

LIQUID CRYSTALLINE SINGLE-POLYMER SHORT-FIBRES COMPOSITES

T. Medeiros Araujo^{*}, A. Pegoretti

Department of Materials Engineering and Industrial Technologies, University of Trento, Via Mesiano 77, 38123 Trento (Italy)

**thiago.medeiros@ing.unitn.it*

Keywords: Single polymer composites, liquid crystalline polymer, Vectran, mechanical Properties.

Abstract

In order to produce single-polymer short-fibers composites (SPSFCs) using Vectran NT fibers, a heat treatment to increase their melting temperature, mechanical properties and thermal stability was optimized. Furthermore, a two-step process was successfully developed to consolidate SPSFCs containing up to 30 wt% of thermally treated Vectran fibres in a matrix of untreated Vectran. The results exhibited a remarkable improvement on the tensile modulus of the composites (up to 161%) and, as expected, a decrease of elongation at break in comparison with the unfilled matrix. Through SEM observations the pull-out phenomena could be noted, attesting the poor fibers-matrix adhesion. A plasma surface treatment was used in order to improve the matrix-fiber adhesion. Tensile modulus increased up to 178% in comparison with unfilled matrix, and fiber breakage could be noted in the SEM observations, attesting the treatment effectiveness.

1 Introduction

Due to an increasing attention to environment preservation, it recently emerged a general interest to improve the recyclability of composites materials. One possibility is offered by the development of so-called "single-polymer composites" (SPCs), i.e. composite materials in which both matrix and reinforcement have the same chemical composition. The main advantage of SPCs is that, unlike traditional heterogeneous composites (such as glass- or carbon reinforced polymer composites), they can be entirely melted down at the end of the product life for recycling. Besides recyclability, the interfacial bonding on SPCs should be improved based on the principle that matrix and fiber are made of the same polymer. On the other hand, one of the main problems in SPCs production arises from the small difference between the melting temperatures of fiber and matrix [1, 2].

Liquid crystalline polymers (LCPs) represent a class of polymers well known for their excellent mechanical properties, thermal and chemical resistance, and low density, which result in exceptional specific properties [3]. Unlike conventional polymers, they crystallize from an ordered and oriented molecular phase, intermediate between a liquid and a solid or glassy phase.

Among the main uses of LCPs, the following applications should be mentioned: production of high precision moldings for use in the electronics industry, multi-way electrical connectors, components in printers and disk drives, transformer bobbins and encapsulation for surface

mounted silicon chips[4]. LCPs can be broadly classified in three classes: (a) aromatic polyamides, (b) aromatic heterocycles, and (c) aromatic copolyesters [3]. Aromatic polyamide fibers, commonly known as aramid fibers, are obtained from polyamides containing aromatic rings along the main chain, and the commercial products most known are Kevlar®, and Twaron®. Aromatic heterocyclic polymers represent themselves lyotropic materials and are characterized by wholly aromatic molecular structures with fused heterocyclic rings along the main chains; PBI and Zylon® are two examples in this category. Aromatic copolyester polymers are characterized by a molecular structure with a high degree of linearity and rigidity that allows formation of ordered phases over a wide temperature range; among them the three examples are Vectra®, Xydar® and Ekonol® [3]. Vectran, in particular, is superior to aramid fibers in several ways: it is very resistant to creep, it resists flex or fold fatigue and abrasion, and it has better long-term resistance to UV degradation [4, 5].

Vectran fibers are melt-spun LCPs that exhibit excellent mechanical properties, coupled with good thermal and chemical resistance. Previous investigations have shown that SPCs can be successfully produced using commercially available continuous LCP fibers having different thermal transitions [6-8].

In the last decades several strategies have been studied, in order to improve the interfacial adhesion between matrix and reinforcement in composite materials. The fibers surface preparation is the key to the successful creation of a composite material, this preparation is performed to remove weak boundary layers and to increase wettability of the fibers. Certain low-energy fibers surfaces must be modified by plasma treatment, acid etching, flame treatment, or some other means to create attractive forces necessary for good matrix adhesion. With some polymeric materials, the fibers are chemically modified to encourage wetting and to achieve acceptable bonding. Thermoplastic materials are generally difficult to bond and some kind of treatment, such as oxidation by flame treatment, plasma or corona treatment, ionized inert gas treatment, or application of primers or adhesion promoters, is usually necessary [9]. Plasma treatments using different gases were successfully performed in Vectra in previous works [10].

The aim of this work is to develop single-polymer short-fibers composites (SPSFCs) using Vectran® NT fibers and investigate their tensile mechanical properties.

2 Materials and testing methods

2.1 Materials

Kuraray supplied the Vectran used in this work under the trade name of Vectran NT. Vectran is a melt-spun LCP fibers having linear density of 750 denier and 150 filaments per yarn. Vectran is a copolymer of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphtonic acid (HNA) with a molar ratio of 73/27, respectively [11, 12]. The fibers possess an almost circular cross-section with an average diameter of $25.5 \pm 2.1 \mu\text{m}$ [7] and have been chopped in 12 mm short fibers with an automated cutting device.

2.2 Heat treatment

To prepare the SPSFCs, a processing window is required between matrix and reinforcement in terms of melting temperature. In order to increase the mechanical properties and improve the thermal stability of LCP fibers, heat treatments have been widely used on the last two decades [13-16]. In this study, an thermal treatment was optimized in order to increase the melting temperature and tensile properties of commercially available Vectran® NT fibers. The annealing consisted in increasing the fibers temperature close to the melting temperature, and keeping them under these conditions for a pre-determined amount of time. The annealing was performed in an oven under inert atmosphere in the temperature range of 240 - 300°C and treatment times lasting between 2 and 24 hours.

2.3 Plasma treatment

The plasma apparatus, consisting of a glass cylinder reactor (500 mm in length and 150 mm in diameter) equipped with semi cylindrical copper electrodes, was assembled in this laboratory. A radiofrequency generator RF5S (maximum power 500J.s⁻¹ and frequency 13.56 MHz) matching network AM-5 and controller AMNPS-2A supplied by RF Plasma Products, (Marlton, NJ, USA) were used. Vacuum, produced by a double stage pump, was controlled and measured by Edwards devices. The working pressure was ca. 1 atmosphere [17]. The voltage of 30V and a treatment time of 3 min were used in the fibers treatment; oxygen flowed along the reactor axis at a flow rate of 10 ml/min.

2.3 Sample preparation

SPSFCs were prepared by a two-step process, in a first step both untreated and thermally treated short-fibers were mechanically mixed at weight fractions of 10, 20 and 30%. The next step is the SPSFCs consolidation; an aluminum square mold of 120 x 120 mm² and 1 mm thick was used. The mixture was placed between two 1 mm thick PTFE sheets and hot-pressed using a Carver Laboratory Press at a temperature between the melting points of the constituents (295°C) once the consolidation temperature was reached the pressure was increased until 4.4 MPa during 30 seconds and then the SPSFCs were cooled under pressure (1.8 MPa). In this way single-polymer composites plates of LCP reinforcing fibers embedded in a LCP matrix were prepared.

2.4 Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed using a modulated DSC 2920 TA instrument. The heating rate was 10°C/min under a nitrogen flux of 100 mL/min.

2.5 Tensile Testing

All the tensile tests were conducted using an Instron model 4502 universal testing machine. Tensile tests on the single fibers were executed according to ASTM standard C 1557 with a 10N load cell. The gage length used was 25 mm under a cross-head speed of 1 mm/min. Single fibers were randomly extracted from a bundle and mounted on cardboard frames using a quick-setting glue. The diameter of individual fibers was measured using an optical microscope.

Tensile tests on composites were performed on ISO 527 1BA specimen with a 25 mm gage length at a crosshead speed of 1 mm/min with a 1 kN load cell.

2.6 Observations

Scanning electron microscopy (SEM) images were obtained using a Zeiss Supra 40 device operating in high vacuum. Secondary electron and In-Lens detectors were used.

3 Results and Discussion

3.1 Heat Treatment

The first step to optimize the heat treatment on the fibers requires studying the influence of the temperature on the process. For this purpose, DSC analyses on fibers treated at 240°C, 260°C, 280°C and 300°C for 2 hours were performed. In Figure 1(a), the untreated fibers show two wide endothermic peaks probably related to an orthorhombic to nematic transition [11, 13, 18]. After the heat treatment a new endothermic peak (T_{m1}) appears at a temperature increasing with the treatment temperature.

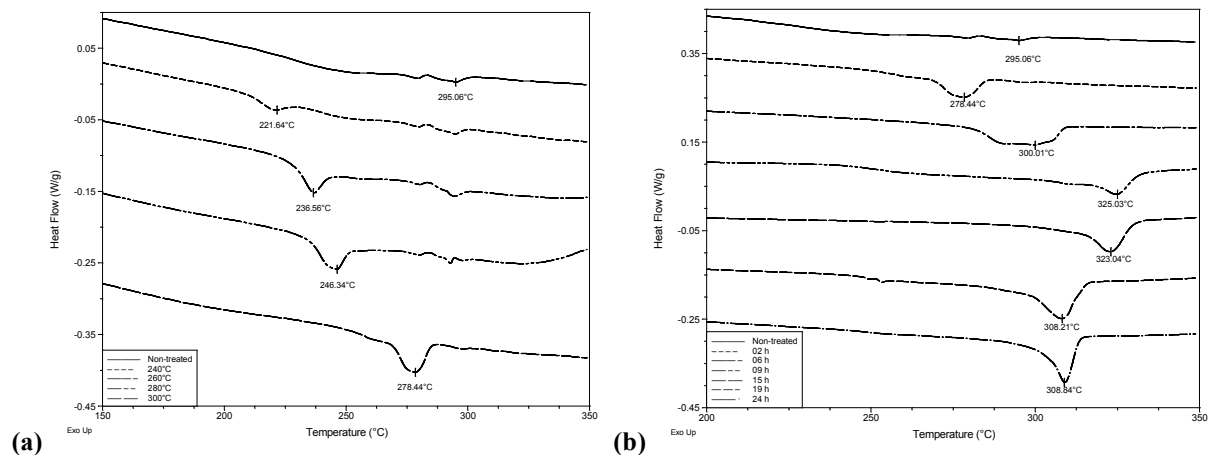


Figure 1. (a) DSC traces of Vectran fibers as a function of treatment temperature for 2 hours. (b) DSC traces of Vectran fibers as a function of treatment time at 300°C.

As reported in previous studies T_{m1} could be attributed to inter-chain transesterification reactions [11, 18]. When the treatment was performed at 300°C, T_{m1} overlaps the two endothermic peaks present in the untreated fibers becoming the new melting temperature of the fibers and due to a largest increment in T_{m1} temperature, 300°C was chosen as an optimal heat treatment temperature. In order to establish the most effective treatment time, DSC analysis were also performed on fibers treated at 300°C for 2, 6, 9, 12, 15, 19 and 24 hours. DSC traces of Vectran fibers as a function of the treatment time at 300°C are presented in Figure 1(b). It is interesting to observe that until 15 hours of treatment T_{m1} moves to higher temperatures with increasing treatment times. After this time, T_{m1} starts to decrease, probably due to degradative phenomena. The heat treatment at 300°C for 15 hours in inert atmosphere effectively increased the melting point of Vectran NT fibers by almost 30 °C. At this point, tensile tests were conducted to verify the effect of the selected heat treatment (300°C for 15 hours) on the mechanical properties of the fibers. In Table 1 mechanical properties of treated and non-treated single fibers are compared.

Besides the increment in the melting temperature, the thermal treatment increases the tensile strength by 51% and elongation at break by 16%. However, the tensile modulus of the fibers does not change significantly.

Property	Vectran NT	Treated Vectran
Tensile modulus [GPa]	61.6 ± 3.2	61.4 ± 8.8
Tensile strength [MPa]	1007 ± 44	1521 ± 123
Elongation at break [%]	2.17 ± 0.15	2.43 ± 0.23

Table 1. Tensile properties of single Vectran treated and non-treated fibers.

In the existing scientific literature, the thermally induced improvement of the tensile mechanical properties of LCP fibres has generally been attributed to an increase in molecular weight after the treatment [13-15].

3.2 SFSPCs characterization

Once confirmed the effectiveness of the heat treatment to increase the melting temperature and the mechanical properties of the Vectran fibers, the SPSFCs were consolidated and their mechanical properties evaluated.

Table 2 compares the tensile properties of the unfilled matrix against the composites produced using different weight fractions of reinforcements.

Property	Unfilled Matrix	SPSFC (10 wt%)	SPSFC (20 wt%)	SPSFC (30 wt%)
Tensile modulus [GPa]	1.31 ± 0.14	1.30 ± 0.12	1.77 ± 0.10	3.42 ± 0.67
Tensile strength [MPa]	37.69 ± 9.17	33.85 ± 5.59	33.16 ± 4.64	29.30 ± 4.03
Elongation at break [%]	5.00 ± 1.44	3.71 ± 0.77	2.59 ± 0.56	0.79 ± 0.20

Table 2. Tensile properties of unfilled matrix and SPSFCs at different weight fractions.

It is worthwhile to note that composites with 10 wt% of reinforcement do not manifest a significantly improvement of the tensile properties. On the other hand, when the filler content is raised to 20 wt% the tensile modulus increases by 35% and with a further increase of the reinforcement content (30 wt%) an increment of 161% in the tensile modulus can be observed. At the same time, all the SPSFCs produced manifest an expected decrease in the elongation at break and a slight decrease of the tensile strength with respect to the unfilled matrix.

The scanning electron microscope (SEM) observations (Figure 2(a) and (b)) show diffuse pull-out phenomena instead of fibers breakage, this behavior could be tentatively explained by the presence of a poor fiber-matrix interface.

This poor interface between matrix and reinforcement could be related to the presence of a sizing. The sizing is added to the fibers during their production, its function is to avoid that the single fibers attach each other. This cause an incompatibility with the matrix, also chemical changes could occur in the sizing during the heat treatment developed in this work, hindering a good matrix-fiber interface.

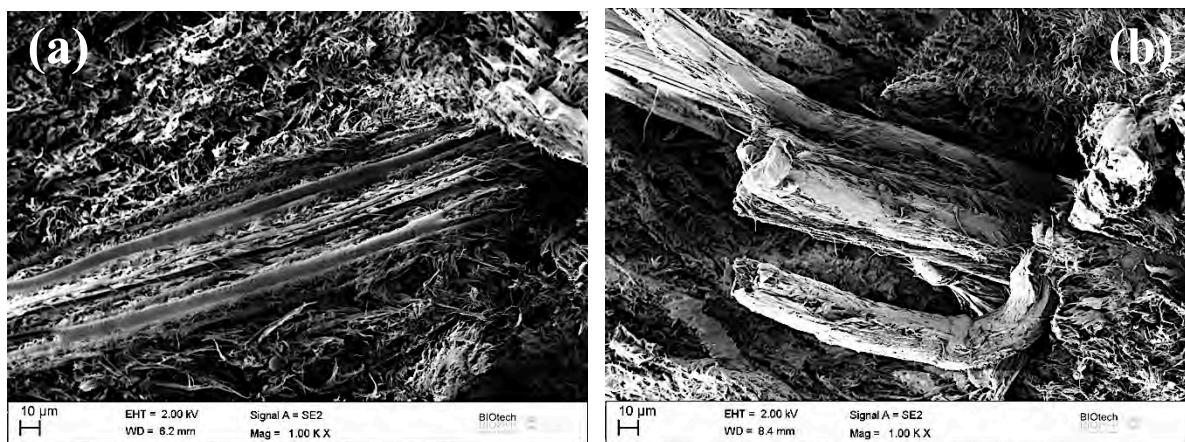


Figure 2 (a) and (b). SEM micrographs of SPSFC (20 wt%) brittle fracture.

In order to improve the interfacial fiber-matrix adhesion, surface modifications and the use of additives are commonly used, due to the SPCs concept the use of additives will be avoided in this work and a plasma treatment on the heat-treated fibers had been used instead.

The results of the tensile properties containing the plasma treated fibers are summarized in Table 3. The composite using 20 wt% of plasma treated Vectran fibers indicates a remarkable improvement of 178% in the tensile modulus with respect to the unfilled matrix and 106% in comparison with the composite using the same amount of non-plasma treated fibers. In terms of tensile strength the composite with plasma-treated fibers maintained the same behavior of the composite with non-plasma treated reinforcement. As a predictable result, the elongation at break show a decrease in its value, this property is directly related to the interface matrix-reinforcement attesting that the plasma treatment is efficient.

Property	Unfilled Matrix	Non-Plasma Treated (20 wt%)	Plasma Treated (20 wt%)
Tensile modulus [GPa]	1.31 ± 0.14	1,77 ± 0,10	3,64 ± 1,30
Tensile strength [MPa]	37.69 ± 9.17	33,16 ± 4,64	31,68 ± 11,01
Elongation at break [%]	5.00 ± 1.44	2,59 ± 0,56	0,73 ± 0,16

Table 3. Tensile properties of unfilled matrix, non-Plasma treated and Plasma treated SPSFCs at 20%wt.

The effectiveness of the plasma treatment could be evidenced by SEM observations (Figure 3 (a)) where the SPSFCs shows a predominant fiber breakage, in other words, the matrix is transferring the load to the reinforcement and, due to the improvement of the matrix-fiber interface; the fibers are not pulled-out, thus increasing the tensile modulus of the SPSFCs and reducing the elongation at break of the composite. Nevertheless, some pull-out phenomena still could be found in the composite (Figure 3 (b)), this can be tentatively explained by a non-homogeneous plasma treatment over all the heat treated fibers.

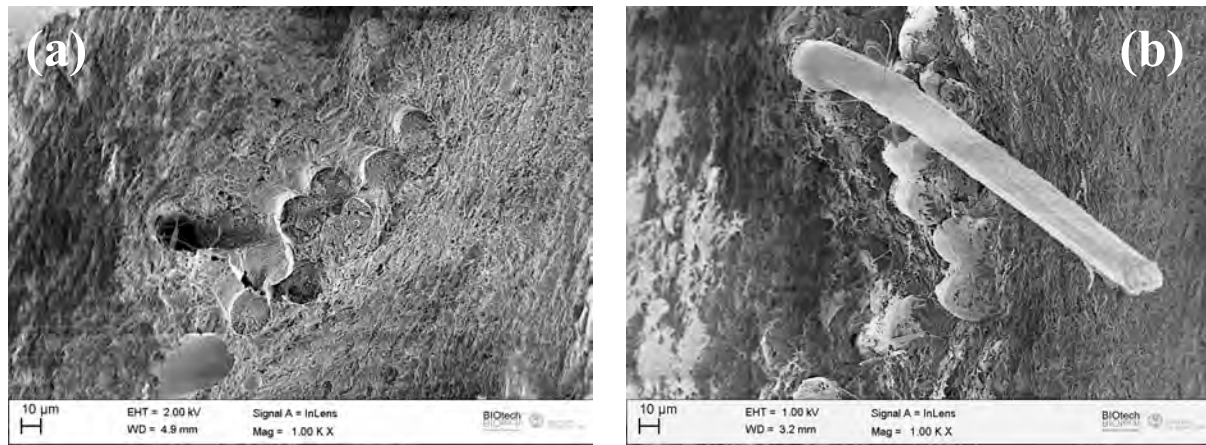


Figure 3 (a) and (b). SEM micrograph of Plasma treated SPSFCs (20%wt) brittle fracture.

In order to compare the experimental results with theoretical prevision models, the following empirical equation (1) for the modulus (E_R) of a composite containing fibers randomly oriented was used:

$$E_R = \frac{3}{8}E_{LL} + \frac{5}{8}E_{TT} \quad (1)$$

Where E_{LL} and E_{TT} can be estimated by the Halpin-Tsai micromechanics equations (2) and represents respectively the longitudinal and transverse tensile moduli for a unidirectional aligned fiber composite having the same fiber volume fraction and fiber aspect ratio of the composite under evaluation.[19, 20]

$$E_{LL} = E_m \frac{1+\zeta_L\eta_L V_f}{1-\eta_L V_f} \quad E_{TT} = E_m \frac{1+\zeta_T\eta_T V_f}{1-\eta_T V_f} \quad (2)$$

Where E_m is the matrix modulus, V_f is the fiber volume fraction, and:

$$\zeta_L = 2 \frac{1}{d} \quad \zeta_T = 2 \quad \eta_L = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta_L} \quad \eta_T = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta_T} \quad (3)$$

Nevertheless, an increment of more than 160% was obtained in the tensile modulus of the composite prepared with untreated fibers in comparison with the unfilled matrix, at Figure 4 it can be observed that the experimental results in terms of tensile modulus are far from the theoretical values. After the Plasma treatment, the SPSFCs show a great improvement, getting closer of the theoretical values for tensile modulus.

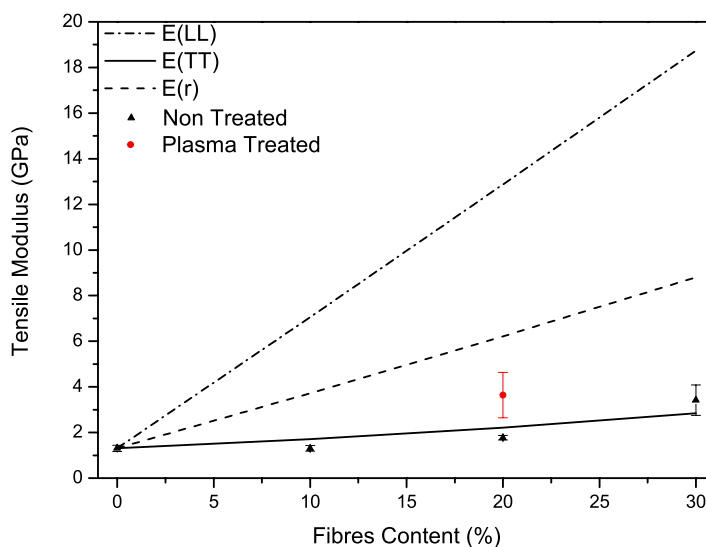


Figure 4. Comparison between theoretical and experimental results of plasma treated and non-treated SFSPCs

One of the reasons to the gap between the theoretical and experimental result after the plasma treatment, could be explained by assuming a deterioration of the surface functionalization of the fibers as a consequence of the elevated temperature they are exposed to during the composite preparation. Several strategies are under currently investigation to improve the fiber-matrix adhesion, such as the use of proper compatibilizing agents.

3 Conclusions

A thermal treatment was optimized to increase the melting point and tensile properties of Vectran NT fibers. Therefore, a processing method has been successfully developed for the production of SPSFCs. SPSFCs containing up to 30wt% of treated fibers were successfully produced and a significantly improvement (up to 161 %) of the composite tensile modulus was observed. Nevertheless, a slightly decrease of tensile strength and elongation at break was obtained. This is probably related to the presence of a poor fiber-matrix interface.

A plasma treatment was used to increase the interfacial adhesion between matrix and reinforcement, and a further increase (up to 178%) in the tensile modulus was obtained.

References

- [1] A. Pegoretti. Editorial corner – a personal view. Trends in composite materials: the challenge of single-polymer composites. *Express Polymer Letters*, **1**, pp. 710-710 (2007).
- [2] K. P. Matabola, A. R. De Vries, F. S. Moolman and A. S. Luyt. Single polymer composites: a review. *Journal of Materials Science*, **44**, pp. 6213-6222 (2009).
- [3] A. Pegoretti and M. Traina. *Liquid crystalline organic fibres and their mechanical behaviour*. in "Handbook of tensile properties of textile and technical fibres", edited by A. R. Bunsell. Woodhead Publishing Ltd, Cambridge, UK, pp. 354-436 (2009).
- [4] A. M. Donald, A. H. Windle and S. Hanna. *Liquid crystalline polymers*. Cambridge University Press, (2006).
- [5] X. Wang, Q. F. Zhou and Q. Zhou. *Liquid crystalline polymers*. World Scientific Pub. Co., (2004).
- [6] A. Pegoretti, A. Zanolli and C. Migliaresi. Flexural and interlaminar mechanical properties of unidirectional liquid crystalline single-polymer composites. *Composites Science and Technology*, **66**, pp. 1953-1962 (2006).

- [7] A. Pegoretti, A. Zanolli and C. Migliaresi. Preparation and tensile mechanical properties of unidirectional liquid crystalline single-polymer composites. *Composites Science and Technology*, **66**, pp. 1970-1979 (2006).
- [8] A. I. Isayev. Self-reinforced composites involving liquid-crystalline polymers - Overview of development and applications. *Liquid-Crystalline Polymer Systems*, **632**, pp. 1-20 (1996).
- [9] S. K. Mazumdar. *Composites Manufacturing: Materials, Product, and Process Engineering*. CRC Press, (2002).
- [10] S. L. Kaplan, P. W. Rose and D. A. Frazier. in "Proceeding of Forth Annual Conference on Advanced Composites", (1988).
- [11] J. D. Menczel, G. L. Collins and S. K. Saw. Thermal analysis of Vectran(R) fibers and films. *Journal of Thermal Analysis*, **49**, pp. 201-208 (1997).
- [12] H. N. Yoon, L. F. Charbonneau and G. W. Calundann. Synthesis, Processing and Properties of Thermotropic Liquid-Crystal Polymers. *Advanced Materials*, **4**, pp. 206-214 (1992).
- [13] J. Sarlin and P. Tormala. Heat-Treatment Studies of a Tlcp Fiber. *Journal of Applied Polymer Science*, **50**, pp. 1225-1231 (1993).
- [14] J. Sarlin and P. Tormala. Isothermal Heat-Treatment of a Thermotropic Lcp Fiber. *Journal of Polymer Science Part B-Polymer Physics*, **29**, pp. 395-405 (1991).
- [15] E. Kalfon-Cohen, A. Pegoretti and G. Marom. Annealing of drawn monofilaments of liquid crystalline polymer vectra/vapor grown carbon fiber nanocomposites. *Polymer*, **51**, pp. 1033-1041 (2010).
- [16] T. Medeiros Araujo and A. Pegoretti. *Preparation and characterization of liquid crystalline single-polymer short-fibres composites*. in "Proceeding of XX Convegno Italiano di Scienza e Tecnologia delle Macromolecole", Terni, (2011).
- [17] C. Dellavolpe, L. Fambri, R. Fenner, C. Migliaresi and A. Pegoretti. Air-Plasma Treated Polyethylene Fibers - Effect of Time and Temperature Aging on Fiber Surface-Properties and on Fiber-Matrix Adhesion. *Journal of Materials Science*, **29**, pp. 3919-3925 (1994).
- [18] E. Kalfon-Cohen, G. Marom, E. Wachtel and A. Pegoretti. Characterization of drawn monofilaments of liquid crystalline polymer/carbon nanoparticle composites correlated to nematic order. *Polymer*, **50**, pp. 1797-1804 (2009).
- [19] J. C. Halpin and J. L. Kardos. Halpin-Tsai Equations - Review. *Polymer Engineering and Science*, **16**, pp. 344-352 (1976).
- [20] A. Pegoretti and T. Ricco. Fatigue fracture of neat and short glass fiber reinforced polypropylene: Effect of frequency and material orientation. *Journal of Composite Materials*, **34**, pp. 1009-1027 (2000).