



## **A METHOD FOR PET MECHANICAL PROPERTIES ENHANCEMENT**

*Raffaella Aversa*  
*University of Naples, Italy*  
*E-mail: raffaella.aversa@unina2.it*

*Relly Victoria Virgil Petrescu*  
*IFTToMM, Romania*  
*E-mail: rvvpetrescu@gmail.com*

*Antonio Apicella*  
*University of Naples, Italy*  
*E-mail: antonio.apicella@unina2.it*

*Florian Ion Tiberiu Petrescu*  
*IFTToMM, Romania*  
*E-mail: fitpetrescu@gmail.com*

*Submission: 12/9/2018*  
*Accept: 1/5/2019*

### **ABSTRACT**

A method for PET mechanical properties enhancement by reactive blending with HBA/HNA Liquid Crystalline Polymers for in situ highly fibrillar composites preparation is presented. LCP/PET blends were reactively extruded in presence of Pyromellitic Di-Anhydride (PMDA) and then characterized by Differential Scanning Calorimetry, Thermally Stimulated Currents and tensile mechanical properties. Moderate amounts of LCP in the PET (0.5 and 5%) and small amounts of thermo-active and reactive compatibilizer in the blend (0.3%) were found to significantly improve LCP melt dispersion, melts shear transfer and LCP fibril formation and adhesion. An unexpected improvement was probably due to the presence of two distinct phases' supra-molecular structures involving PET-LCP and PMDA.

**Keywords:** Biotechnology; Bioengineering; PET; Reactive Compatibilizer; Situ Composites; Differential Scanning Calorimetry; LCP melt dispersion; Recycle.



## 1. INTRODUCTION

After a slight decline as a result of the 2008 financial crisis, plastics production is increasing and in 2010 it has reached 265 million tonnes worldwide and 57 million in Europe (PLASTICS EUROPE, 2011).

In the same year, plastic converters in Europe processed 46.4 million tonnes of products, of which approximately 40% were short-term applications, especially for packaging purposes, which resulted in 24.7 million tonnes of plastic waste from post-consumable Europe (2011). It is not surprising that environmental concerns have also increased over the last decades, reinforcing efforts to reduce the impact of polymer materials on the environment. In 2009, for the first time in Europe, the amount of plastic waste used exceeded the quantity entering the landfill. This favorable trend continued the following year and 6 million tons were recycled for new products, 8.3 million tons of energy and 10.4 million tons of waste (PLASTICS EUROPE, 2011).

However, for the treatment of certain waste streams, composting has proven to be the most advantageous method (Kale et al., 2007), so that biodegradable and compostable polymers have found applications in various fields.

Although the magnitude of the process is often controversial, a consensus has been reached on the potential depletion of petrochemical raw materials (HOEL; KVERNDOKK, 1996; SHAFIEE; TOPAL, 2009).

As in other areas, the plastics industry has begun to seek alternative sources of raw materials over the past decades, and its special interest is natural and renewable solutions. Polymers based on polymers, ie polymers produced from renewable raw materials, biomass in general, could replace fossil sources and also have considerable environmental benefits such as low carbon emissions.

Although the term "biopolymer" is used in several different ways, depending on the scope, the generally accepted definition covers polymers belonging to the abovementioned categories, ie they are either renewable, biodegradable or both. The global production capacity of these materials is dynamic (SHEN et al., 2009).



Both environmental concerns and market trends are behind this trend, as in the case of oil prices, conventional polymers will become more and more expensive. Consumers' expectations cannot be neglected, as many customers consider the ecological effect of the products they buy. The proportion of biodegradable polymers compared to non-degradable biodegradable types has also recently increased. One of the reasons that have led to this trend could be considerable changes to legislation on compostable products in recent years. Long-term projections, however, predict the dominance of non-degradable biopolymers.

The relative importance of biological and biodegradable classes in polymer production could further increase as production technology improves and becomes more cost-effective. According to different estimates, only 4% of the world's biomass is used by mankind, mainly for food, being only a fraction for chemical production and production of plastics (SHEN et al., 2009) capacity increase.

Biopolymers have great potential and many advantages, but they also have some disadvantages. Despite the increase in production capacity, they are still quite expensive compared to commodity polymers, and their properties are also often inferior or at least not in line with the expectations of converters or users. Although natural polymers are available in large quantities and are also cheap, their properties are even further away from those of the base plastics. Consequently, biopolymers must often be modified to meet market expectations.

In order to use its potential and penetrate new markets, the performance of biopolymers must increase considerably. Consequently, the modification of these materials is at the heart of scientific research. Unlike the development of new polymeric materials and new polymerization paths, blending is a relatively inexpensive and rapid method of adapting the properties of plastics. As a result, this approach can play a crucial role in increasing the biopolymer's competitiveness. In our present paper, we try to provide a summary of recent trends and achievements in the field of biopolymer blends, with a special focus on compatibility-compatibility- ownership relationships (AVERSA et al., 2018a; AVERSA et al., 2018b; AVERSA et al., 2017a; AVERSA et al., 2017b; AVERSA et al., 2016a; AVERSA et al., 2016b; AVERSA et al., 2016c; AVERSA et al., 2016d;



AVERSA et al., 2016e; AVERSA et al., 2016f; AVERSA et al., 2016g; AVERSA et al., 2016h; AVERSA et al., 2016i; AVERSA et al., 2016j; AVERSA et al., 2016k; AVERSA et al., 2016l; AVERSA et al., 2016m; AVERSA et al., 2016n; ANNUNZIATA et al., 2006; APICELLA et al., 2018a; APICELLA et al., 2018b; APICELLA et al., 2018c; ARMAH, 2018; MARQUETTI; DESAI, 2018; TAMBURRINO et al., 2018; WILK et al., 2017).

As mentioned in the introductory part, the term "biopolymer" refers to polymers that are biodegradable, biodegradable or both. Before discussing the different aspects of biopolymer blends, we define these categories in this section to help understand subsequent discussions.

### **1.1. Biopolymers**

Replacement of fossil raw materials with renewable raw materials is one of the main actions of the modern plastics industry. Natural polymers are a specific class of materials among polymers based on natural resources. They appear in nature as macromolecules and include natural or physically modified polymers in this class. Typical examples are cellulose, hemicellulose, lignin, silk and starch.

Another class of materials consists of synthetic polymers based on natural or biological bases, whose monomers come from renewable resources. This category includes poly (lactic acid) (PLA) as well as conventional biological polymers such as polyethylene (PE), poly (ethylene terephthalate) (PET) and polyamide (PA), because the polymer is produced by the bacterial fermentation process. Biodegradability, on the other hand, is independent of the above mentioned categories, so that biodegradable polymers are not necessarily of natural origin.

The conditions for determining the content of bio-based polymer materials are described in European Standard CEN / TS 16295: 2012. The approach is based on the carbon content of biofuels as a fraction of the total organic carbon content. However, precise legislative details and precise protocols for determination should be developed in the future.

### **1.2. Degradation, biodegradation**

Each polymer degrades to a certain degree over a period of time, depending on environmental conditions. However, a precise definition of this



feature is necessary to obtain a useful description of the degradation of the polymer. According to the related standard (CEN / TR 15932: 2010), these polymers can be called degradable, where degradation results in molecular weight loss by dividing the chain into the backbone, and degradation is complete, ie the final products are low biosynthesis. It does not consider either the chain failure mechanism or the environmental effect of the final products.

In biodegradable polymers, on the other hand, chain cleavage is caused by cellular activity (human, animal, fungus, etc.), so it is an enzymatic process, although it is usually accompanied and promoted by physicochemical phenomena. The two types of processes, ie physical and enzymatic processes, can not be distinguished and/or separated in general, their combined effect results in complete polymer degradation (CEN / TR 15932: 2010).

The assessment and laboratory testing of the biodegradability of the polymeric materials are well defined in the European standards (EN ISO 14851: 2004, EN ISO 14852: 2004, EN ISO 17556: 2004, EN ISO 14855-1: 2007/2: 2009). The tests are based on the measurement of the oxygen demand or the amount of carbon dioxide that has evolved in the process. It is important to note that most polymers containing various degradation agents (oxo-biodegradable polymers) (SCOTT, 2000; CHIPELLINI et al., 2006) cannot be considered biodegradable according to the standards mentioned above. Although fragmentation and disintegration may occur, degradation is never complete under test conditions that simulate natural environments (soil, water, and compost).

The environmental effect of the high molecular weight residual fractions is not satisfactorily described and is therefore of serious concern. Consequently, these agents could help solve pollution problems, but not the fundamental problem arising from the slow degradation of synthetic polymers.

The use of such plastics has been widespread and encouraged in the past by imperfect legislation. Early standards (ASTM D3826-98 (2008)) have determined a certain decrease in traction resistance as a condition of degradability, which can easily be achieved by the use of pro-oxidants, for example without a real environmental advantage (Imre and Pukánszky, 2013).

## 2. METHODS AND MATERIALS



A method for PET mechanical properties enhancement by reactive blending with HBA/HNA Liquid Crystalline Polymers for in situ highly fibrillar composites preparation is presented. LCP/PET blends were reactively extruded in presence of Pyromellitic Di-Anhydride (PMDA) and then characterized by Differential Scanning Calorimetry, Thermally Stimulated Currents and tensile mechanical properties.

The formation of specific macromolecular structures, where the PET, the LCP, and the reactive additive are involved, has been hypothesized in the reactively extruded blends from TSC analysis evidence.

The use of a reactive additive improved the matrix LCP compatibilization and adhesion as indicated by the SEM analysis and mechanical testing. Moderate amounts of LCP in the PET (0.5 and 5%) and small amounts of thermo-active and reactive compatibilizer in the blend (0.3%) were found to significantly improve LCP melt dispersion, melts shear transfer and LCP fibril formation and adhesion.

Blends of PET and LCP containing the compatibilizer favored the formation of a well dispersed and homogeneous fibrillar phase whose particle size distribution did not show great coarsening and coalescence leading to significant elastic properties improvements from 0.8 for not compatibilized to 3.1 GPa for compatibilized 0.5% LCP loaded PET blends that were even higher than those expected from ordinary theoretical calculation. This unexpected improvement was probably due to the presence of two distinct phases' supra-molecular structures involving PET-LCP and PMDA.

The post-consumer PET is mainly derived from injection molded bottles prepared using high intrinsic viscosity and a high molecular weight PET fiber. Intrinsic viscosity (IV) is a measure of polymeric molecular weight (MW) and therefore reflects the melting point of the material, crystallinity and tensile strength. The length of the polymer chain in PET determines the molecular weight of the material and the mechanical properties that determine large IV PET useful for high strength applications (The higher the traction, impact, or operating temperature, the higher the intrinsic viscosity of the polymer).

Applications of this high molecular weight PET and intrinsic viscosity include



carbonaceous bottles, solder bands, films, and photographic bands, while low-density IV molds are used in the fiber and textile industry.

However, high molecular weight PET suffers a significant reduction during the recycling process due to the reduction in molecular weight due to spontaneous melting processes which greatly reduce the intrinsic viscosity and the final mechanical properties of the material.

These recycled materials can only be used for smaller structural value applications such as carpet fibers, geotextile or extruded into a forming sheet by thermoforming and by blowing non-food containers.

Mixing with glass or carbon fiber could help improve the mechanical and thermal stability of these materials.

However, the processing of these composites does not have always had immediate results in improving mechanical properties (APICELLA et al., 1980; NICOLAIS et al., 1981).

Breaking fibers and high viscosity of composite material during the process severely limit their application. Liquid crystalline polymers can have great potential as high strength modifiers which can be easily processed because they tend to dissolve in the matrix at high processing temperatures, reducing the melt viscosity, and facilitating extrusion and injection processes.

Pure LCP (not in a mixture with a polymer the matrix) can be potentially used in many industrial fields such as electronics, composites, and packaging, where high dimensional stability, low environmental sensitivity is required. However, once oriented, their very anisotropic structure, while increasing their power in the direction of orientation, greatly reduces their resistance in the transverse direction.

Therefore, it is necessary to mix with other engineering thermoplastic materials. However, the morphology of these mixtures is unstable; the distribution and size of the dispersed phase, in fact, tend to increase when they are melted reduced shear conditions, for example, as may occur during certain injection molding conditions, resulting in deleterious effects on the final properties of the blend.



The shear viscosity of the high-temperature isotropic phase is, in fact, higher than the viscosity of the mosquito phase at lower temperatures. During the flow, the eye leaks easily between them when it is the anisotropic phase is oriented along the flow due to the fact that LCPs have four times greater relaxation times than the regular polymers, the elongational flow of an anisotropic melt containing local orientation domains induces stretching and alignment which is kept cool in a solid state.

Some research (DUTTA et al., 1996) also showed that the potential level or LCP order close to the unit (0.90) that can be reached for a specific stretch on the pure LCP is never approached when mixed with a matrix host; the current level of control in the same degree is 0.4/0.5. This may be related to the weak interactions between the two phases present in the melt; However, interactive interaction/interaction is better through chemical changes, the greater will be the improvement (CRUZ; FIU, 2015; ZHANG et al., 2000).

So-called in-situ composites formed from a polymeric curing polymer matrix have been extensively investigated in the past (APICELLA et al., 1989, NICODEMO et al., 1981, SKOVBY et al., 1991, ZHANG et al., 2000, GOH; TAN, 2012, CRUZ; SON, 2015).

Even in such cases, however, the properties of the resulting materials were lower than expected. This was primarily due to poor control of interaction and adherence between oriented LCP and array host. This lack of adhesion is related to Van der Waals's weak forces, which have links between the LCP segments and the host matrix.

In our investigation, the melt phase interactions and solid phase adhesion between the two components were improved and controlled by reactive alloy processes in which LC polymer molecules containing reactive groups (such as OH, NH and the like) are mixed with PET-based host polymers in the presence of an anhydride-specific reaction promoter.

Commercial commercial HBA / HNA extrusions (VECTRA 950) were made with recycled PET to produce composite composites in situ which, after thermal expansion at an appropriate temperature improving adhesion of LCP / host polymer fibers and superior mechanical properties (AVERSA; APICELLA, 2016).



### **3. MATERIALS, APPARATUS AND PROCEDURES MATERIALS**

LCP fillers and reactive additives: Vectra A 950 (Hoechst) prepared from HBA and HNA and Pyromellitic Anhydride (PMDA) has been used as a reactive additive.

Matrix: Recycled PET's of IV-0.60 dl/g have been used. Intrinsic viscosity has been measured at 25°C in phenolortodichlorobenzene (60/40 weight fraction) solutions.

#### **3.1. Apparatus and Procedures**

##### **3.1.1. Blending and Reactive Extrusion**

The PET matrix, the dispersed LCP, and the reactive additive (PMDA) compounds were plasticized after previous drying (24 h at 140°C under vacuum) in a Haake counter-rotating intermeshing twin screw extruder. Mixtures containing 0.5 and 5.0% of LCP with and without the reactive additive (0.30%) were extruded at 290°C, quenched in a water bath and then pelletized.

##### **3.1.2. Filming and Orientation**

Base polymer and mixtures in the form of pellets were dried in a vacuum oven at 140°C for 16 h and then extruder in a single screw extruder Haake equipped with a flat die. The strand of the blends and neat resin were extruded into a water bath and then calendered without stretching. General purpose tensile tester (Instron model 4500) equipped with a thermostatic chamber set at 190°C has been used to stretch under nitrogen the extruded strands up to two times the initial length at the crosshead speed of 1 mm/min.

##### **3.1.3. Mechanical Testing**

The tensile modulus of the stretched samples was measured on the same Instron 4500 mechanical tester with a constant crosshead speed of 10 mm/min on 3 cm samples.

##### **3.1.4. Differential Scanning Calorimetry**

An ADSC Mettler Differential Scanning Calorimeter has been used for the thermo- calorimetric characterization. Samples films of 0.5 mm containing 0.5 and 5% of LCP before and after stretching and annealing were tested. Thermal scans from 0 to 300°C were carried out at 5°C/min.



### **3.1.5. Thermally Stimulated Depolarization Currents (TSDC)**

A Solomat model 41000 spectrometer equipped with liquid nitrogen cooling system has been used on samples films of 0.5 mm containing 0.5% of LCP before and after stretching and annealing was tested. Thermal scans from 0 to 200°C were carried out were carried out at 5°C/min on samples polarized for 5 min at 40, 60 and 90°C in a polar field of 200 V/mm and quenched to -100°C.

### **3.1.6. Scanning Electron Microscopy (SEM)**

A Hitachi electron microscope has been used for surface morphology characterization. Namely, samples containing 0.5 and 5% of LCP were both fractured in brittle mode under nitrogen and in the plastic mode in tensile tests. Fracture surfaces of the samples of extruded and extruded/stretched films were observed at 400 to 6000 X magnification (AVERSA; APICELLA, 2016).

## **4. RESULTS AND DISCUSSION**

The reactive reaction was carried out on polymer blends of PET and LCP previously mixed in a double extruder by the addition of 0.3% of poly-anhydride (PMDA). The resulting material was extruded and films with different LCP content were obtained.

A preliminary thermo-calorimetric investigation on those samples indicated that for the investigated compositions this technique was not able to detect any difference between the samples with and without the reagent additive. The thermogram against the PET / LCP (Vectra) blend with and without the reagent additive was compared. In both situations, the resulting curves exhibit an inflection of about 60 ° C which (for a directed film) is representative of the glass transition temperature range of the polymer.

The intense tip at 250 ° C is relative to the melting of the crystalline phase. The test materials exhibit a crystallinity of about 50%, taking them as reference crystallization heat for 100% crystalline PET 28.1 cal / g or 117 J / g (GROENINCKX et al., 1980).

To verify that the LCP and the host polymer have undergone some chemical interaction during reactive extrusion, a highly sensitive analytical technique (TEYSSÉDRE; LACABANNE, 1995), heat-stimulated sample



depolarization currents were used. Under an external electric field, the polymer (which is a dielectric medium) accumulates electrical charges in a form that can be retained for a long time, where increasing internal segmental mobility can release these loads that produce a depolarization current.

The peaks observed in the diagram that report the intensity of such depolarization currents as a function of temperature during a thermal scan are related to the release of electrical charges in the samples in the physical events occurring in the (molecular) and phase (super-molecular).

Characteristics of TSC diagrams of mixtures containing 0.5% of LCP (with and without PMDA) and pure LCP were also compared. This method offers high sensitivities even with currents in the order of 10-13 amps and decreases.

Diagram of the mixture in the absence of the reagent (PMDA) is characterized by a peak of about 30° C above the polarization temperature that characterizes the PET transition glass (about 60° C), and that the LCP (VECTRA) which, measured by the same technique, given a higher peak at 71.5° C.

The test carried out under the same experimental conditions but on the same admixture with the reagent (0.3%) is compared and analyzed. Surprisingly, the new chart shows no peak in the glass transition region of the two component mixtures, in addition, a second thermal event takes place around 110-140 ° C (which is obviously widening the tip).

Therefore, TSC analysis indicates that the presence of the reagent additive changes the internal structure (molecular structure) of the mixture. Even if in a very small amount, only 0.5%, LCP was still detected by TSDC analysis, the tip being probably related to the presence of LCP while the presence of the peak at 140 ° C in the thermogram over the additive the mixture is representative of a structural macromolecular feature where PET, LCP, and the additive is involved.

This second thermal event, which may be characteristic of this particular segment rearrangement of the PET / LCP reaction mixture was further confirmed in a TSDC test performed on an additive polarized mixture at a higher temperature of 90° C. At this elevated temperature, electrical charges are accumulating and associated with events that have place at temperatures above 90° C.



Thermal tests (DSC and TSDC) associated with mechanical analysis and electronic scanning microscopy (SEM).

SEM analyzes were performed on PET containing 5% LCP fractured in liquid nitrogen.

Figure 1 shows the liquid crystalline polymer in (this hypothesis is validated by the presence of spherical voids on fracture surfaces that eventually contain decoded LCP particles). Extrusions and shooting procedures in the absence of the reagent additive did not lead to significant LCP orientation, as indicated by the almost spherical inclusion model.

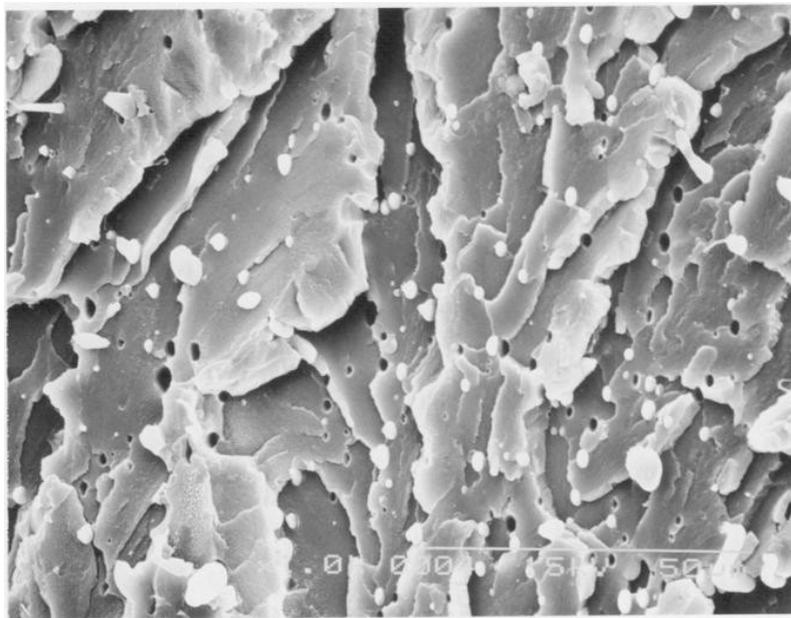


Figure 1: SEM image of PET/5.0%LCP blends without PMDA reactive additive

The surface of the ET / 5.0% LCP sample containing 0.3% of the reactive additive is shown in Figure 2.



Figure 2: SEM image of PET/5.0%LCP blends with 0.3% of PMDA reactive additive

The same extrusion and extrusion processes used for the sample described above, homogeneously obtained in this case and elongated LCP fibers. Extrusion by reactive extrusion promotes better dispersion by improving phase interactions between the two molten components.

SEM analysis was performed on the surfaces of the same PET/LCP mixtures with and without the reagent additive which was broken in traction tests at room temperature. As shown in Figure 3, situ does not contain the additive, it is characterized by the presence of ellipsoidal particles (approximately  $8 \times 4$  microns) from the dramatic phase of the liquid crystal yields and does not increase plastic around LCP inclusions.

The presence of non-adherent ellipsoidal inclusions that remain undeformed after the matrix breaks lead to intense stress concentration and to a plastic flow at the matrix / PET filter interface. Due to the lack of interaction during processing and the lack of a solid state, the LCP filler does not act as a curing agent.



Figure 3: SEM image of PET/5.0%LCP blends without PMDA reactive additive. Room temperature fracture is accompanied by plastic flow around poor adhering LCP fillers

In the presence of PMDA, the better it is dispersed (about 2 microns in diameter) and well directed LCP phases, as shown in Figures 4 and 5, improving the mechanical properties of the matrix.

This occurrence was probably due to the fact that improved physical dispersion in the presence of the reactive additive leads to higher surface/volume ratios, playing a significant role in fracture tests performed at room temperature.

Figure 5 is a top elevation of the previous image showing as an LCP fiber that adheres to matrix and plastic.

This is an indication of the active role of the additive in improving both the mechanical processing properties and the final mechanical properties of the PET/LCP blends.

This emergence further confirms the macromolecular nature of hypothetical structural change by analyzing TSC diagrams.

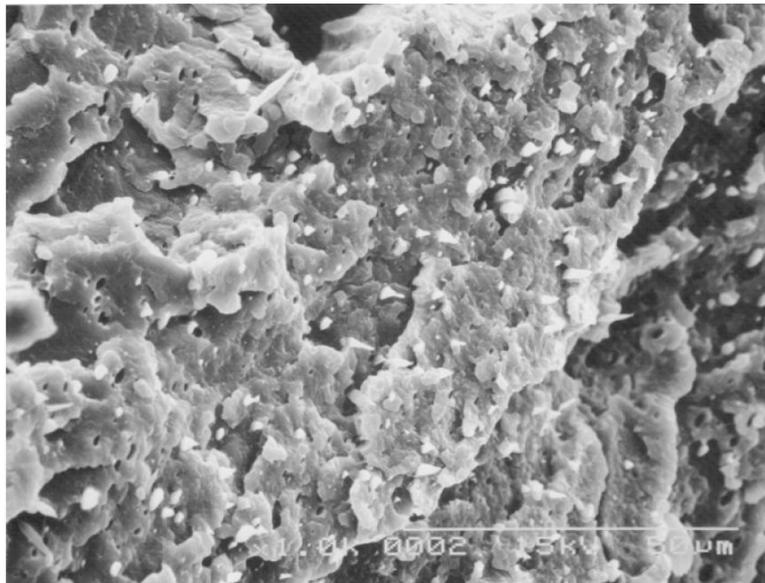


Figure 4: SEM image of PET/5.0%LCP blends with PMDA reactive additive. Good adhering and plastically deforming LCP fillers

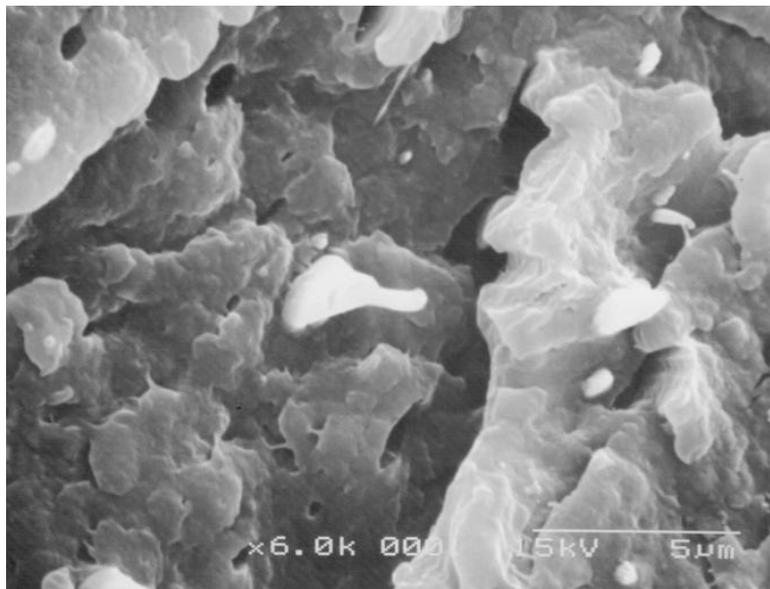


Figure 5: Higher magnification of the previous SEM image showing the plastic deformation of the LCP filler

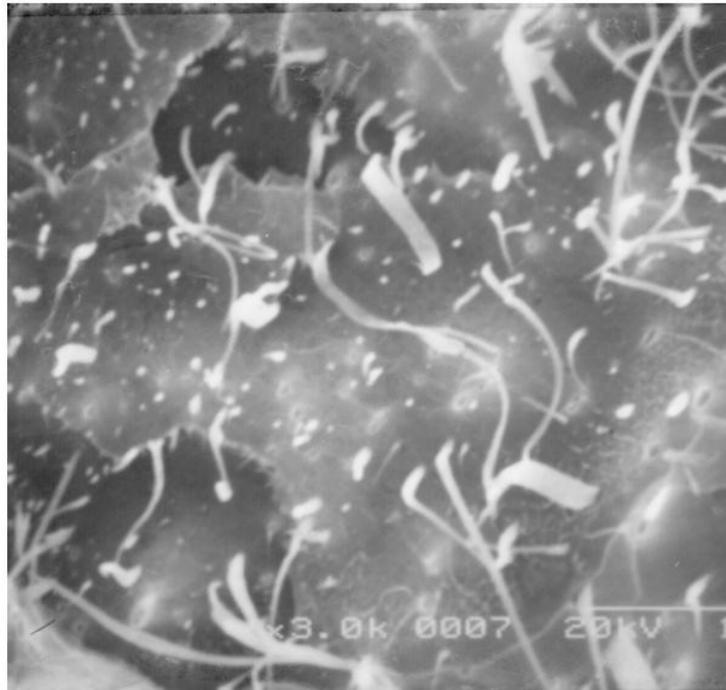


Figure 6: High dispersion and yield of the LCP filler in the reactive additive compatibilized PET/LCP blends

As previously mentioned, the LCP in the extruded blend orients much less than the optically measured or SEM dimensional changes indicates, this may be due to the lack of shear stresses transfer between LCP and matrix.

The increases of elastic moduli calculated according to the well-accepted Halpin- Tsai relationships are, generally, much lower than expected: Values of 0.8 GPa instead 1.0 GPa were in fact calculated). Nevertheless, the presence of the reactive compatibilizer favored both processes of shear transfer and post cure chemical bonding between LCP the host polymer.

In this investigation blend with 0.5 and 5% of LCP were utilized in the presence and absence of specific reaction promoters. Moreover, tests on the net resin in the same conditions of thermal stretching filming and processing were carried out as a control.

Improvement of adhesion and mechanical properties in presence of the reaction promoters were always observed after stretching of the films (Figure 6).

Surprisingly the best result (even as absolute values) were observed for the blends of lower content of LCP (0.5%) with increase of elastic moduli that were even twice higher than those expected from the mechanical H.T. theory (i.e., 3.9 GPa Vs the expected 2.1 GPa and the 2.0 GPa in absence of LCP under the same overall processing conditions).

This unexpected high value could be due to a higher level of LCP internal order and corresponding limiting elastic moduli near to the theoretical.

This was probably due to the fact that the ameliorated physical dispersion in presence of the reactive compatibilizer, which increases the number and dispersion of fibrils, plays a significant role in the LCP orientation even in the preliminary filming procedures.

For the as-cast films, it was observed, in fact, that the presence of the reacting promoter produced films of higher moduli than the ordinary blending procedures: The expected moduli (according to Halpin Tsay theory) were only 10% lower expected for the activated 0.5% LCP blend and 50% lower for the richer blend while the corresponding values in absence of the reacting promoter were respectively 30 and 80% lower.

An increase of the LCP orientation shown in Fig. 8 (or level of order) depends both on physical and chemical adhesion; a good physical dispersion during the extrusion leads to thinner fibers presenting a high surface to volume ratio. A good shear transfer will improve local LCP order and hence LCP elastic moduli. Moreover, additional chemical bonding under thermal stretching should further increase the mechanical properties of the LCP/Polymer blend.

## 5. CONCLUSIONS

The continued growth of electronic component applications is expected to increase the market growth of liquid crystal polymers in the coming years.

Increased demand for microinjection by casting coupled with high-temperature resistance and flow properties is expected to drive demand. Thin wall design is, in fact, essential during microinjection of electronic components. LCP is



then preferred for which produce ultra-thin components up to 0.1 mm from other technical resins, such as polyphenylene sulfide (PPS), polycyclohexylated imine terephthalate (PCT) and polyphthalamide (PPA) and nylon. Due to their higher processing viscosities (SON et al., 2004), these engineering resins require longer manufacturing cycles and can produce components with a thickness of 0.25 mm.

Reactivation of the mixture of these engineering polymers with LCP in the presence of a reactive compatibilizer may result in both processing aids and mechanical improvements (WEISS et al., 1987, ZHANG et al., 2000).

In general, in situ LCP composites are composed of an incompatible liquid crystalline polymer and a conventional thermoplastic polymer forming a molten matrix which includes and disperses as the melting temperature is reduced, the separation of the phases in anisotropic and isotropic states. After subsequent cooling and solidification of the components, the structure of the two phases is retained. The resulting in-situ composite exhibits a morphology that strongly depends on the two rheological components properties and processing conditions (APICELLA et al., 1989).

The liquid crystalline nematic anisotropic phase, in fact, slightly aligns in the direction of the melted flow with a level of orientation that depends either on the relative ratio between the two viscosities of the molten phases, the expanded flux character, and the liquid fill matrix dispersion capacity. In the present study, as shown in the TSC tests, the use of a reagent compatibilizer improved the liquid phase interactions through a macromolecular structure involving PET, LCP and reactive compatibilizer. The mechanical properties of mixtures, which are defined by the morphology and LCP / matrix content resulting in the solid state, significantly improved by the presence of the reagent compatibilizer.

Independent and isotropic anisotropy a character of the two polymer melts, a partial or total solubility of LCPs in the molten host thermoplastic matrices cannot, however, be excluded a priori.

A liquid crystalline material is one which, in addition to having a liquid isotropic phase, also has one or more anisotropic liquid phases; In the case of a high chemical affinity of the two blend components, the LCP may be partially or totally dissolved in the matrix. A plasticizing effect was then (thermo-calorimetric) measured



from the presence of the LCP isotope melt that is dissolved in the matrix resulting in a decrease in the viscosity of the molten mixture and hence lighter processed into films in the form of thin film.

At high processing temperatures, chemically similar to PET LCP polymer is probably completely dissolved in it further increasing flexibility and softness melt by weakening intermolecular binding forces and by separating the host polymer chains. As material cooling, however, LCP solubility may decrease significantly, ultimately leading to phase separation and crystallizing the liquid LCP in the molten matrix still.

Although in some cases solid solid solid mixtures such as bis- 4-n-butylaniline terephthalate (TBBA) in polystyrene (APICELLA et al., 1986), p- hydroxybenzoic acid LCPs (HBA) in the authors' tests and recycled polyethylene Terephthalate (PET) had a partial (even limited) solubility (Baird) and was measured thermo-calorimetric by differential scanning calorimetry as PET reducing the transition of glass. This possibility, however, has been demonstrated in our tests to be amplified by the presence of specific reagent additives.

The use of reactive mixing agents (acting in such cases as a reagent compatibilizer) and the choice of appropriate LCP and host polymers (even if there is evidence that the mixture does not react extensively during premixing and film processing) improves LCP dispersion and orientation (especially for very low LCP content).

The reason for the deviation from the law of mixtures is not clear. Partially miscible systems may have superior mechanical properties because the solid PET / LCP solution coexists with the free LCP phase. The matrix itself is strengthened to a certain extent, LCP at a structural level. Moreover, due to partial miscibility, the superior interfacial adhesion between the solid PET/LCP solution and the free LCP phases strongly orients the growth curing effect.

Another possibility is that, due to the partial miscibility, there is superficial surface tension which results in a finer appearance with a higher aspect ratio, providing superior surface efficiency and fibrillation. It is possible for both mechanisms to happen in our reactive mixing system.

SEM of fractured surfaces of PET/LCP the sample mixed with PMDA (which is considered less miscible) has a large gap between the incised spheroidal



inclusions and the PET matrix, and these voids exhibit low interfacial adhesion / low fibrillation and a superior matrix interfacial surface voltage. The higher aspect ratio of fibrils present in PET/LCP mixed systems in the presence of PMDA, indicates the possibility of larger matrix / fill interactions and surface superficial surface tension of the interfacial matrix favoring better dispersion of LCP.

The influence of the LCP level of dispersion, orientation, and thermally activated reaction during stretching is under study to define their effect on the poor physical aging characteristics of amorphous PET. Furthermore, an optimization is made between the LCP content and the reaction promoter content, the film processing conditions and the thermal expansion of an operation.

## 6. ACKNOWLEDGEMENT

This text has been acknowledged and appreciated by Assoc. Pro. Taher M. Abu-Lebdeh, North Carolina A and T State Univesity, United States.

## REFERENCES

- ANNUNZIATA, M.; AVERSA, R.; APICELLA, A.; ANNUNZIATA, A.; APICELLA, D. (2006) In vitro biological response to a light-cured composite when used for cementation of composite inlays. **Dental mater.**, v. 22, p. 1081-1085. Doi: 10.1016/j.dental.2005.08.009
- APICELLA, A.; AVERSA, R.; PETRESCU, F. I. T. (2018a) Hybrid Ceramo-Polymeric Nano-Diamond Composites. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p. 766-782. Doi: 10.3844/ajeassp.2018.766.782
- APICELLA, A.; AVERSA, R.; PETRESCU, F. I. T. (2018b) Biomechanically Inspired Machines, Driven by Muscle Like Acting NiTi Alloys. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p. 809-829. Doi: 10.3844/ajeassp.2018.809.829
- APICELLA, A.; AVERSA, R.; TAMBURRINO, F.; PETRESCU, F. I. T. (2018c) About the Internal Structure of a Bone and its Functional Role. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p.914-931. Doi: 10.3844/ajeassp.2018.914.931
- APICELLA, A.; NICODEMO, L.; NICOLAIS, L.; WEISS, R. A. (1989) Dimensional stability of thermoplasticpolymeric liquid crystal blends. **Polymer Sci. Technol.**
- APICELLA, A.; NICODEMO, L.; NICOLAIS, L. (1980) Recoil kinetics of uniaxially oriented polystyrene. **Rheological Acta**, v. 19, p. 291-298. Doi: 10.1007/BF01543141
- ARMAH, S. K. (2018) Stress Analysis of an Artificial Human Elbow Joint: Application of Finite Element Analysis. **Am. J. Eng. Applied Sci.**, v. 11, n. 1, p. 1-18. Doi: 10.3844/ajeassp.2018.1.18
- AVERSA, R.; APICELLA, A.; TAMBURRINO, F.; PETRESCU, F. I. T. (2018a) Mechanically Stimulated Osteoblast Cells Growth. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p. 1023-1036. Doi: 10.3844/ajeassp.2018.1023.1036
- AVERSA, R.; PARCESEPE, D.;TAMBURRINO, F.; APICELLA, A.; PETRESCU, F. I.



T. (2018b) Cold Crystallization Behavior of a Zr44-Ti11-Cu10-Ni10- Be25 Metal Glassy Alloy. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p. 1005-1022. Doi: 10.3844/ajeassp.2018.1005.1022

AVERSA, R.; PETRESCU, R. V. V.; APICELLA, A.; PETRESCU, F. I. T. (2017a) Nano-diamond hybrid materials for structural biomedical application. **Am. J. Biochem. Biotechnol.**, v. 13, p. 34-41. Doi: 10.3844/ajbbbsp.2017.34.41

AVERSA, R.; PARCESEPE, D.; PETRESCU, R. V. V.; F. BERTO, F.; CHEN, G. (2017b) Process ability of bulk metallic glasses. **Am. J. Applied Sci.**, v. 14, p. 294-301. Doi: 10.3844/ajassp.2017.294.301

AVERSA, R.; PETRESCU, F. I. T.; PETRESCU, R. V.; APICELLA, A. (2016a) Biomimetic FEA bone modeling for customized hybrid biological prostheses development. **Am. J. Applied Sci.**, v. 13, p. 1060-1067. Doi: 10.3844/ajassp.2016.1060.1067

AVERSA, R.; PARCESEPE, D.; PETRESCU, R. V.; CHEN, G.; PETRESCU, F. I. T. (2016b). Glassy amorphous metal injection molded induced morphological defects. **Am. J. Applied Sci.**, v. 13, p. 1476-1482. Doi: 10.3844/ajassp.2016.1476.1482

AVERSA, R.; TAMBURRINO, F.; PETRESCU, R. V.; PETRESCU, F. I. T.; ARTUR, M. (2016c) Biomechanically inspired shape memory effect machines driven by muscle like acting NiTi alloys. **Am. J. Applied Sci.**, v. 13, p. 1264-1271. Doi: 10.3844/ajassp.2016.1264.1271

AVERSA, R.; BUZEA E. M.; PETRESCU, R. V.; APICELLA, A.; NEACSA, M. (2016d) Present a mechatronic system having able to determine the concentration of carotenoids. **Am. J. Eng. Applied Sci.**, v. 9, p. 1106-1111. Doi: 10.3844/ajeassp.2016.1106.1111

AVERSA, R.; PETRESCU, R. V.; SORRENTINO, R.; PETRESCU, F. I. T.; APICELLA, A. (2016e) Hybrid ceramo-polymeric nanocomposite for biomimetic scaffolds design and preparation. **Am. J. Eng. Applied Sci.**, v. 9, p. 1096-1105. Doi: 10.3844/ajeassp.2016.1096.1105

AVERSA, R.; PERROTTA, V.; PETRESCU, R. V.; MISIANO, C.; PETRESCU, F. I. T. (2016f) From structural colors to super-hydrophobicity and achromatic transparent protective coatings: Ion plating plasma assisted TiO<sub>2</sub> and SiO<sub>2</sub> nano- film deposition. **Am. J. Eng. Applied Sci.**, v. 9, p. 1037-1045. Doi: 10.3844/ajeassp.2016.1037.1045

AVERSA, R.; PETRESCU, R. V.; PETRESCU, F. I. T.; APICELLA, A. (2016g) Biomimetic and evolutionary design driven innovation in sustainable products development. **Am. J. Eng. Applied Sci.**, v. 9, p. 1027-1036. Doi: 10.3844/ajeassp.2016.1027.1036

AVERSA, R.; PETRESCU, R. V.; APICELLA, A.; PETRESCU, F. I. T. (2016h) Mitochondria are naturally micro robots - a review. **Am. J. Eng. Applied Sci.**, v. 9, p. 991-1002. Doi: 10.3844/ajeassp.2016.991.1002

AVERSA, R.; PETRESCU, R. V.; APICELLA, A.; PETRESCU, F. I. T. (2016i) We are addicted to vitamins C and E-A review. **Am. J. Eng. Applied Sci.**, v. 9, p. 1003-1018. Doi: 10.3844/ajeassp.2016.1003.1018

AVERSA, R.; PETRESCU, R. V.; APICELLA, A.; PETRESCU, F. I. T. (2016j) Physiologic human fluids and swelling behavior of hydrophilic biocompatible



hybrid ceramo-polymeric materials. **Am. J. Eng. Applied Sci.**, v. 9, p. 962-972. Doi: 10.3844/ajeassp.2016.962.972

AVERSA, R.; PETRESCU, R. V.; APICELLA, A.; PETRESCU, F. I. T. (2016k) One can slow down the aging through antioxidants. **Am. J. Eng. Applied Sci.**, v. 9, p.1112-1126. Doi: 10.3844/ajeassp.2016.1112.1126

AVERSA, R.; PETRESCU, R. V.; APICELLA, A.; PETRESCU, F. I. T. (2016l) About homeopathy or «Similia Similibus Curentur». **Am. J. Eng. Applied Sci.**, v. 9, p. 1164-1172. Doi: 10.3844/ajeassp.2016.1164.1172

AVERSA, R.; PETRESCU, R. V.; APICELLA, A.; PETRESCU, F. I. T. (2016m) The basic elements of life's. **Am. J. Eng. Applied Sci.**, v. 9, p. 1189-1197. Doi: 10.3844/ajeassp.2016.1189.1197

AVERSA, R.; PETRESCU, F. I. T.; PETRESCU, R. V.; APICELLA, A. (2016n) Flexible stem trabecular prostheses. **Am. J. Eng. Applied Sci.**, v. 9, p.1213-1221. Doi: 10.3844/ajeassp.2016.1213.122

AVERSA, R. ; APICELLA, A. (2016) Liquid Crystalline Polymers Compatibilization and Adhesion Enhancement by Reactive Blending in Post- Consumers PET's. **Am. J. Eng. Applied Sci.**, v. 9, n. 3, p. 530-539. Doi: 10.3844/ajeassp.2016.530.539

CHIELLINI, E.; CORTI, A.; D'ANTONE, S.; BACIU, R. (2006) Oxo-biodegradable carbon backbone polymers – oxidative degradation of polyethylene under accelerated test conditions. **Polym Degrad Stabil**, v. 91, n. 11, p. 2739-2747.

CRUZ, H.; SON, Y. (2015) Reactive compatibilization of liquid crystalline polymer/ethylene-acrylic acid ionomer blends. **J. Korea Academia-Industrial Cooperat. Society**, v. 16, p. 3653-3659. Doi: 10.5762/KAIS.2015.16.5.3653



DUTTA, D.; WEISS, R. A.; HE, J. (1996) Compatibilization of blends containing thermotropic liquid crystalline polymers with sulfonate ionomers. **Polymer**, v. 37, p. 429-435. Doi: 10.1016/0032-3861(96)82912-0

GOH, K. L.; TAN, L. P. (2012) Micromechanical fiber recruitment model of liquid crystalline polymer reinforcing polycarbonate composites. **Damage. Fract. Comp. Mater. Struct.**, v. 17, p. 85-106. Doi: 10.1007/978-3-642-23659-4\_7

GROENINCKX, G.; REYNAERS, H.; BERGHMANZ, H.; SMETS, G. (1980) Morphology and melting behavior of semicrystalline poly(ethylene terephthalate). Isothermally crystallized PET. **J. Polymer Sci.**, v. 18, p. 1331-1324. Doi: 10.1002/pol.1980.180180612

HOEL, M.; KVERNDOKK, S. (1996) Depletion of fossil fuels and the impacts of global warming. **Resour Energy Econ**, v. 18, n. 2, p. 115-136.

IMRE, B.; PUKÁNSZKY, B. (2013) Compatibilization in bio-based and biodegradable polymer blends. **European Polymer Journal**, v. 49, n. 6, p. 1215-1233.

KALE, G.; KIJCHAVENGKUL, T.; AURAS, R.; RUBINO, M.; SELKE, S. E.; SINGH, S. P. (2007) Compostability of bioplastic packaging materials: an overview. **Macromol Biosci**, v. 7, n. 3, p. 255-277.

MARQUETTI, I.; DESAI, S. (2018) Adsorption Behavior of Bone Morphogenetic Protein-2 on a Graphite Substrate for Biomedical Applications. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p. 1037-1044. Doi: 10.3844/ajeassp.2018.1037.1044

NICODEMO, L.; APICELLA, A.; NICOLAIS, L. (1981) Dimensional stability and tensile properties of drawn polystyrene composites. **J. Applied Polymer Sci.**, v. 26, p. 129-139. Doi: 10.1002/app.1981.070260111

NICOLAIS, L.; APICELLA, A.; NICODEMO, L. (1981) Filler effect on the recoil kinetics of drawn polystyrene. **Polymer Eng.**, v. 21, p. 151-154. Doi: 10.1002/pen.760210307

PLASTICS EUROPE. **Plastics – The Facts 2011 – An analysis of European plastics production, demand and recovery for 2010.**

<<https://www.plasticseurope.org/en>>

SCOTT, G. (2000) 'Green' polymers. **Polym Degrad Stabil**, v. 68, n. 1, p. 1-7.

SHAFIEE, S.; TOPAL, E. (2009) When will fossil fuel reserves be diminished? **Energy Policy**, v. 37, n. 1, p. 181-189.

SHEN, K.; HAUFE, J.; PATEL, M. K. (2009) Product overview and market projection of emerging bio-based plastics. **Final report of Utrecht University to European Bioplastics.**

SKOVBY, M. H. B.; KOPS, J.; WEISS, R. A. (1991) Studies on a diphenyl ether modified poly(phenyl-1,4, phenylene terephthalate) liquid crystalline polymer and its blends with polycarbonate and polysulfone. **Polymer Eng. Sci.**, v. 31, p. 954-962. Doi: 10.1002/pen.760311305

SON, Y.; CHUN, Y. S.; WEISS, R. A. (2004) Improvement of the processability of poly (ether ketone) by the addition of a liquid crystalline polymer. **Polymer Eng. Sci.**, v. 44, p. 541-547. Doi: 10.1002/pen.20048

TAMBURRINO, F.; APICELLA, A.; AVERSA, R.; PETRESCU, F. I. T. (2018)

Advanced Manufacturing for Novel Materials in Industrial Design Applications. **Am. J. Eng. Applied Sci.**, v. 11, n. 2, p. 932-972. Doi: 10.3844/ajeassp.2018.932.972

TEYSSEDE, G.; LACABANNE, C. (1995) Some considerations about the analysis of thermo stimulated depolarization peaks. **J. Phys. D**, v. 28, p. 1478-1478. Doi: 10.1088/0022-3727/28/7/029

WEISS, R. A.; HUH, W.; NICOLAIS, L. (1987) Novel reinforced polymers based on blends of polystyrene and a thermotropic liquid crystalline polymer. **Polym. Eng. Sci.**, v. 27, p. 684-691. Doi: 10.1002/pen.760270913

WILK, J.; SANDERS, G.; MARKS, S.; PAOLICELLI, S. A.; DICAPRIO, M.; BUCINELL, R. (2017) The Optimization of a Porous Ti6Al4V Bone Construct Using Additive Manufacturing. **Am. J. Eng. Applied Sci.**, v. 10, n. 1, p. 13-19. Doi: 10.3844/ajeassp.2017.13.19

ZHANG, H.; WEISS, R. A.; KUDER, J. E.; CANGIANO, D. (2000) Reactive compatibilization of blends containing liquid crystalline polymers. **Polymer**, v. 41, p. 3069-3082. Doi: 10.1016/S0032-3861(99)00469-3