Synthetic Metals 245 (2018) 51–60

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Influence of melt spinning parameters on electrical conductivity of carbon fillers filled polyamide 12 composites

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ARTICLE INFO

Keywords:
Smart textiles
Conductive polymer composites
Electrical conductivity
Melt spinning
Drawing ratio
Twisting

ABSTRACT

Nowadays, the market is flooded by smart textiles due to the major advances made in the development of flexible materials. Electrical conductivity is one of the most important properties, which can be assured by the introduction of metallic filaments in the yarns. However, such introductions of metallic filaments can cause a decrease of the characteristics of textile (flexibility, durability). Thus, a lot of studies focus on the development of electrical conductivity that does not decrease the characteristics of textile. An alternative to develop conductive polymer composites (CPC), is conductive fillers which can be integrated into the polymer. The current technic a bulk functionalization of the polymer during melt spinning allowing a thermoplastic yarn to become electrically conductive. In this study, the electrical conductivity of carbon black (CB) fillers filled multifilaments based on polyamide 12 (PA12) was optimized. The CPC were prepared in two steps: the first step was the incorporation of the fillers in PA12 by twin screw extrusion, and the second step was the melt spinning to obtain multifilament yarns. After extrusion, the blend has an electrical conductivity of 101 S/m. However, after the melt spinning of this blend, the electrical conductivity dropped sharply to 10-6 S/m. Several experimental parameters during the melt spinning can modify the structure filaments and impact on their electrical conductivity, which could explain this loss of electrical conductivity. Drawing out of rod during extrusion, as well as different melt spinning parameters, such as volumetric pump output and speed variation of the drawing rolls, were identified as key factors that not only influence the electrical conductivity but also the mechanical properties of the yarn. A low drawing ratio combined with a low pump output can increase the electrical conductivity. With the same value of volumetric pump output and the same supply roll speed, if the drawing roll speed increases from 225 rpm (rpm) to 450 rpm, the electrical conductivity decreases by a factor of 10, respectively 7.10-5 S/m and 7.10-6 S/m. Observations by transmission electron microscopy (TEM) of the two CBs inside PA12 give insight the dispersion of nanofillers, which effects on the CB physical network and its subsequent electrical conductivity. At the scale of the yarn, twisting can increase the contact path between the monofilaments and increase (from 10-6 S/m to 10-5 S/m) the global conductivity until a plateau for the multifilament. Thus, the key factors explaining this loss of electrical conductivity between the rod and the multifilament were identified. However, these parameters also effect the mechanical characteristic of the materials too.

1. Introduction

Customer satisfaction is one of the main target of the textile industries which made more and more innovation in the smart textiles due to an increasing range of applications. These applications are for instance made by the functionalisation of the textile which allows bringing new properties. One of the main properties is the electrical conductivity of the textile materials. In fact, this conductivity can be used in fashion for aesthetics [1], but also in technical fields, for sensor material [2–6], heating textiles [7], or for electromagnetic interference properties [8,9]. To obtain these kinds of textiles, several manufacturing processes exist such as the surface treatment which can be mainly made by two different methods. First, as illustrated by Malinauskas et al. [10], the coating can be used on the textile surface. The authors showed the possibility to have an electrical conductivity through the coating with several conducting electroactive polymers like polyaniline which was an intrinsic conductive polymer (ICP) [11,12].A Second method is the surface metallisation of polymer by a vacuum coating system an e-beam gun [13]. Other method to achieve electrical conductivity in the smart textile is the introduction of conductive elements in the textile, such as metallic material or carbon fiber, or in the polymer, such as a conductive polymer composite (CPC) by adding

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https://doi.org/10.1016/j.synthmet.2018.08.003
Received 20 March 2018; Received in revised form 10 July 2018; Accepted 5 August 2018

conductive fillers in insulated polymer. Several kinds of fillers can be used, such as metallic particles, ICP, or carbon black. Mamunya et al. [14] proved that metallic powders were able to give a high electrical conductivity with a low filler content. They showed that with 0.3 wt.% of copper powders filled polyvinyl chloride, the electrical conductivity was 5.2 log(S/m), whereas without filler the electrical conductivity was -13.2 log(S/m). The second example is based on the use of intrinsically conducting polymers (ICP) as shown for instance by a study made by Zhang et al. [15].They found that 5 wt.% of polyaniline filled polyamide 11 showed an increase in the electrical conductivity from 10^{-6} S/cm to 10^{-1} S/cm. Numerous studies were carried out on carbonaceous fillers, as carbon nanotubes (CNT), carbon black particles (CB) or graphene, due to their stability, the absence of oxidation and good conductivity. Each of these fillers has its own special characteristics which can change the resulting electrical conductivity. For example, Kwon et al. [16] have shown that different fillers can modify the electrical conductivity of polymer due to their different specific areas. Dorigato et al. [17] have proved that the filler content has an important influence on the conductivity and conductive network capabilities of the CPC. They increased the electrical conductivity of the acrylonitrile-butadiene (ABS) from 10^{-12} S/cm to 10^{-6} S/cm with 0.8 wt.% of CNT. Moreover, in this study, authors have illustrated that the percolation threshold was near to the 2 wt.% of CNT. However, when the filler content became superior to the percolation threshold, the conductivity remained steady [18,19]. Bauhofer et al. [20] reviewed on the percolation threshold in a polymer filled with CNT and they demonstrated that the CNT addition in polymer had an insignificant effect on the percolation threshold, contrary to the chemical nature of polymer and dispersion method used. They indeed explained that a polymer followed the theoretically predicted percolation if the fillers were well dispersed. Other studies demonstrated that the dispersion and the orientation of fillers were also significant [21–23] for the value of electrical conductivity. Bouchard et al. [24] have illustrated, for a polyester sulfone filled with 1 wt. % of MWCNT, that the dispersion time has an influence on the electrical conductivity. For 5 min of dispersion time, the electrical conductivity was approximately -1.5 log(S/m) and for a 60 min of dispersion time, the electrical conductivity was -8.5 log(S/m). Bouchard et al. [25] have observed on a multifilament of poly ((hydroxyl-ether) of bisphenol A) that the filler content have an influence the mechanical properties. They have found that when the filler content increase from 0 wt. % to 1.5 wt. %, the elongation at break decreases, 121.8% and 59.9% respectively. Vilmow et al. [26] studied the influence of temperature profile, rotation speed and screw profile in order to evaluate the variation of the dispersion and the distribution in the CPC. Miles et al [27], have explained that the dispersion in particular depends on the polymer viscosity. During melt spinning, the draw ratio of rolls and shear rates of the volumetric pump can have an effect on the CNT alignment and mechanical properties. Cayla et al. [28] illustrated that the mechanical properties were influenced by the draw ratio on a nanocomposite of 90 wt.% of polypropylene and 10 wt.% of polycaprolactone filled with 4 wt.% of CNT. With this CPC, when the draw ratio increases the elongation at maximum force decreases. When the draw ratio was at 1, the elongation at maximum break was at 350% whereas when the draw ratio was at 5, the elongation at maximum force was approximately at 75%. Due to melt spinning process, filler agglomeration and presence of defects can be reduced and the crystallisation rate of the polymer can be increased [29,30]. Feller *et al.* [31] demonstrated that the extrusion parameters were important in order to enhance the CPC's conductivity for various thermoplastic polymers. In fact, they have shown that the screw rotation speed and the temperature can decrease the electrical conductivity of a nanocomposite based on poly (butylene terephthalate)/poly (amide12-b-etramethyleneglycol)-carbon black (PBT/PEDAX-CB). They measured that when the screw speed was 25 rpm (rpm), the electrical resistivity at room temperature, 1.3 log(Ω/m), was higher than when the screw speed was 5 rpm, 0.9 log(Ω/m) at 239 °C. The electrical conductivity being the opposite of electrical resistivity, so at 25 rpm the electrical conductivity was lower than 5 RPM. The implementation during the extrusion and the melt spinning must then be studied carefully for each CPC, in order to optimize the electrical conductivity.

The drawback of using CPC is the influence of the conductive fillers on the rheological properties of the material. The melt flow index (MFI) decreases if fillers are added into the polymer [25,32,33]. And addition of fillers makes the melt spinning process of polymeric material harder. However, the MFI must not be too low or too high as demonstrated by Straat et al. [34]. A compromise between the MFI and the targeted electrical conductivity has to be found to ensure the spinning process. In this way, the filler content must lead to a satisfactory value of the MFI and be just above the percolation threshold. In order to find a compromise, synergy between several fillers to optimize the conductive network has to be established [19,35,36]. He et al. [37] showed that using several type of fillers in the nanocomposite enables an improvement of the electrical conductivity of polymer with a synergy of fillers between multiwalled carbon nanotube (MWCNT) and graphene nanosheets (GNs) in an epoxy resin. Indeed, the electrical conductivity at 1% filler content with the synergy was -1 log(S/m) as opposed to 1% filler content with only GNs which electrical conductivity was -3 log(S/m). In fact, the different fillers allow to create more network conductivity thanks to their different specific area. Moreover, the rheological properties are less affected due to the low fillers content. The rule of mixture behaviour as proposed by Marom and Fischer can evaluate the efficiency of this synergy [38].

In this paper, polyamide 12 (PA12) filled with two kinds of carbon black particles was studied: Ketjenblack (CB Ket) on one hand and Printex L6 (CB L6) on the other hand. PA12 filled with a blend of 3 wt.% CB Ket and 8 wt.% CB L6 was the optimal formulation for the nanocomposite, corresponding to a filler content just above the percolation threshold and an acceptable MFI of 20.9 g/10 min at 230 °C under a load of 2.16 kg (ISO 1133 standard). During the melt spinning process, some parameters such as the draw ratio, the output of the volumetric pump, the speed of the drawing rolls and the multifilament twisting can vary and be adapted. The aim of the study was to understand how these parameters can change the electrical conductivity and the mechanical properties of the multifilaments. In order to observe these different modifications, transmission electron microscopy, tensile tests and electrical characterizations were used.

2. Experimental

2.1. Materials

PA12 AMNO TLD supplied by Arkema (spinnable grade), use in this study had a melting temperature (Tm) of 180 °C and a glass transition temperature (Tg) of 40 °C. Two kinds of carbon blacks were studied: Ketjenblack EC-300 (CB Ket) provided by AkzoNobel and Printex L6 (CB L6) supplied by Orion Engineered Carbons. These two classes of carbon blacks, CB Ket and CB L6, have bulk densities of 0.125 g/cm^3 and 0.09 g/cm^3, specific areas of 800 m^2/g and 270 m^2/g, and primary particles diameters of 40 nm and 18 nm respectively. Moreover, the shape of CB L6 are spherical as opposed to CB Ket which have a possessing a branched structure. Several blends with different filler content of CB Ket and CB L6 have been made. For each one, the electrical conductivity was measured following the process explain in the paragraph 2.3.1. The MFI at 230 °C under a load of 2.16 kg (ISO 1133) was also measured. Fig. 1 displays the electrical conductivity and MFI of each blend.

This figure shows that when the filler content increased, the electrical conductivity increased and the MFI decrease. However, it is necessary to have a compromise between the MFI and the electrical conductivity to obtain a conductor multifilament. Thus, the optimized blend has been determined by a formulation of PA12 + 3 wt.% CB Ket + 8 wt.% CB L6, with a MFI of 20.9 g/10 min at 230 °C under a load of