# COMPOUNDING AND SPINNING OF POLYPROPYLENE NANOCOMPOSITES WITH KAOLINITE

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**Keywords:** nanocomposites, polypropylene, kaolinite, fiber spinning

**Abstract**
*Isotactic polypropylene (PP) was melt compounded with the various amount of kaolinite nanoparticles (from 3% up to 30% wt). Nanofilled fibers with low and high filler amount were successfully produced by melt-spinning process through a co-rotating twin screw extruder and drawn at 145°C in air at increasing draw ratio (up to 15). The dispersion of nanoparticles enhanced the elastic modulus of PP, positively affected the stress at break, and decreased the strain at break for compositions at high nanofiller content (20% and 30% wt.). Moreover, kaolinite significantly improved the crystallinity content, acting as a nucleating agent, and it increased the thermal stability.*

## 1. Introduction

Polypropylene (PP) have been known for its good mechanical properties, corrosion resistance, low density, low cost and easy processability to allow it to be used in a wide areas such as automotive, construction and other industrial applications [1]. The introduction of particulate filler into PP matrix improves their thermal stability, mechanical properties and also shrinkage and flammability. The effects of the fillers on the final properties of the composite depend on their shape, aggregate size, surface characteristic and degree of dispersion. In particular interests are nanocomposites containing organically modified layered silicate because they often exhibit remarkable properties in comparison to those of neat polymer. In the plastic and rubber industry, kaolin has been used as filler because of its great reinforcing effect in mechanical properties, such as stiffness and strength. It was reported by the other researches that the introduction of kaolin improved the stiffness and strength of PP but the elongation at break and impact properties were lower [2, 3]. Recent literature evidences a lot of progress in the nanofilled bulk materials; on the contrary, there are relatively a few publications on the PP fibers nanocomposites. For instance, various nanofillers, such as layered silicates, carbon nanotubes, and montmorillonite [4-9] were used for the production of PP fibers, whereas till now no published data has been found on nanocomposites fiber of kaolin/polypropylene. The aim of the present work is to study the effect of low and high kaolin content on the mechanical and thermal properties of PP fibers.

## 2. Experimental section

### 2.1. Materials

Polypropylene PP505P (MFI at 230°C and 2.16kg = 3.6dg/min) was supplied by Sabic (Sittard, The Netherlands). Kaolinite – Paralux (density $2.6g/cm^3$, surface area $12m^2/g$, average diameter 0.9μm) supplied by Vale, Brazil was added to the PP and compounded with in a co-rotating intermeshing twin-screw extruder Cextral BC21 (Firminy, France) with increasing temperature profile from hopper to rod die in the range 150-200°C and with 250 rpm in the form of masterbaches containing from 10% up to 30% by wt. of the filler.

### 2.2. Nanocomposites fibers preparation

Polypropylene fibers at various kaolinite content in the range 1 and 30% wt. were produced after direct mixing polypropylene and masterbatch, and compounding of selected formulation by using a Thermo Haake PTW16 intermeshing co-rotating twin screw extruder (screw diameter=16 mm; L/D ratio=25; rod die diameter 1.65 mm; temperature profile in the range 130-230°C). The screws rotation speed was regulated depending on the melt flow of material in order to produce as-spun filaments of 500μm and to maintain residence time of 20 min. Fibers were then drawn in air at 145°C, at various draw ratios (DR) from 5 up to 15. Nanocomposites were designated with the matrix and the amount of filler; for instance, the code PP-K10 indicates formulation at 10% by wt. of kaolinite.

### 2.3. Experimental techniques

TEM analysis has been performed on the ultramicrotomed cross section of as-spun nanocomposites fibers in order to get information about nanofiller distribution and their orientation when a strain was applied. The observations were performed by using FEI Quanta 200 SEM microscope, operated under high vacuum at a voltage of 7.5kV. Thermal degradation was studied in the range 50-600 °C by using thermobalance Mettler TG 50 (sample of about 15 mg; heating rate 10 °C/min; air flow 100 ml/min). Differential scanning calorimetry (DSC) analysis was performed on samples of about 15 mg by using a Mettler DSC30 calorimeter, in the range 0-250 °C with a heating-cooling cycle at ±10 °C/min flushing nitrogen at 100 ml/min. Crystallinity of PP was calculated from the melting enthalpy referring to 209 J/g [10]. Mechanical properties of PP fibers were performed at room temperature by using a dynamometer Instron 4502, equipped with a load cell of 100 N. Fiber with diameter from 500 up to 125 micron and gauge length of 30 mm were tested at a cross-head speed of 50 mm/min. Creep test were performed on as-spun and drawn (DR15) fibers at 25°C by using a dynamic mechanical analyzer DMA Q800- TA Instruments® (constant stress : 3 MPa; creeping time: 3600 s; gage length: 10 mm).

## 3. Results and discussion

### 3.1 Morphology

The effect of compounding and the quality of kaolinite dispersion in PP matrix was tested by TEM analysis. The transversal cross section of as-spun PP-K20 fibers with 500μm is depicted in Figure 1. According to these TEM observations, PP-K20 composite fiber evidences homogeneous nanofiller dispersion within the polymer matrix. The nanofiller dimensions are between 3μm and 100nm.

(a)  (b)

(c)  (d)
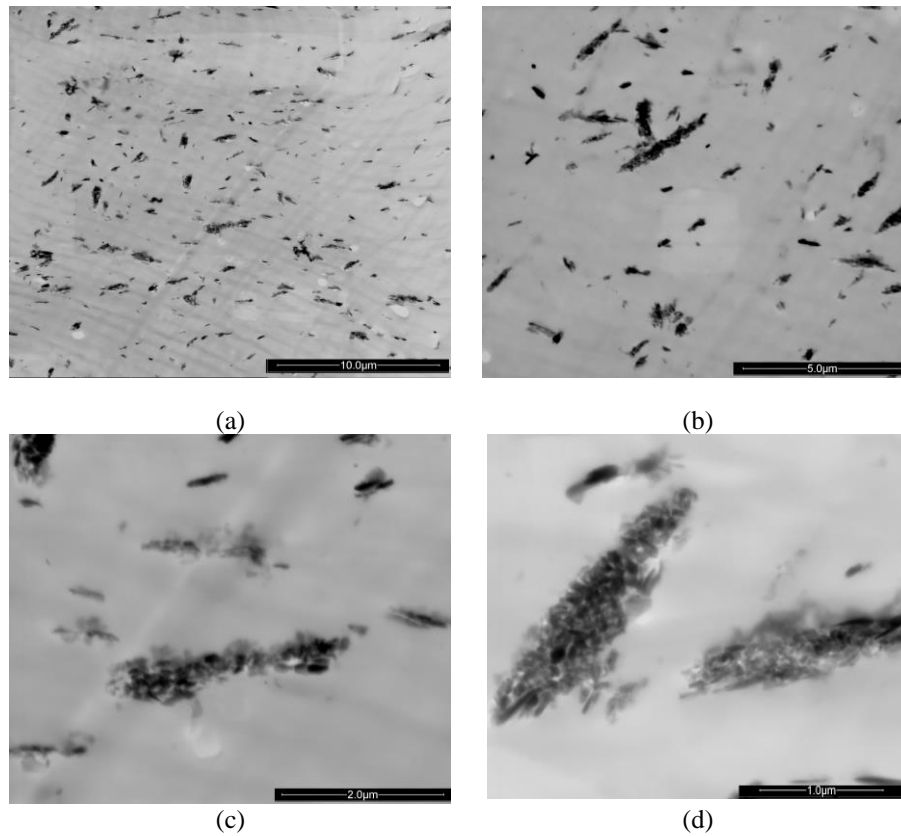
**Figure 1a-d.** TEM micrographs of PP-K20 as-spun fiber performed at different magnification (a) 10000x, (b) 20000x, (c) 50000x and (d) 100000x.

## 3.2. Thermal properties

In order to study the influence of nanofiller content on the thermal stability of polypropylene, TGA analysis was performed. Representative TGA curves of as-spun fibers are reported in Figure 2. The results show one-step degradation for all samples evidencing the beneficial effect of kaolinite on the thermal stability for all the nanocomposite fibers in comparison to neat PP. In the initial step up to 10% of mass loss, it can be observed a higher initial degradation temperature for the compositions PP-K20 and PP-K30 with respect to neat PP.
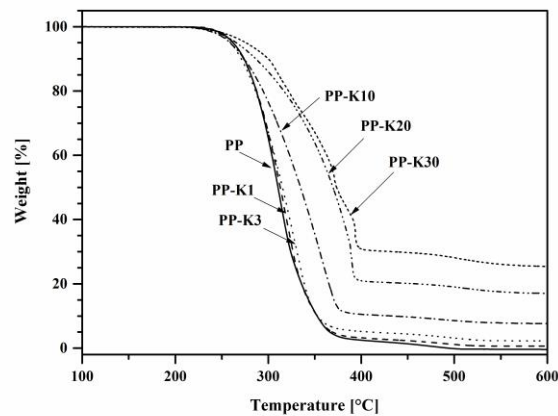


**Figure 2.** TGA curves of neat and nanofiller PP-K fibers under air atmosphere.

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The effect is more relevant at 50% of mass loss, where the compositions at 1-3% wt. of kaolinite evidenced degradation temperature 5 degrees higher than that of neat PP, and furthermore an even higher degradation temperature (about 25-60 degrees) was found for compositions PP-K10, PP-K20 and PP-K30. The residual mass at 600°C ranged between 1% for PP-K1 and about 25% for PP-K30 fibers. The incorporation of kaolinite into the polymer matrix enhances the thermal stability of nanofilled polypropylene.

*3.3 DSC analysis*

DSC thermograms of neat and nanofilled polypropylene as-spun fibers and fibers drawn 15 times are reported in Figure 3, while the most important results are summarized in Table 1. The multiple melting peaks observed for fibers with DR=15 (Fig. 3b) are related to the difference of crystal forms or degree of their perfection obtained during drawing.
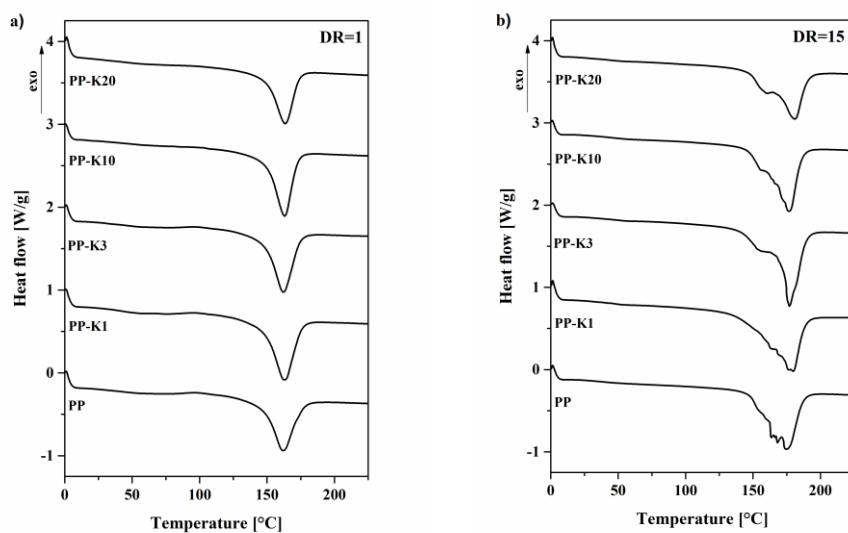


**Figure 3.** DSC thermograms of neat and nanofilled PP fibers at draw ratio a) DR=1 and b) DR=15.

| Sample | Draw Ratio | Melting Temperature [°C] | Crystallinity Content [%] | Crystallization Temperature [°C] |
|--------|------------|--------------------------|---------------------------|----------------------------------|
| PP | 1 | 162.0 | 41.3 | 113.2 |
| | 15 | 175.0 | 50.4 | 123.5 |
| PP-K1 | 1 | 162.7 | 46.5 | 117.8 |
| | 15 | 179.8 | 58.7 | 116.0 |
| PP-K3 | 1 | 162.2 | 44.4 | 122.3 |
| | 15 | 177.1 | 57.7 | 119.4 |
| PP-K10 | 1 | 164.2 | 44.7 | 124.2 |
| | 15 | 178.1 | 56.7 | 123.1 |
| PP-K20 | 1 | 163.7 | 42.8 | 121.0 |
| | 15 | 181.1 | 54.0 | 123.1 |
| PP-K30 | 1 | 163.5 | 44.6 | 123.4 |
| | 10 | 173.3 | 52.7 | 122.4 |

**Table 1**. Results of the DSC analysis: melting temperature ($T_m$), crystallinity content ($X_c$) and crystallization temperature ($T_c$) for neat and nanofilled PP-K fibers before and after drawing at different draw ratio (DR).

From DSC analysis it can be observed that the melting temperature ($T_m$) and crystallinity content of drawn fibers increase with the draw ratio. According to the literature references, the applied drawing induces an ordering of the crystalline phase along the strain direction [11]. The introduction of nanoparticles determined an increase of not only melting and crystallization temperatures, but also the crystallinity content in comparison to the neat fibers. These findings confirm that kaolinite behaves as a nucleating agent in polypropylene [12].

*3.4. Mechanical properties*

Elastic modulus versus draw ratio of nanocomposite PP-K fibers with low and high nanofiller content are represented in Figure 4a and 4b, respectively. In case of low nanofiller content (1% and 3% wt.) no improvement in modulus was observed at low draw ratio (DR<10). At DR=15, a slightly higher elastic modulus of nanofilled fibers was obtained, i.e. 8.2 GPa for PP-K1 and 8.5 GPa for PP-K3 with respect to 7.9 GPa for neat PP. In case of higher nanofiller content (Fig. 4b), a significant enhancement of elastic modulus in all draw ratio range was observed. For example at DR=10, elastic modulus raised from 5.3 GPa for neat PP up to 5.9 GPa, 6.5 GPa and 7.1 GPa for PP-K10, for PP-K20 and for PP-K30 nanocomposite fibers, respectively.
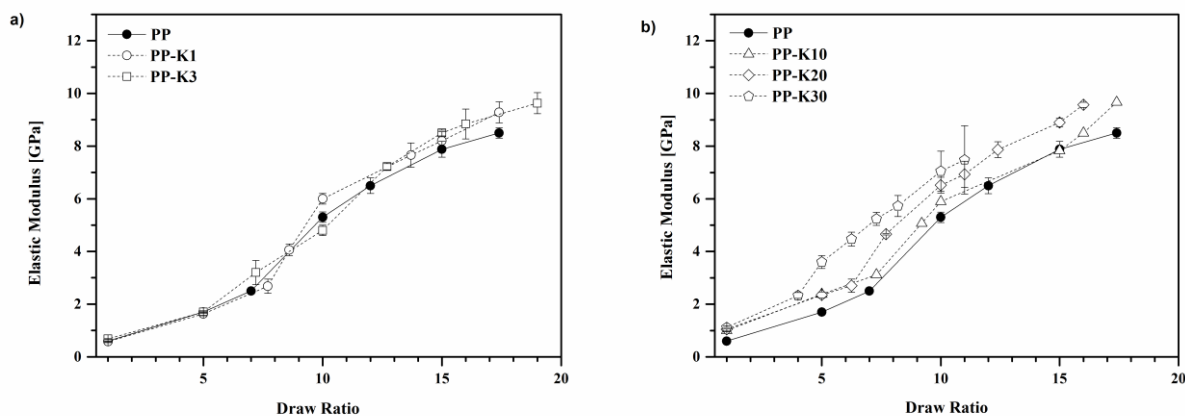


**Figure 4.** Elastic modulus of neat PP and nanofilled fibers at low (a) and high (b) kaolinite content.

It is well known that the stress at break of compositions usually decreases with the addition of the nanofiller. Stress at break for low and high nanofiller content fibers was reported in Figure 5a and 5b, respectively. For compositions with nanofiller content up to 3% wt., the similar values to neat PP were observed for low DR<10, as shown in Figure 5a, analogously to modulus. It is worth noting that the higher the drawing process, the higher the stress at break increases and for DR=15 significant improvement was obtained. In particular at DR=10, neat PP exhibited strength of 775 MPa, whereas 923 MPa and 900 MPa were obtained for PP-K1 and PP-K3 fibers respectively. At higher DR (DR=15) this improvement is even more significant and stress at break reached values of 1240 MPa and 1166 MPa for PP-K1 and PP-K3 respectively, in comparison to 906 MPa for neat PP.

If the results for fibers with high kaolinite content will be taken into consideration, it can be seen that higher stress at break was observed only at higher draw ratio. In particular for DR=15, stess for neat PP (906MPa) was lower than reported for PP-K10 (990MPa), PP-K20 (932MPa) and PP-K30 (924MPa). It is important to underline that differently from common cases where the stiffening effect is accompanied by reduction of the tensile strength, in this case of polypropylene kaolinite drawn fibers a parallel enhancement of both modulus and stress at break was observed, even at high nanofiller content (see Figures 4b and 5b).

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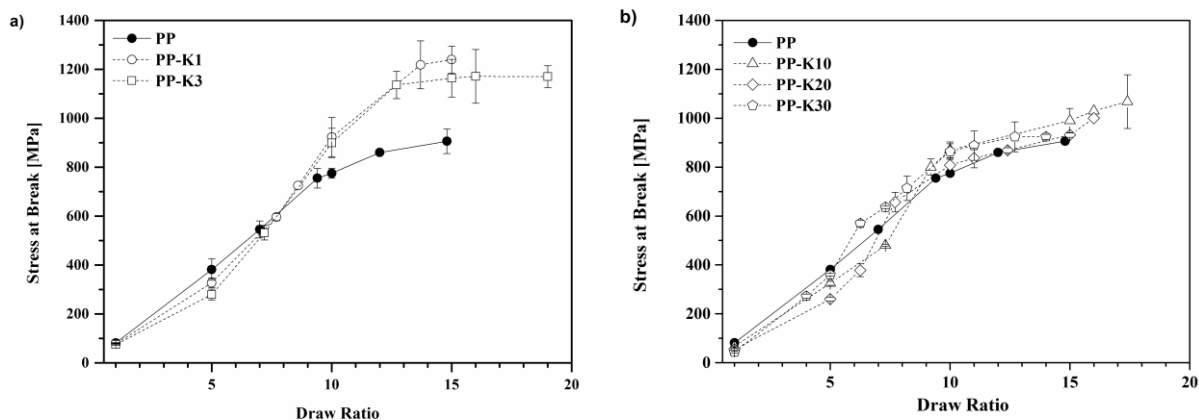
**Figure 5.** Stress at break of neat PP and nanofilled fibers at low (a) and high (b) kaolinite content.

In Figure 6 strain at break for nanocomposites PP-K fibers with a) low and b) high nanofiller content are reported. As expected at low nanofiller content (Fig. 6a), no reduction in elongation at break was observed for PP-K1 and PP-K3 fibers. However, for fibers with high nanofiller content (Fig. 6b) significant reduction of strain at break was detected for low draw ratio, while with drawing process the behavior of neat and nanofiller fibers was very similar.
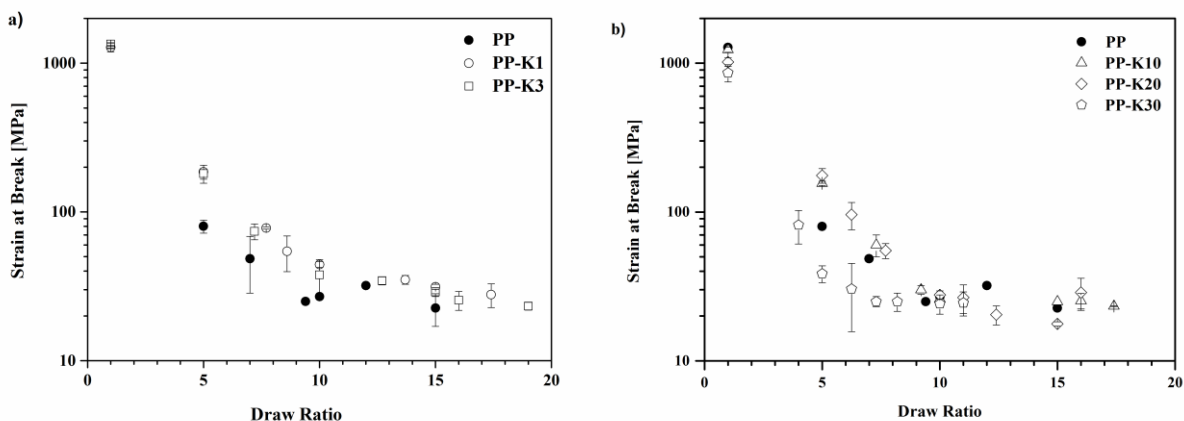


**Figure 6.** Strain at break of neat PP and nanofilled fibers at low (a) and high (b) kaolinite content.

It can be concluded that for fibers drawn at higher draw ratio (DR≥10) a significant improvement of modulus was obtained, together with the enhancement in stress at break, without affecting strain at break. This behavior could be related to the homogeneous kaolinite dispersion inside the polymer matrix, that significantly enhanced the filler-polymer interfacial adhesion and it is responsible for the improvement of mechanical properties.

*3.5. Creep test*

Creep compliance curves for neat and nanocomposite polypropylene fibers, tested at the same stress level of 3MPa, are depicted in Figure 7.
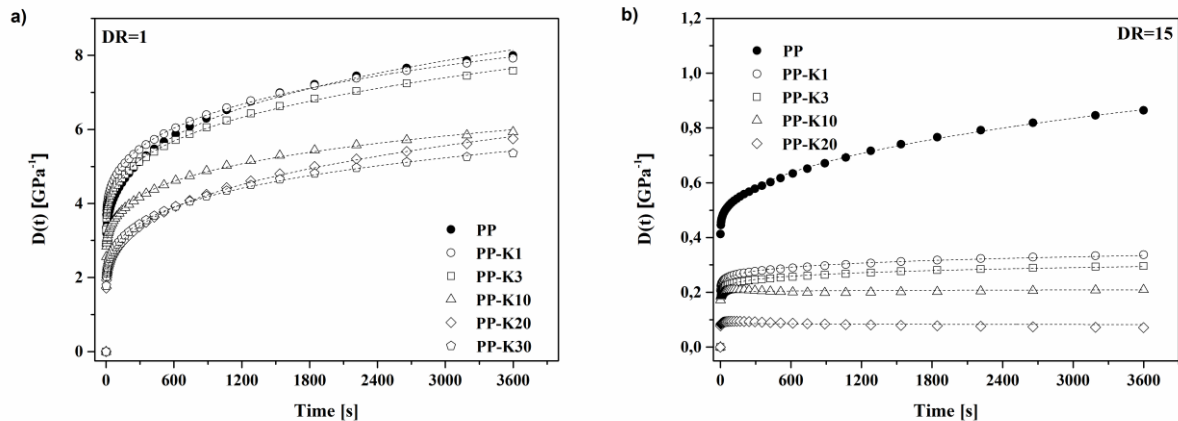
**Figure 7.** Creep test on neat PP and nanofilled fibers for different draw ratio a) DR=1 and b) DR=15 at 25°C.

If the data for as-spun fibers (DR=1) will be compared the creep compliance for the compositions with low nanofiller content (1-3% wt.) was only slightly lower, while for high kaolinite content (10-30% wt.) the reduction of creep compliance was significant. Moreover, a remarkable improvement of the creep stability of nanofilled fiber drawn at DR=15 was observed, for all the compositions with kaolinite content in the range 1-20%. Similar results were already observed in case of polyethylene – fumed silica nanocomposites fibers [13]. The relevant improvement has been related to the intercalation of nanoparticles, which may effectively reduce the polymer chain motion, affecting the stress transfer at a nanoscale level, which has positive effect on the final creep stability of the composite material [4].

## 4. Conclusions

Polypropylene nanocomposites with kaolinite content up to 30% wt. were successfully compounded and spun by combined melt-extrusion and hot-drawing process. Thermo – mechanical properties of polypropylene nanocomposite fibers, prepared by using kaolinite nanoparticles, were evaluated and compared with those of neat polypropylene fibers. Thermal stability of the nanofilled fibers was remarkably improved, especially at high kaolinite content, above 10% by wt. The introduction of nanoparticles induced an increase of both melting and crystallization temperatures, and crystallinity content, confirming the nucleating effect of kaolinite in polypropylene. From the mechanical analysis, a higher elastic modulus of nanofilled polypropylene fibers without affecting the ultimate tensile properties was observed. The stabilizing effect provided by kaolinite was confirmed also in creep tests, where an evident reduction of the creep compliance with respect to the neat PP fibers was obtained for as-spun and expecially drawn fibers. The improvements of mechanical properties for nanofilled fibers were attributed to the good dispersion and ordering of kaolinite particles along the strain direction, promoting the molecular orientation and the crystallization of the amorphous regions.

## 5. References

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