necessary to gain all the advantages of nanoparticles. To achieve a proper dispersion, melt compounding is used to create a masterbatch [5, 6]. Within the melt compounding, a separation of particles has to be achieved to gain the surface contact of nanoparticles with the polymer that is higher than 80% [7]. In the use of two-dimensional nanoparticles, the separation of particle layers by intercalation and exfoliation is meant in detail.

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Some of the particles, e.g. organoclays, are modified to ease the exfoliation and dispersion in the melt [3]. Proper dispersion of nanoparticles is further necessary to achieve a stable extrusion process. In the fibre process, metal filter elements are used with the pore sizes from 20–70 μm, depending on the filament diameter. Especially in the use of particles, the filters have to be sufficiently coarse to allow a stable extrusion and filament winding without filament breaks [4].
Recent studies on fibre extrusion show that the use of functional particles in fibre extrusion lead to reduced lifetime of spin packs or reduced spinning speed during the melt spinning. The reduced lifetime of spin packs and melt filtration derives from filter clogging due to the agglomerations of functional additives or nanoparticles in the melt filters [4]. As soon as the filter is clogged, the pressure in the spin pack increases and leads to the end of the process. In industry, the filter lifetime of at least 1 day is reached using particles or colour batches [4]. The reduced spinning speed is the result of agglomerations that are not filtered in the spin pack. An agglomeration of 10 μm is larger than half the size of a Nylon 6 filament with 3 dtex. The tension around the agglomeration can be double as high as in the virgin polymer. The stress peaks due to the increase in tension lead to filament breaks and process instabilities.
Apart from the processing problems, the properties of fibres are diminished by using additives. This is a problem for the fibres in high demanding technical applications, e.g. technical nonwovens. The fibres are coarser than the mentioned fineness; hence, there are fewer problems in the process stability, however, the properties, especially tenacity, are reduced.

2 Experimental

Within the experimental part, the spinability and reproducibility in the production process of Nylon 6 and abrasion resistant materials were studied. A highly viscous Nylon 6 provided by EMS-CHEMIE AG was used as a polymeric matrix. Nylon 6 was modified by two different two-dimensional nanoparticles, graphene platelets and organoclays. The effects of different concentrations were studied within the range of 0.1 wt% up to 5 wt% additive content in the polymer. The investigated concentrations are shown in Table 1.

Table 1: Investigated particle concentration

Concentration [wt%]	0.1	0.5	1	3	5
Organoclays	x	x	x	x	x
Graphene platelets	x	x	x		

The nanocomposites were melt spun into fibres using the masterbatch route. Therefore, masterbatches with 10 wt% additive were produced by melt compounding. The final concentration was gained by dry blending, which means mixing the polymers on a granule level. The meltspinning experiments were performed on a lab scale meltspinning plant designed by Fourné Polymertechnik GmbH, Alfter, Germany (Figure). The winding speed was set to 400 m/min.

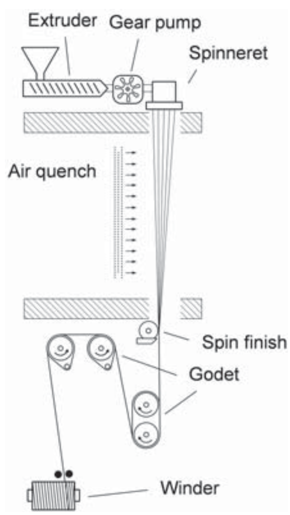

Figure 1: Lab scale melt spinning plant

Subsequently to fibre spinning, hot drawing was performed on a draw stand. The yarns were stretched using the following draw ratios:
- $\lambda_D = 1$
- $\lambda_D = 1.75$
- $\lambda_D = 2.5$
- $\lambda_D = 3.25$
- $\lambda_D = 4$.

To stretch the yarn, it was heated above the glass transition temperature to the temperature of 80 °C. After the stretching, the yarn was tempered on the following godets at 120 °C. The temper process is necessary to reduce the induced tension in the yarn so it can be wound up on a bobbin again.

Due to their structure and geometrical shape, the nanoparticles influence the processing and the tribological behaviour of the fibre. The relationship among the processing conditions, material composition and resulting material properties was investigated. Therefore, the abrasion and mechanical properties were analysed. Moreover, Wide Angle X-ray scattering experiments were performed to gain the insight into the structure of nanocomposites. The properties were compared to a virgin Nylon 6 material.

The abrasion resistance was studied using the bechlenberg test device that was developed at ITA (Institute of Textile Technology at RWTH Aachen University). It studies the bearable abrasion of a fibre against itself under additional loading. The yarns were wound four times around themselves at the angle of 90° and slid against each other with 300 slides per minutes. The bechlenberg test device is schematically shown in Figure 2. The mechanical properties were determined by Statimat 4 U from Textechno H. Stein GmbH & Co. KG, Mönchengladbach, Germany.

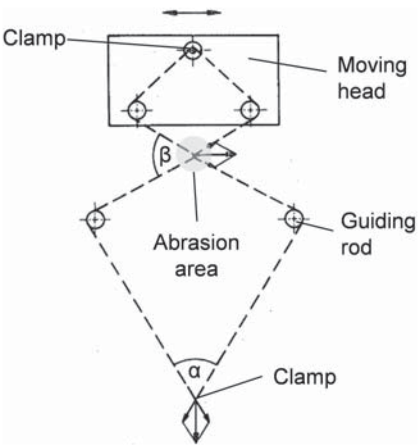

Figure 2: Bechlenberg test device

3 Results

The use of graphene platelets in the meltspinning process was limited to the amount of up to 1 wt%. Further enhancement was not possible as the graphene platelets led to filter clogging in the spinning plant and reduced the fibre properties. Especially during the spinning, the use of a higher concentration led to filament breaks and instabilities during the processing. Even the loadings below 1 wt% led to filter clogging and problems in the process stability over time. Furthermore, the material did not show improvements in terms of abrasion resistance or mechanical properties.

Organoclays led to the results that were more promising. Up to the additive content of 1 wt%, no negative effects were detected and up to 5 wt%, no limitations in the processing were found apart from the reduced drawability. During the abrasion studies, it became obvious that only low amounts of organoclays (up to 1 wt%) lead to the improvement of the fibre. The endurance of the fibre was increased by 100% comparing the best and worst value of the virgin material to the material containing 0.1 wt% organoclays (Figure). The investigation clearly indicates that low amounts of organoclays show better properties than the materials containing more than 1 wt%.

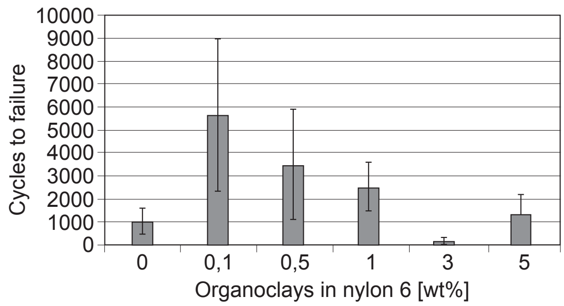

Figure 3: Abrasion resistance with bechlenberg

The analysis of properties show that the mechanical properties were diminished by the presence of organoclays. Particularly the performance was lost at particle contents > 1 wt%, which is shown in Figure 6.

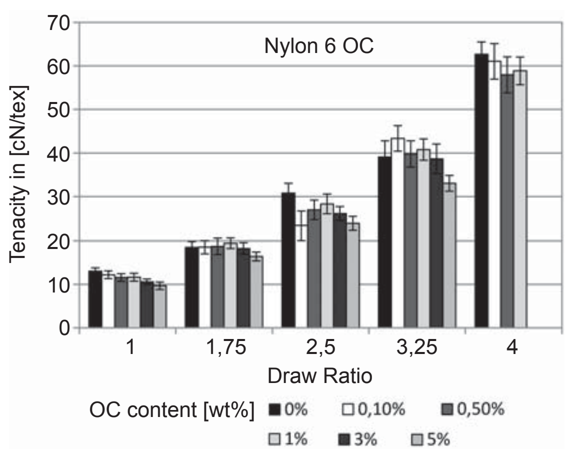

Figure 4: Tenacity over draw ratio (λ_D) and organoclay (OC) content

On the other hand, the modul of the fibre increased with the organoclay content, which is shown in Figure 5.

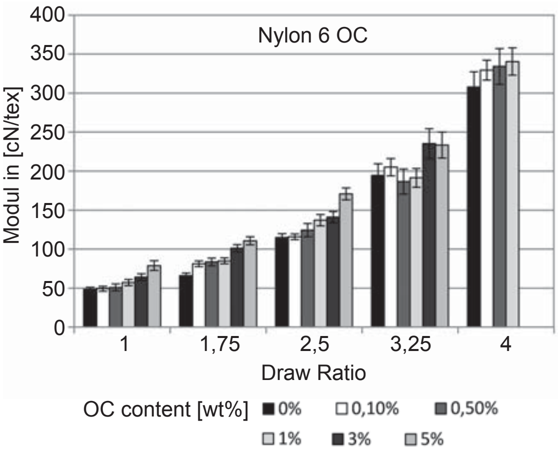

Figure 5: Module over draw ratio (λ_D) and organoclay (OC) content

There was no fibre specimen at the draw ratio λ_D = 4, containing more than 1 wt%, as they did not bear the stretching in the drawing process. This was already visible at tenacity, as it decreased over the particle content.

Due to the WAXD investigation, it became obvious that the presence of organoclays influences the formation of the crystal phases in Nylon 6. The γ-phase was stabilised up to the draw ratios λ_D = 2.5. An example of this investigation is shown in Figure 6. In the virgin Nylon 6 material, there was a steady conversion from the γ-phase in the beginning to the α-phase. The α-phase grows due to stretching and temperature in the drawing process. In comparison, the growth of the α-phase was inhibited in the Nylon 6 material containing 1 wt% of organoclays.

4 Discussion

The results of the investigations are reasonable concerning the fact that the fibre properties in virgin fibres were determined by the orientation and growth of crystal phases. Therefore, it is obvious that nanoparticles are impurities to the fibre, which cannot transfer the forces within the polymeric phase. Hence, the bearable force is reduced due to the stress peaks over the fibre cross-section. The negative effects of nanoparticles are more severe if the particles used are not modified to fit into the Nylon 6 matrix. These particles do not disperse in the matrix and form an agglomeration that leads to filter clogging and instabilities in the process. This is found by the use of graphene platelets. Further negative effects are found by overloading the fibres with particles as found in organoclay contents above 1 wt%.

The results from the WAXD study show that the particles also hinder the crystallisation behaviour. Due to their presence, the polymeric chains are not able to align to each other into crystal phases. Only high drawing leads to the stretching forces necessary to

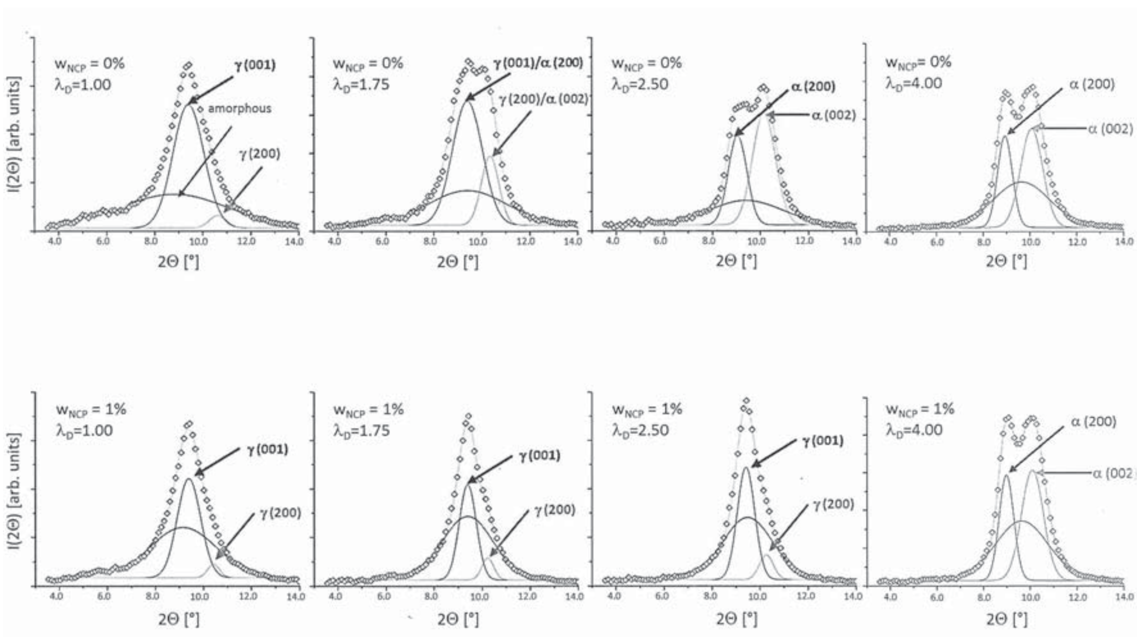

Figure 6: Crystal structure over draw ratio (λD) and organoclay (OC) content

align the polymeric chains around the two-dimensional particles. The change in crystallisation behaviour will influence especially the properties in the draw ratios below $\lambda D = 2.5$. At higher draw ratios, it is found that the crystalline structure becomes similar to a material without additives.

Moreover, the abrasion properties cannot be explained by crystallisation behaviour. The increased abrasion resistance most likely results from the sheer presence of organoclays in the matrix that are less destroyed by the abrasion than the polymer. The increased abrasion resistance is a balance from the increased abrasion properties by using small amounts of additive and the few impurities by the additives not leading to decreased material properties.

5 Conclusion

It was established in the research that there is a balance between the properties gained by the particles and the properties diminished by the use of particles. In the properties, e.g. abrasion resistance, which depend on the mixture of fibre properties, e.g. the module and tenacity, a balance of both properties has to be found. The changes in the crystallisation behaviour caused by the particles mainly influence the fibre at lower draw ratios. In a high drawn state, the properties of the nanocomposites and the virgin materials are similar. The addition of too many particles to the fibre lead to property loss. The inhibition of the $\gamma \rightarrow \alpha$ change is caused by the sheer presence of particles.

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