EXAMINING THE EFFECTIVENESS OF DIFFERENT MIXING ELEMENTS IN THE TWIN SCREW COMPOUNDING OF LIQUID CRYSTAL POLYMER AND POLYPROPYLENE

By

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for any proprietary material contained therein.

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Examining the Effectiveness of Different Mixing Elements in the Twin Screw Compounding of Liquid Crystal Polymer and Polypropylene

Abstract

by

AKASH AGRAWAL

Thermotropic Liquid Crystalline Polymers, which are materials made up of semi rigid rod-like molecules, have this unique property of orienting themselves during flow. This results in the formation of a very ordered melt phase which gives these materials a plethora of superior properties like high tensile modulus, good chemical resistance, very high thermal stability, flame retardant characteristics, dimensional stability etc. However, their cost prohibits their wide scale use and limits it to niche applications. This has engendered a lot of interest in the preparation of Thermoplastic/Liquid Crystal Polymer blends. Moreover, the fact that Liquid Crystal Polymers tend to reduce the melt viscosity, making the blend easier to process, is an added incentive in addition to their properties.

Extension dominated flows have been long known to be more efficient in mixing as compared to shear dominated flows. Exploiting this concept, Carson and et al. at Case Western Reserve University have developed new mixing elements for the Twin Screw Extruder. These elements were proven to impart extensional forces as opposed to the shear forces imposed by the Kneading Blocks, resulting in better dispersive and dissipative mixing.

This thesis aims to use these novel extensional mixing elements on a system of Polypropylene and Liquid Crystal Polymer compatibilized by a compatibilizer, to enhance mechanical and thermal properties of Polypropylene on addition of a low quantity of Liquid Crystal Polymer. Furthermore, this research also intends to compare the extensional mixing elements to the kneading blocks, which are the industry standard. All the extrusions were carried out on a co-rotating twin screw extruder, at two different temperatures of 285-295 °C and 220-230 °C. The purpose of using two different temperatures was to melt the Liquid Crystal Polymer to prepare blends in one case, whereas to keep it a solid and prepare composites in the other case.

Chapter 1: Introduction

The field of material science and engineering is represented broadly by three fundamental materials, metals, ceramics and polymers. While ceramics and metals have made steady progress through the years, it is the field of polymer science and engineering that has made exponential progress in the past few decades. Although they started their journey as cheap substitutes for other materials, today they are used in high technology applications where no other material can be used. The rate at which this field is growing, it won't be surprising to see some ground breaking breakthroughs in the years to come. Polymers have become an integral part of our everyday life and it would be impossible to imagine living in a world without them.

However, the applications today are getting so demanding, that it is impossible for a single polymer to have all the properties. This has given birth to the field of polymer blends and composites. Polymer blending is an inexpensive method of blending two polymers together in order to get the best of both worlds. A polymer composite on the other hand is a material having continuous phase of a polymer and a dispersed phase (generally filler or fiber). Using Polymer Blends and Composites, it is now possible to tailor mechanical, electrical and optical properties of a polymer.

Thermotropic Liquid Crystalline Polymers, which are materials made up of semi rigid rod-like molecules, have this unique property of orienting themselves during flow. This results in the formation of a very ordered melt phase which gives these materials a plethora of superior properties like high tensile modulus, good chemical resistance, very high thermal stability, flame retardant characteristics, dimensional stability etc. However, their cost prohibits their wide scale use and limits it to niche applications. This has engendered a lot of interest in the preparation of Thermoplastic/Liquid Crystal Polymer blends. Moreover, the fact that Liquid Crystal Polymers tend to reduce the melt viscosity, making the blend easier to process, is an added incentive in addition to their properties.

According to the report from IHS, Asia was by far the biggest consumer of Liquid Crystalline Polymer in 2015 (Figure 1.2) [1].

Important points to be noted in the LCP market are [1]:

- Flame retardants are materials that inhibit the occurrence of fire in a material by restraining the chemical reactions which lead to it, or by forming a layer on the surface. These materials have always had halogens present in them, which are not eco-friendly materials. Over, the recent years there legislations have only gotten very strict with regard to their use amid environmental concerns. LCP's can be strong candidates to be used as eco-friendly flame retardants.
- The packaging industry is expected to be a $ 975 billion dollar industry by 2018 [2]. While the industry is growing exponentially, so are its challenges. One such challenge the industry faces is in the form of tighter packaging. This is bound to result in higher temperature electronics, and the development of thinner parts, which will ultimately happen only with higher flowability in the mold. These challenges can be surmounted by the use of LCP's.
- Based on the current trends and market reports, it seems that the LCP market is going to continue to increase in Asia, with the highest increase expected to be in China and Japan in particular. No significant expansions seem to be coming up for the United States and Europe.

- Developing lightweight materials for automobile components to increase fuel efficiency and reduce carbon emissions is likely to aid LCP growth.
- The focus on finding newer materials of choice for construction of various vehicles, seems to be increasing with each passing day. The importance of using a material which is light and strong cannot be stressed enough as it could lead to the better fuel efficiency leading to a cost saving running into millions of dollars.

World consumption of LCP is expected to grow at a rate of 4-5% during 2015-2020. This estimation is after taking in to consideration the deceleration in China's economy.

Prior Work

Blending of LCP's with a thermoplastic has engendered a lot of interest and has been an active area of research since quite some time. Two primary reasons for it to become an exciting avenue of research are the in-situ fibrillation of the LCP's in the extrusion direction thereby leading to substantial enhancement of the properties of the base matrix and the fact that these materials have a very low viscosity, helps to reduce the viscosity of the melt during extrusion and hence facilitates processability. However, one of their biggest drawbacks is that these materials are very incompatible with most of the polymer matrixes. Hence finding the right compatiblizer to compatibilize LCP blends is quite a challenging task. Hence a lot of the research in the preceding years has been on the identification of the right compatibilizer. MAH-g-EPDM was used as a compatibilizer by Seo [4], for compatibilizing different Polyamide/LCP blends. Seo reported of the possibility of a chemical reaction going on between the MAH group of the compatibilizer and the LCP which led to compatibilization of the blends. G.C. Nayak et al. [5] used Silicon

Carbide modified Multiwall carbon nanotubes and polyphosphazene in an effort to compatibilize the otherwise incompatible blend of Polyetherimide and LCP.

As mentioned before LCP's are very difficult to blend with polymers. Things get complicated further when you try to blend it with a polymer like Polypropylene due to its non-polar nature. Hence the use of a compatibilizer is a necessity. Mandal et al. [6] have explored the use of Ethylene Acrylic Acid (EAA) as a compatibilizer to blend a system of PP and LCP Vectra A950. The compatibilizer was found to work by forming a Hydrogen bond (Figure 1.6). They reported significant improvements in the properties of the base polymer on the addition of a small amount of compatibilizer. 5 different compatibilizers were used to compatibilize a PP/LCP (LC Rodrun 3000) system by J. Maia et al. [7]. Good Tensile modulus improvements were achieved at the cost of Elongation at break and toughness. They further went ahead and studied how the rheological and morphological properties evolve along the length of the extruder [8] and the influence of different parameters on the Mechanical, Rheological and Morphological properties [9]. Compatibilized and incompatibilized PP/LCP blends were also looked at under extension [10]. Though this system was the first choice, the non-availability of the Rodrun LC3000 grade of LCP supplied by Unitika made this choice unviable.

Owing to the cheap raw materials (PP and EAA), ease of processability and good results this system was chosen for research in this work. However, due to the non-availability of Vectra A950, Vectra A130 which is nothing but Vectra A950 with an additional 30% (by weight) glass fibers.

Liquid Crystals and Life

"Liquid Crystals stand between the isotropic liquid and the strongly organized solid state, life stands between completely disorder, which is death and complete rigidity, which is death again" D.G. Dervichian [11].

Anistropy, which is the characteristic of not having the same properties in both directions, is a trait which is shown by some living things. Whichever living things, do show this property are either currently in the liquid crystal state or have been in one during some point of their life. Liquid crystallinity can be induced either by temperature (liquid crystals produced in this fashion are referred to as thermotropic liquid crystals), or by a dissolving in a solvent (liquid crystals produced in this fashion are referred to as lyotropic liquid crystals). Biological systems in nature are generally found to be lyotropic in nature.

Although, there are numerous number of examples of liquid crystals presence in the nature, only a few of them have been highlighted here (Figure 1.7) [12].

Liquid Crystals are integral to life. Probably one of the most prominent example of this is their presence in the cell membrane. The lamellar structure can be seen in the diagram. This particular structure of the cell membrane plays a crucial role in the photoreceptors in a fish. The orientation which is a characteristic of liquid crystals also helps in orienting the molecules which absorb light. This ultimately helps the fish in polarized night vision.

One of the most visually appealing sights due to liquid crystals, can be seen in the iridescent colors seen in beetles. It is important to note that not all beetles exhibit this kind of a behavior. Scarab beetles for instance, are one kind of beetles which show iridescent lights. How this basically works is that these beetles secrete liquid crystals in the cholesteric state, during the late chrysalis phase. The resulting coat is found to reflect circularly polarized light and is found to show iridescence.

Myelin, which is the material sheathing the nerves, is quintessential in transmission of electrical impulses. This material although discovered in 1853 was proved to be a liquid crystal much later. Other biological materials which are found to possess liquid crystals include various vitamins (A,E & K), bile acids, retinols etc.

Liquid crystals are also found in DNA. Blood in some cases is capable of forming liquid crystalline phase. However, this scenario is not desirable at all as it can cause the viscosity of the blood to increase, which will ultimately lead to hindrance to the flow. The case when the blood is found to behave in this fashion, is referred to as sickle cell anemia.

Introduction to Liquid Crystal Polymers

Often referred to as the fourth state of matter, Liquid Crystals are substances which have properties intermediate between solid crystal and conventional liquid. After a late start in 1950, of theoretical proving of the Liquid Crystal phase by Onsager and Flory, it was only in 1970 that aromatic polyamides were synthesized and their ability to form LC solution in some solvents was found.

Liquid crystalline Polymers (LCP) are a very interesting class of materials, representing advanced organic based functional materials. These materials form the best of both worlds by combining the molecular order in liquid crystals with the superior mechanical properties of polymers. These advanced organic materials have the unique capability of self-organization [13]. This capability can be attributed to the presence of molecular architectures possessing anisotropy. However, the property which sets this material apart from the rest is their morphological state. This state cannot be described entirely as crystalline (or glassy) or as liquid. They are found to be in a morphological state which is intermediate between the two. Self-organization of their chains can lead into the formation of a broad range of ordered structures (nematic, semectic etc.).

Liquid Crystalline polymers are materials, whose properties are dependent on their final physical form (fibers, films, sheets) and the way they have been processed (extrusion, injection molding and fiber spinning).

In any ordinary liquid, the molecules have sufficient thermal energy, to overcome the intermolecular attractive forces and move around freely. This random motion of the molecules makes it isotropic, which means it is equally disordered in all the direction. The material exhibiting this kind of a behavior is known to be isotropic in nature. On the other hand, liquid crystals are materials which are known to possess an anisotropic behavior. This means that the properties of the material will vary depending on the direction from which it is viewed. Therefore, liquid crystal polymers retain some degree of order, and possess anisotropy.

This characteristic can be explained by the primary bonds and the secondary bonds. The primary bonds lead to a high degree of attractive force to be formed within the molecule itself. The forces responsible for bonding between the molecules are secondary forces. Secondary forces happen to be less than the primary forces, making it more susceptible to separation. On application of a force, transverse to the molecular orientation, most of the load is directed towards the secondary bonds, leading to a comparatively easier separation. On the other hand, if a load was applied in the longitudinal instead of the transverse direction, it would cause loading of the primary bonds making the separation more difficult.

Low value of thermal expansion coefficient coupled with high melt flow in the direction of molecular orientation facilitates LCP’s to showcase excellent cycle repeatability. This ultimately offers the big advantage of being able to manufacture a thin-walled part without warping. These materials show good flame retardant properties and tend to remain unaffected by weather and UV rays. LCP’s also show a high degree of chemical resistance across a broad range of temperatures. They are well known for their superior mechanical properties and good electrical insulation properties.

Though LCP’s offer a number of advantages, like any other material they come with their own set of disadvantages [14]. Since this material is anisotropic in nature, wherever this material meets it causes weak weld lines. The main reason for this is due to the fact that the when the material meets, it is having molecular orientation different from the bulk of the material. As thermal expansion is directly affected by the molecular orientation, the weld lines can have different warpage as compared to the rest of the material. These problems can however be solved by carefully designing and placing the gates. Anisotropy also causes properties like tensile strength, thermal expansion, elastic modulus etc. to be approximately 3 times more in the longitudinal directional as compared to the transverse direction. Apart from that, as these are niche materials with superior properties, they are obviously more expensive. One other minor drawback is that these materials need to be properly dried before processing.

One of the biggest initial practical applications of LCP, which continues on to this day, came in the form of manufacturing a very high modulus material known as KEVLAR. The reason behind KEVLAR's high modulus is the order in the Liquid Crystal phase. Since then, the applications of Liquid Crystals has grown exponentially. Today, they are the most versatile materials finding applications in electronics, photonics, plasmonics metamaterials, automotive, industrial machinery etc.

Amongst the newer applications of LCP, their use in the medical industry is garnering quite a bit of attention. Magnetic Resonance Spectroscopy (MRI), is an imaging technique which upon using the concept of Nuclear Magnetic Spectroscopy (NMR) is able to generate images of the body. Developed in 1970's, MRI has today become the standard for diagnosis. However, certain medical procedures like catheterization for instance, are still found to use X-Ray due to the presence of metals in some of the medical equipment, which is incompatible with MRI. The use of X-Ray is not very advisable, as it exposes the client directly to ionizing radiation.

To overcome this challenge, Zeus has managed to process LCP in the form of a monofilament fiber in order to capitalize on all its unique properties and build a catheter tube as a substitute for metals, which is now compatible with MRI [15]. However, their primary application is in the electrical and electronics industry [16].

There are certain applications which are specific only to LCP's. Other polymers are generally not feasible to use in these kind of applications. One such application for instance, is their use in oven handles and engine shields. Since they have an operating temperature range of greater than 200 C (which is not very common amongst polymers), it make them a good choice for this application. Their high degree of resistance to chemicals along with high tensile modulus, makes them ideal to use in high pressure fuel line connectors in the automotive industry. Good electrical insulating properties makes them a material of choice for electrical device housing and semiconductor components.

Properties of LCP [14, 17-20]

The increment of the knowledge in various aspects like the chemistry of liquid crystals, its molecular structure, the different techniques which are used for its processing, and its applications coupled with the great amount of progress from theoretical studies and the computer simulations standpoint has contributed to a great extent into making this an exciting arena of scientific research. Through its fundamental challenges, the field of Liquid Crystalline Polymers has managed to prick the curiosity of the entire scientific community. Recent revelations on the possibility of synthesizing these materials from a myriad different sources has created a sense of awareness. In spite of all the advances, the study of these mystery materials still poses a great deal of a challenge, as with newer and newer technologies coming up there is a new found need to come up with advanced materials having as broad a range of properties as possible. Today upon realizing the need for advanced organic materials and their potential applications, industrialists are collaborating with scientists to come up with new classes of liquid crystalline polymers. Today it is one of the most rapidly growing branches of Polymer Science and Technology is Liquid Crystal Polymers.

Classification of Liquid Crystals

There are two different ways to form Liquid Crystals. One way is by dissolving the polymer in an appropriate solvent. Liquid crystals formed in this manner are termed as lyotropic (concentration dependent). The other way in which Liquid crystals can be formed is by heating the polymer above its glass transition temperature. These class of Liquid Crystals are referred to as Thermotropic (temperature dependent) [17-20].

Lyotropic liquid crystals are materials which are sensitive to concentration (Figure 1.9). They exhibit liquid crystallinity only in a narrow range of concentration. In lyotropic liquid crystals flowability is gotten in the system by the solvent molecules. These molecules tend to fill all the spaces around the compound. Based on the amount of concentration, a lot of different phases can be induced.

Thermotropic liquid crystals are highly sensitive to temperature (Figure 1.10). They are found to show ordering only in a small range of temperature. Increasing the temperature beyond the range, would lead to the heat energy causing increased thermal motion in molecules leading to disruption of the ordered state. This would eventually lead the material to go in the liquid phase. Thermotropic liquid crystals are broadly divided in to High Molar Mass and Low Molar Mass materials (Figure 1.8).

High Molar mass class of liquid crystals are generally the liquid crystal polymers. Based on the structure of these macromolecules and the position that they take with respect to the polymer chain, they are generally categorized as, Main-chain Liquid Crystal Polymers (MCLCPs), side chain Liquid Crystal Polymers (SCLCPs) and the third category is a combination of main chain liquid crystal polymers and side chain liquid crystal polymers (MCSCLCPs) depending on the placement of the mesogenic units [18]. Main-chain Liquid Crystal Polymers are materials where the molecular chains are all aligned in a particular direction. On the other hand, Side Chain Liquid Crystal polymers, as the name suggests, are materials having chains branching out on the side from the main chain. They have a structure that resembles one of a comb. The general direction, which is given by the director, is oriented either in the direction of the side chains or in the direction of the main chains.

Low Molar Mass liquid crystals are materials which can be broadly divided into rod like and disc like molecules. Rod like molecules form the calamitic liquid crystals while the disc like molecules form the discotic phase. Rod like molecules are further sub-divided into Nematic and Smectic. Within Nematic there are Ordinary Nematic and Twisted Nematic (cholesteric). Smectic, which are also referred to as book shelf liquid crystals, are divided into perpendicular and tilted long axis. Perpendicular semectics, as the name suggest are those which tend to align perpendicularly. While tilted long axis smectic are those which tend to line up tilted on the long axis.

The differences in the different phases of a liquid crystal polymer are mainly based on order. Two types of low molar mass thermotropic liquid crystal, mesophases are [17-22]:

a) Calamatic: LCP's falling under this category have a rigid polarizable core, with an aliphatic tail which is generally flexible, on one of the sides. While the function of the core is to make them align, the flexible aliphatic tail helps in helps them to flow. They may have polar groups like Cyanide along the main axis fluorine groups along the main axis, or a dipole moment along the rings caused by Nitrogen. All this becomes very important when we try to orient a material using an external stimuli (for example: applied electric field). Calamatic consist of the following phases:

1. Nematic Liquid Crystals: Nematic is derived from the word Nematon in greek, which means thread-like. These liquid crystals generally have a single axis, the direction of which is given by the average of individual axis of the liquid crystals. However, there is this rare case in which liquid crystals have two axis. These nematic liquid crystals having two axis are known as biaxial nematics. The important characteristic to note about these molecules is that, although they do not have short term order they have long range directional order. In general these molecules possess the flowability of a liquid, however they can be aligned with the help of external magnetic fields. This property of liquid crystals is exploited in liquid crystal displays.
2. Cholesteric phase: Cholesterol derivatives were first seen to exhibit this phase and hence this phase was named the cholesteric phase. Molecules which show chirality, are the only ones capable of showing this phase. Hence this phase is also often referred to as the chiral phase. This phase is nothing but the nematic phase itself superimposed layer by layer, having a slight twist with each layer. The time it takes for a director to rotate a full 180 degrees, is known as the pitch. And this pitch is found to be dependent on the temperature. It is due to this reason that this phase is found to possess temperature sensitive optical properties.
3. Smectic phases: This phase is found to exist at temperature lower than that of the nematic phase. The origins of the word smectic lies in the latin word “smecticus”, which means soap like characteristics. While the origins of the word may seem a little odd at first, it is the fact that this phase has layers which are well defined and

are found to glide one on top of the other, in a soap like fashion that gives it that name. In fact it is interesting to note that the slimy material seen at the very bottom of a soap tray is actually a type of a smectic liquid crystal. These phases are found to have what we refer to as “bookshelf ordering”. That is to say that they have more order in the direction normal to the director. This phase, unlike the nematic phase has some extent of translational order. Smectic phases are further subdivided based on positional and orientational order. Out of which Smectic A and Smectic C are the most common phases. In the case of Smectic A, the director is found to be normal to the plane, while in the case of Smectic C, though the molecular arrangement is similar to the former, the director is found to be at an angle to the plane. Just as seen in the case of the Nematic phase, the smectic C phase is found to have a chiral state which is represented as C*. True to the smectic C phase, the director is found to make an angle with respect to the plane. However the only difference is that, the director is found to rotate while moving on from one layer to the other ultimately leading to the formation of a helix.

b) Discotic Liquid Crystals: In this phase, flat liquid crystal molecules, as the name suggests, generally in the shape of discs having a three-fold and sometimes even a four-fold symmetry having a somewhat rigid core and side chains stacked with their planes being almost parallel. Therefore, the director is approximately normal to the plane. The discotic liquid crystals are further subdivided into nematic discotic phase and columnar discotic phase. The nematic discotic phase is found to have very little positional order but great amount of orientational order. On the other hand, in the case of columnar discotic phase the molecules are stacked into columns, and hence are found to have some degree of positional order. These discs often tend to make hexagonal patterns, and hence these phases are referred to as the hexagonal columnar discotics.

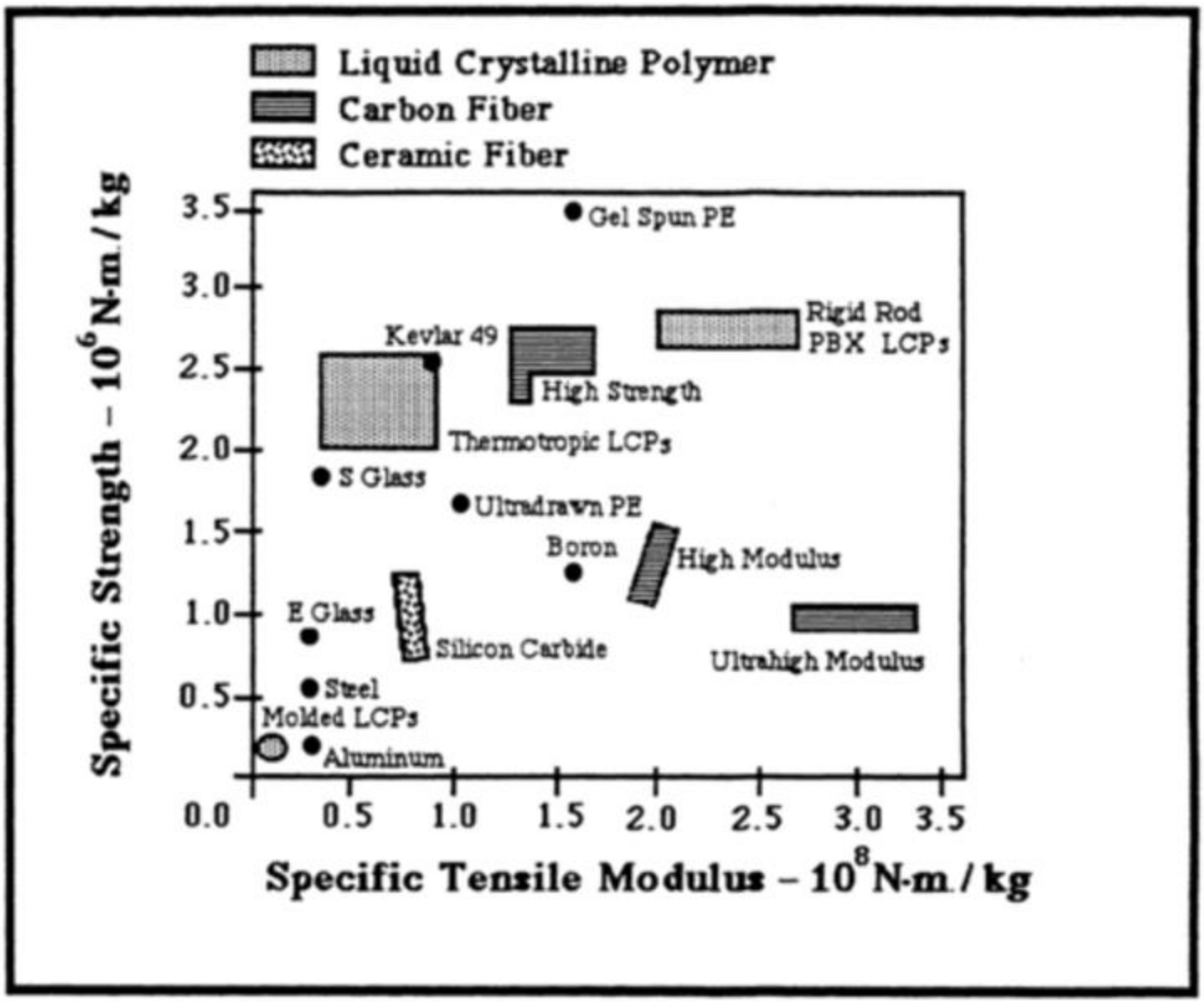
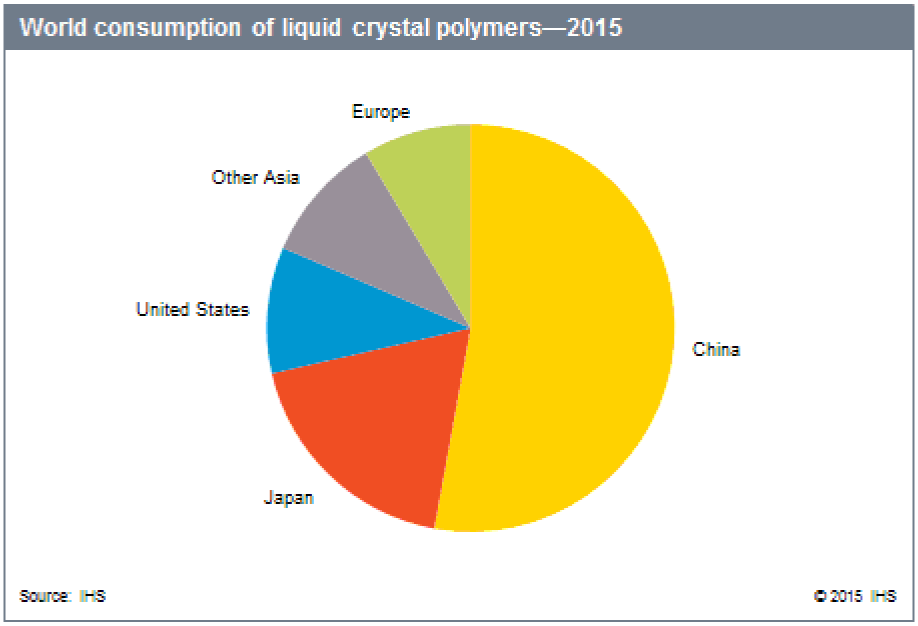


Figure 1.1 - Specific tensile strength vs Specific Tensile modulus of LCP's in context with other materials



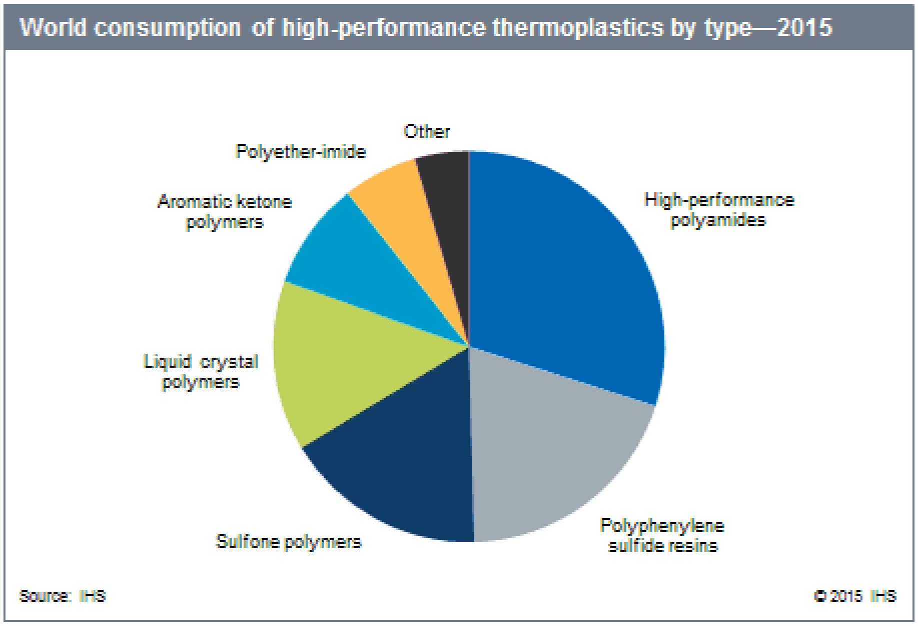


Figure 1.2 – Top – World Consumption of LCP in 2015. Bottom – World consumption of thermoplastics by type in 2015 [1,3].

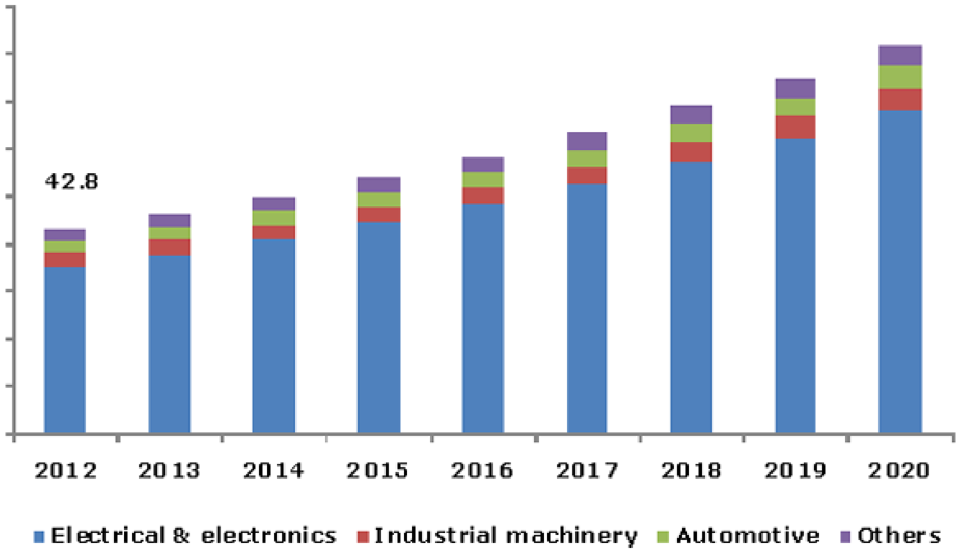
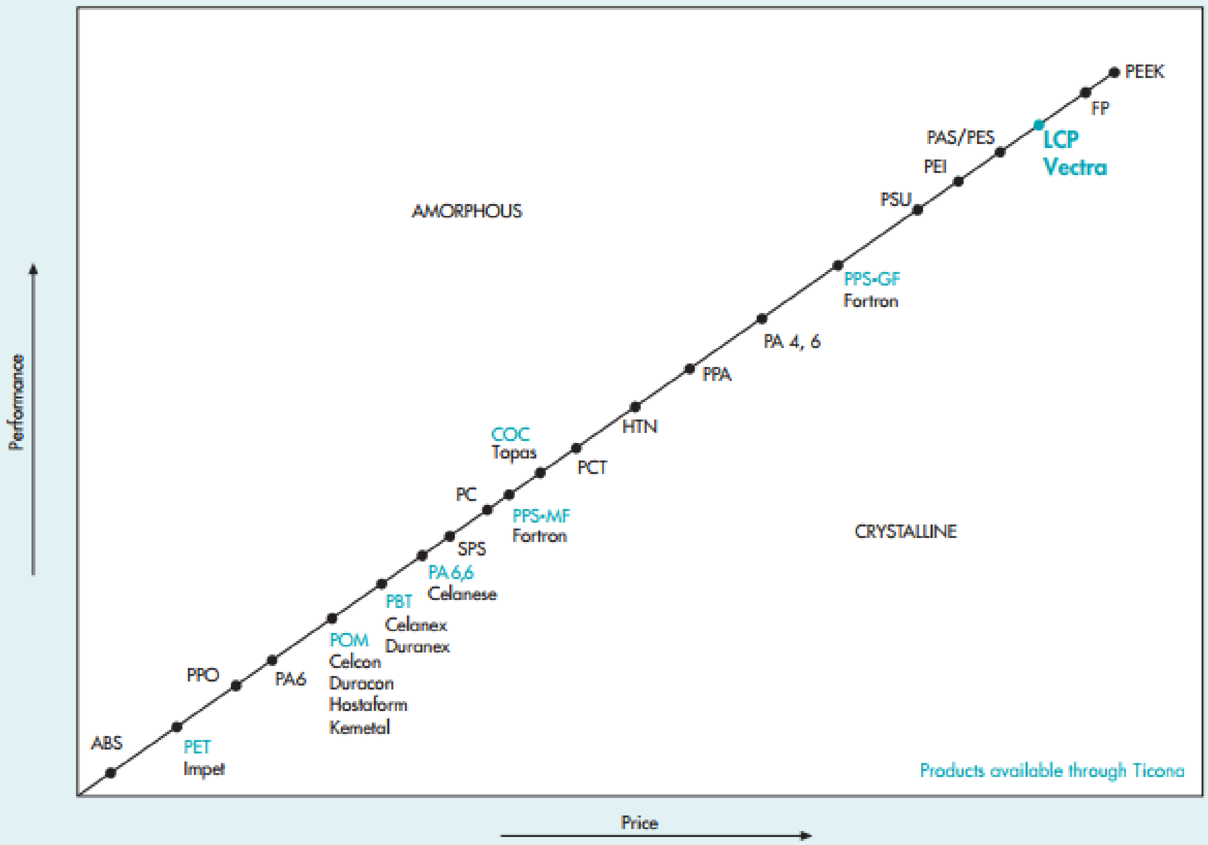


Figure 1.3 – Applications of LCP's in different market segments [16].

Figure 1.4 – Use of LCP as an alternative to metals in MRI [15].

Fig. 1.2 · Price Performance Comparison of Engineering and High Performance Plastics



*** High Performance Plastics Acronyms**

ABS = acrylonitrile-butadiene-styrene
COC = cyclic olefin copolymer
FP = fluoropolymers
PA6 = polyamide 6 (nylon)
PA4,6 = polyamide 4,6 (nylon)
PBT = polybutylene terephthalate
PEEK = polyether ether ketone
PES = polyether sulfone
POM = polyoxymethylene (polyacetal)
PPS-MF = polyphenylene sulfide (mineral filled)
PPA = polyphthalamide
SPS = syndiotactic polystyrene

HTN = high temperature polyamide (nylon)
LCP = liquid crystal polymer
PA6,6 = polyamide 6,6 (nylon)
PAS = polyaryl sulfone
PCT = polycyclohexylenedimethylene terephthalate
PEI = polyether imide
PET = polyethylene terephthalate
PPO = modified polyphenylene oxide
PPS-GF = polyphenylene sulfide (glass filled)
PSU = polysulfone
PC = polycarbonate

Figure 1.5 – Price performance of Engineering and high performance plastics.

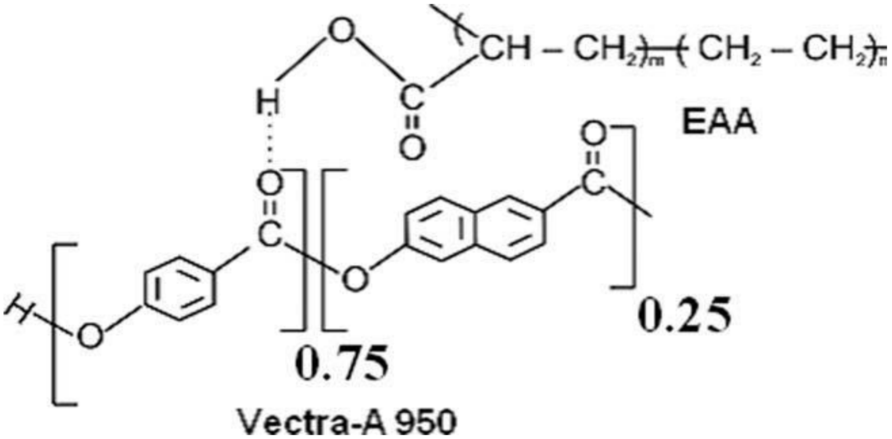


Figure 1.6 – The formation of Hydrogen bond between Vectra A 950 and EAA [6] .

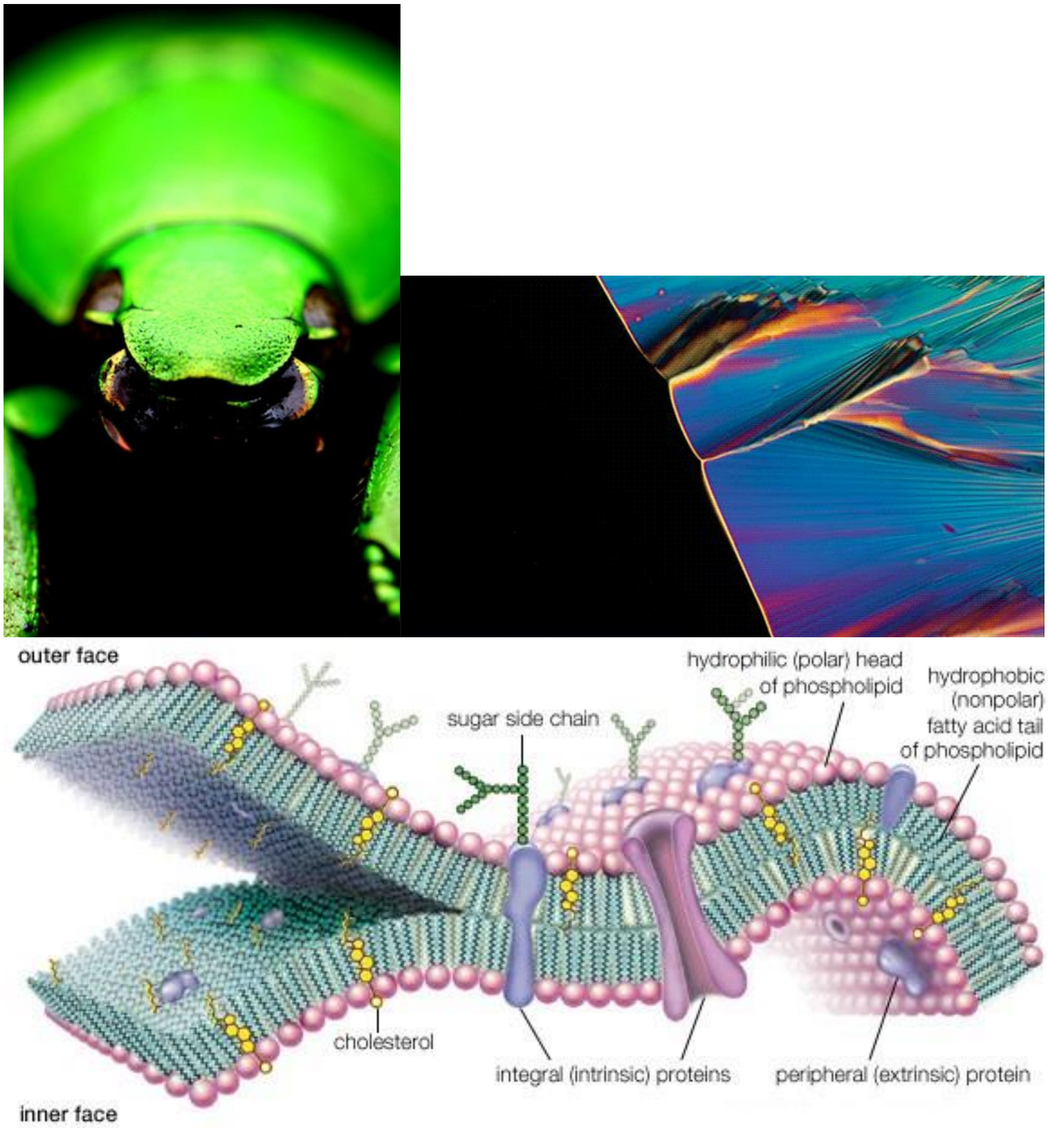
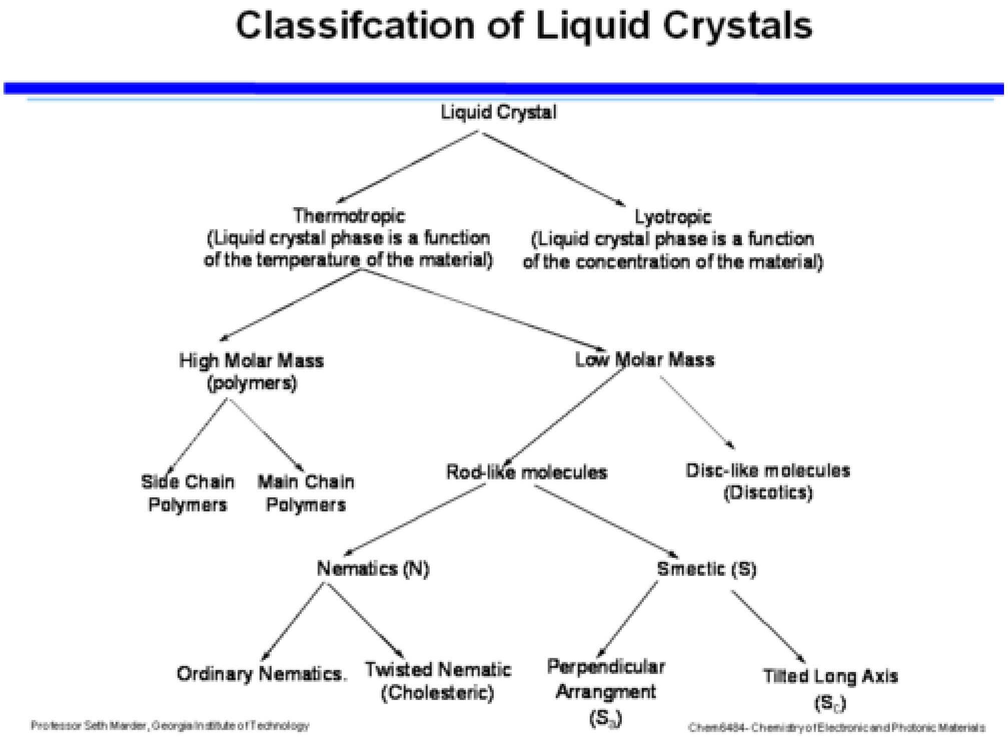


Figure 1.7 – Top left – Irridescence displayed by beetles due to LCP. Top right – Presence of LCP in DNA. Bottom – Cell membrane in a human being.



Classifcation of Liquid Crystals

Liquid Crystal

Thermotropic
(Liquid crystal phase is a function
of the temperature of the material)

Lyotropic
(Liquid crystal phase is a function
of the concentration of the material)

High Molar Mass
(polymers)

Low Molar Mass

Side Chain
Polymers

Main Chain
Polymers

Rod-like molecules

Disc-like molecules
(Discotics)

Nematics (N)

Smectic (S)

Ordinary Nematics.

Twisted Nematic
(Cholesteric)

Perpendicular
Arrangment
(S_a)

Tilted Long Axis
(S_C)

Professor Seth Marder, Georgia Institute of Technology

Chem6484- Chemistry of Electronic and Photonic Materials

Figure 1.8 – Classification of liquid crystals, with a focus on thermotropic liquid crystals [22].

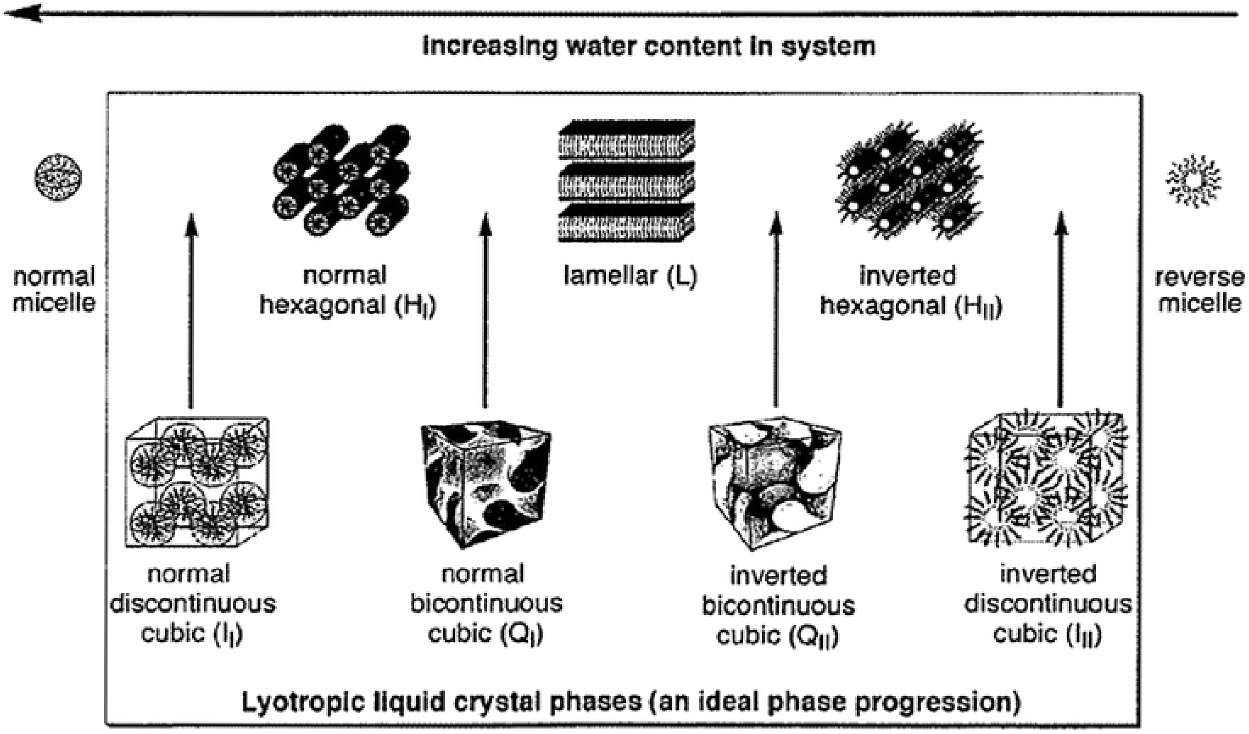


Figure 1.9 – Lyotropic liquid crystal phases as a function of increasing solvent content [13].

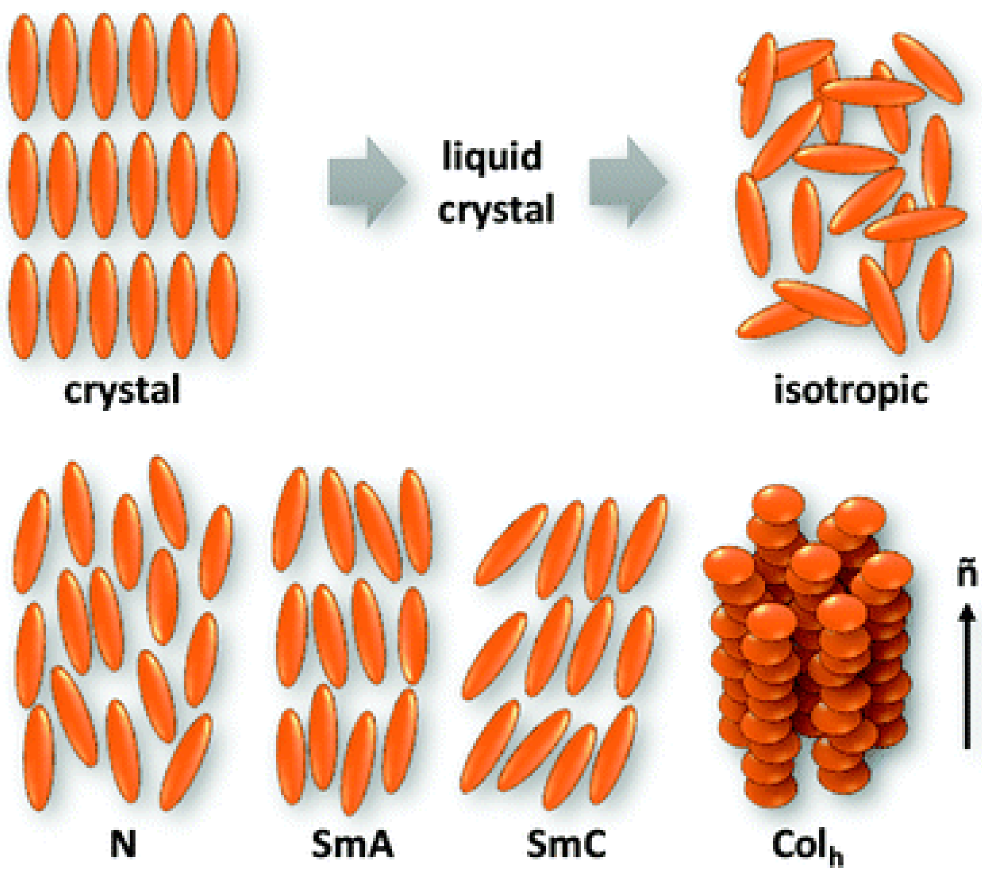


Figure1.10 – Phase change in Thermotropic Liquid Crystals as a function of temperature [23].

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Chapter 2

Processing of PP/LCP Blends and Composites

Introduction

Pure polymers are very rarely processed by themselves. More often than not, they are mixed or compounded with other materials to enhance some properties of the base polymers. These materials could be other polymers, additives (colorants, stabilizers, flame retardants, viscosity modifiers etc.), fillers (to reduce cost) and other processing aids. While in theory single screw or twin screw extruders can be used for this task, Twin screw extruders are by far the favorite choice. The reason for choosing Twin screw extruder (TSE) over the Single screw extruder for compounding operations is because it provides better mixing [1]. TSE is also used exclusively for reactive extrusion, which involves in-situ chemical reaction during extrusion.

There are essentially two different types of mixing dispersive mixing and distributive mixing (Figure 2.1) [2]. Dispersive mixing is the extent of breaking up of the larger domains into smaller domains. Smaller the domain size, better is the dispersive mixing. Distributive mixing on the other hand, as the name suggests is the extent of distribution of the dispersed phase domains.

The extent of distributive and dispersive mixing taking place inside the twin screw extruder can be controlled, by changing the type of the twin screw elements and the screw configuration. Currently, most of the dispersive mixing taking place inside the extruder is a result of the shear dominated flow which is imposed on the material during its passage through the kneading blocks

(KB). Though KB's also impose a small amount of extensional flows on the material during processing.

Grace [3], through his work on high viscosity immiscible fluid systems studied the effectiveness with which rotational (shear) and irrotational (extensional) flows are able to disperse suspended droplets with varying viscosity ratios. The results of his studies confirmed that irrotational (extensional) flows give better mixing as compared to rotational (shear) flows over a wide range of viscosity ratios. Given that it is now well established that extensional flows are way more effective as compared to shear flows when it comes to mixing coupled with the fact that the fact that KBs, which are the industry standard today do not generate enough extensional mixing there was a strong need to find a route to enhance the extensional flows in the twin screw extruder.

While there have been several attempts over the past to achieve this feat in the form of Elongational Flow Mixer (EFM) (Figure 2.2) [4-6], which is an attachment which can be added on to the melt pump in the Single Screw and the Twin Screw Extruder; Elongational Flow Reactor and Mixer (RMX) (Figure 2.2) [7], which is a small scale device used for mixing of materials by forcing the material in the molten form back and forth over the same mixing element by the use of pistons; there was a breakthrough which recently came in the form of the newly developed extensional mixing elements for the twin screw extruder by Carson et. Al at Case Western Reserve University [8,9].

There are three Extensional Mixing Elements which were developed, L2, L4 and S4 (Figure 2.4, Figure 2.5). The numbers 2 and 4 signifies the ratio of contraction to divergence. In the case of S, the length of contraction is half that of L. These EME's were convenient to use and were found to provide good dispersive mixing.

Experimental

Processing Equipment

All the extrusions were carried out on ThermoScientific TSE24MC, which is a 24mm co-rotating twin-screw extruder having L/D ratio of 40:1 (Figure 2.3). This extruder has been constructed to offer 12 ports, throughout the length of the barrel. These ports can be used to measure the pressure or temperature during an extrusion run. Two screw configurations have been used through all the extrusion runs. These screw configurations are exactly the same apart from the mixing elements (Figure 2.6). While one configuration made use of 90° kneading blocks to cover 3.25 L/D. The other configuration covered the same L/D of the mixing section using three different extensional mixing elements, L2, L4 and S4 (Figure 2.7). These identical screw configuration with differences only in the mixing elements, makes it possible to compare the efficiency of the extensional mixing elements with respect to the kneading blocks. Additionally, there was a reverse conveying element which was positioned at the very end of the mixing section for each of the two screw configurations. The purpose of this was to increase the distributive mixing post mixing sections, to ensure that the channels of the mixing elements are full at all times and finally to create enough pressure for sample removal (if required).

The extrusion runs were carried out at a screw rotation speed of 300 RPM. Brabender feeder was used for feeding the raw materials into the extruder. Material extrusion was carried out through a die having a diameter of 3mm. Collection of the polymer melt was done into a Thermofisher water bath and the material was finally pelletized using a Thermofisher pelletizer. Pressure measurements were made during the extrusion runs through two of the 14 ports present. Dynisco MDA422 in connection with Dynisco 1390 instrumentation box was used for the measurement of Pressure. Pyromation JMM-B23U transducers along with Fluke 52 II thermometer was used for measuring the temperature. Temperature and pressure measurements were done through the same ports. Careful attention was paid to the fact that the extrusion process has stabilized before taking pressure, temperature measurements.

Rheological Characterization

All the rheological measurements were carried out on the TA Instruments ARES G2 rotational rheometer. All the measurements were made by using a 25 mm parallel plate geometry. The Small Amplitude Frequency Sweep of the PP/EAA/LCP blends (processed at 285-295 ºC) and the PP/EAA/LCP composites (processed at 220-230 ºC) of varying LCP and EAA content was carried out at a Strain rate of 0.7% and at a temperature of 220 ºC. Temperature Sweep was carried out on the raw materials, Polypropylene and LCP Vectra from temperatures of 280 to 300 ºC. Viscosity ratio was determined in this temperature range.

The material was compression molded into discs of 25 mm in diameter and 1 mm in thickness, using a CAVER press at a temperature of 210 ºC. A pressure of 10 metric tons was applied during the compression molding stage and then released. This cycle was repeated three times and then the discs were cooled using running cold water.

Morphological Analysis

Morphological Analysis on PP/LCP blends and composites was carried out using a JEOL JSM-6510LV SEM using a 30kV beam voltage. Some amount of the extruded strands were collected as such after cooling in the water bath. They were not pelletized, so that the surface of the material is not damaged, when viewed under SEM. Therefore, these extruded strands, were immersed under liquid Nitrogen (supplied by Airgas) and then fractured using hand.

Gold coating, of approximately around 5 nm in thickness, was carried out on the sample using the EMS Quorum Sputter Coater.

Mechanical Characterization

Tensile Testing

The mechanical properties such as Tensile Modulus and Elongation at break, of all the PP/LCP blends and composites were determined using universal testing machine Instron. The test was carried out in accordance with ASTM D638.

The material was compression molded into sheets, using a CAVER press at a temperature of 210 ºC. A pressure of 10 metric tons was applied during the compression molding stage and then released. This cycle was repeated three times and then the sheet was cooled using running cold water. Once the sheet had cooled, dog bone shaped samples were punched out from the sheet. The specifications of the mold were according to ASTM D638. The punched samples were carefully scrutinized to insure that there were no pores and nicks present.

The mechanical testing on the Instron was carried out at Room Temperature pulling the dog bone shaped sample (Figure 2.8) at a constant strain rate of 5mm/min.

Dynamic Mechanical Analysis (DMA)

The samples were cut in a proper rectangle of acceptable range provided by TA instruments. After which the samples edges were polished. The prepared samples were analyzed using a Q800 series DMA which was supplied by TA Instruments. The samples were evaluated over a temperature range of -25 ^{0}C to 70 ^{0}C, with a temperature ramp rate of 3 ^{0}C/min.

Thermal characterization

Thermal properties of PP, LCP and PP/LCP blends & composites, was determined with the help of Thermometric Gravimetric Analysis (TGA) using a Q500 TGA supplied by TA Instruments. The sample was mounted on an Aluminum pan, and air was chosen as the gas under which the test was conducted. A small grain of material was chipped off a pelletized granule and weighed. The weight of the material was ideally kept in between 5 to 10 mg. The material was first allowed to equilibrate at 25 ^{0}C for a couple of minutes, following which the temperature was ramped up to 700 ^{0}C at 10 ^{0}C/min.

Batch mixer Analysis

Torque measurements at different temperatures for PP/LCP blends and composites were taken using the HAAKE Rheomix Lab mixers, which was supplied by ThermoFisher Scientific. A small batch size of about 40 g was put in to the mixer each time. The torque was measured in Nm over a period of 3 minutes. A roller type rotor was used for carrying out the test.

Image Processing

All the image processing was done using Image J. For the measurement of average glass fiber length using different mixing elements post extrusion, long strands were cut and kept in an Aluminum foil inside a furnace at 600 ^{0}C for 2 hours. The remaining glass fibers were put in water and spread across a circular glass tray. As much as possible, good distribution of glass fibers was ensured using naked eye. The glass tray was then taken as such to get images using Olympus microscope.

Results and Discussion:

Differential Scanning Calorimetry (DSC)

DSC on the raw materials PP and LCP was done from 40 ^{0}C to 200 ^{0}C and from 100 ^{0}C to 350 ^{0}C respectively. The results of the test confirm the melting point of the raw materials to be 170 ^{0}C for PP and around 280 ^{0}C for LCP (Figure 2.9).

Compatibilizer Optimization – Based on literature survey, Ethylene Acrylic Acid (EAA) was identified as the compatibilizer to compaibilize the Liquid Crystal Polymer and Polypropylene system. Vectra A 950, supplied by Celanese was used as the Liquid Crystal Polymer, in literature. However due to the non-availability of this grade, 30% (by weight) glass filled version of the same grade was used during this research.

The goal of varying the compatibilizer, was to find the optimum percentage of the compatibilizer to be used in order to get the best mechanical and thermal properties. 12 extrusion runs were carried out at 285-295 ^{0}C, with different amounts of LCP (4%, 8% and 12%) and different amounts of EAA (2%, 5%, 7% and 10%), keeping the same screw configuration (KB) in an effort to evaluate only the effect the varying percentage of compatibilizer is having on the system.

Upon varying the amount of compatibilizer keeping all the other parameters constant, it was found that the mechanical and thermal properties peaked at 5% compatibilizer, and were found to remain almost constant thereafter (Figure 2.11-2.13). Similar trends were observed for 4%, 8% and 12% of LCP.

Based on mechanical and thermal trends (Figure 2.31-2.34), 5% Ethylene Acrylic Acid was chosen as the amount of compatibilizer for all the future experiments.

Batchmixer results:

In order to evaluate if the torque is within safe range for the PP/LCP system to be run at 220 C and 280 C on the Twin Screw Extruder, the PP/LCP samples were first run on the Rheomix. The PP/LCP system was run on the Rheomix at three different temperatures. One was 280 ^{0}C, which was the temperature at which the PP/LCP blends were intended to be processed, second was 250 ^{0}C, to see if keeping the LCP in the solid phase will not generate too high a torque and the third was at 220 ^{0}C, which was the temperature at which the composites were intended to be processed on the 24 mm co-rotating twin screw extruder.

Upon seeing not too great of an increase in the torque on reducing the temperature from 280 ^{0}C to 250 ^{0}C, the temperature was further reduced to 220 ^{0}C. On finding the torque to be only slightly higher than 250 ^{0}C & 280 ^{0}C, and that also for a very short time, 220 ^{0}C was deemed as a safe temperature for processing PP/LCP composites on the 24 mm co-rotating twin screw extruder (Figure 2.10). The general processing temperature of Polypropylene being 220 ^{0}C coupled with the torque being within acceptable range led to this temperature being chosen as the temperature to process PP/LCP composites.

The temperature of processing PP/LCP blends was ultimately chosen to be 285 ^{0}C to 295 ^{0}C as that is the temperature range in which the LCP begins to melt. The temperature of processing is kept at just the temperature at which LCP begins to melt, as going on increasing the temperature would ultimately lead to the degradation of the PP matrix.

Image Processing Results

Image Processing done using Image J on SEM images of pure LCP Vectra Samples, helped in determining the average length of the glass fibers after extrusion. The volume of the glass fibers in the system were known to be 30% by weight. The length of the glass fibers was found to be similar after extrusion.

Comparison Kneading Blocks and Extensional Mixing Elements

For comparing of kneading blocks to extensional mixing elements, extrusion was carried out at two different temperatures, 285-295 ^{0}C and 220-230 ^{0}C.

PP/LCP Blends:

Processing at temperatures of 285-295 ^{0}C leads to the melting of the Liquid Crystal Polymer. The melting temperature of PP and LCP is determined using Differential Scanning Calorimetry (DSC) and Rheology. All in all blends were prepared for different LCP contents (4%, 8% and 12 %) and different compatibilizer contents (2%, 5%, 7% and 10%). However, the optimum concentration of the compatibilizer was identified to be 5%. Therefore, PP/LCP blend of 8% LCP (chosen at random) and 5% EAA were used for the purpose of comparing the Kneading Blocks to the Extensional Mixing Elements for PP/LCP blends.

1) The summary of the mechanical results shows that Kneading Blocks give the highest Tensile Modulus as compared to all the Extensional Mixing Elements (L2, L4, S4) (Figure 2.25).
2) Dynamic Mechanic Analysis (DMA) of the blends shows the same trend (Figure 2.28).
3) Frequency sweep on the blends reveals that the viscosity is the highest for Kneading Blocks and decreases for the Extensional Mixing Elements (Figure 2.14).
4) SEM images of the samples shows the formation of fibers in the case of Kneading Blocks. On the other hand, the Extensional Mixing Elements result in the formation of a very little amount of short fibers (if any) and mostly droplets (Figure 2.30).

5) Image Analysis using Image J reveals that that the average glass fiber length in all the different mixing elements are similar (Figure 2.35, 2.37, 2.38, Table 2.5).

All these results put together make perfect sense. The fact that Kneading Blocks lead to fiber formation, explains why the mechanical properties are higher than that of Extensional Mixing Elements. The reason is that the LCP fibers, which get oriented in the machine direction, give rise to better mechanical properties in the extrusion direction. Frequency sweep gives a higher viscosity for Kneading Blocks than the Extensional Mixing Elements due to the fact that fibers offer greater hindrance to flow as compared to droplets. DMA, which is often considered to be more accurate than Tensile testing using Instron, also shows higher modulus in the case of Kneading Blocks thereby confirming the fact that fiber formation in KB's is responsible for giving better properties than EME's. Moreover, the fact that the average length of glass fibers is found to be similar in all the different mixing elements, goes on to prove that morphology is the reason for the difference in mechanical properties in Kneading Blocks as compared to the other extensional mixing elements. To further provide concrete proof to this theory extrusion of PP/LCP was done, keeping LPC in the solid phase. If the above reasoning is sound, in this case, the mechanical properties of KB should not be higher than the EME's.

PP/LCP Composites:

Polypropylene is generally processed at 220 ^{0}C. Hence after conducting the torque analysis on the system using a Rheomix, 220 ^{0}C was chosen as the temperature to process PP/LCP composites. All in all blends were prepared for different LCP contents (4%, 8% and 12 %) and different compatibilizer contents (2%, 5%, 7% and 10%). However, the optimum concentration of the compatibilizer was identified to be 5%. Therefore, PP/LCP blend of 8% LCP (chosen at random) and 5% EAA were used for the purpose of comparing the Kneading Blocks to the Extensional Mixing Elements for PP/LCP composites.

1) The summary of the Dynamic Mechanic Analysis (DMA) results shows that Kneading Blocks give the lowest Tensile Modulus as compared to all the Extensional Mixing Elements (L2, L4, S4) (Figures 2.26, 2.27).
2) Frequency sweep on the blends reveals that the viscosity is the lowest for Kneading Blocks and increases for the Extensional Mixing Elements (Figure 2.15).
3) Image Analysis using Image J reveals that that the average glass fiber length in all the different mixing elements are similar (Figure 2.36, 2.39, 2.40, Table 2.6).

Putting together all the results proves the theory that superior Mechanical properties in the case PP/LCP blends was a result of fiber formation and the fact that the fibers were oriented, giving the blend higher strength. Moreover, the fact that the average length of glass fibers is found to be similar in all the different mixing elements, goes on to prove that morphology is the reason for the difference in mechanical properties in Kneading Blocks as compared to the other extensional mixing elements. Therefore, the plausible reason for the trends to reverse in the case of PP/LCP composites could be the result of two things. Firstly, that the EME's breaks the LCP into smaller domains and secondly, the EME's offers better dispersive and dissipative mixing as compared to KB's. However, this is a theory which needs to be backed with more data. Hence in order for proving the theory right, image analysis using Image J should be done in order to quantitatively prove everything.

Viscosity Ratio

Results of the Temperature Sweep on raw materials PP and LCP in the 285 ^{0}C to 295 ^{0}C temperature range, gave the viscosity ratio of the system. Viscosity ratio is defined as the ratio of the dispersed phase to the ratio of the continuous phase. For the current system LCP is the dispersed phase while PP is the continuous phase. For the given system, in the corresponding temperature range the viscosity ratio is found to be greater than 10. Looking in the Grace plot for the given viscosity ratio, shows that it is impossible to break up droplets by shear forces. On the other hand, droplet break up is very easily possible with the help of extensional forces. Given the fact that Kneading blocks exert shear forces whereas Extensional Mixing Elements exert extensional forces it is not difficult to expect that in the given processing conditions the former will form fibers while the later will not. The results are confirmed (as mentioned above) with the help of SEM.

Conclusions:

This work involved extruding the mixture of Polypropylene, Liquid Crystal Polymer and a compatibilizer (EAA) on a co-rotating twin screw extruder at two different temperatures, 285-295 ^{0}C and 220-230 ^{0}C. Two different temperatures were chosen in such a manner that the LCP was kept solid in one case, while molten in another. Torque analysis was carefully carried out on a Rheomixer before extruding the system on the extruder, to ensure that the system does not over torque the instrument. Compatibiliser content was varied from 2% to 10%, and the optimum level, based on mechanical and thermal properties was found to be 5%. All the further extrusion runs were carried out at 5% compatibilizer content, with different percentages of LCP’s in them. Same screw configuration with different mixing elements was used in order to compare the industry standard Kneading Blocks with the novel Extensional Mixing Elements. Mechanical and Rheological analysis revealed that the Kneading Blocks give better results in the case of PP/LCP blends processed at 285 ^{0}C to 295 ^{0}C, whereas Extensional Mixing Elements give better results in the case of PP/LCP composites processed at 220 ^{0}C to 230 ^{0}C. On carrying out morphological analysis on these samples, it came to light that the reason KB was giving better properties than the EME's in the case of PP/LCP blends was due to the fact that the morphology of the LCP fibers in the samples processed using KB were long elongated fibrils, while in the case of the blends processed using the EME's the morphology was found to be mainly droplets. The results were in perfect accordance to the Grace Plot, which says that beyond a particular viscosity ratio (i.e. the ratio of the viscosity of the dispersed phase to that of the continuous phase) it is impossible to break a droplet using shear flows. Given that Kneading Blocks exert shear forces, the droplets extend to form long fibrils but fail to break. On the other hand, according to the Grace Plot only a small amount of shear is required to break the droplets, across all viscosity ratios. As it is already well known that the EME's tend to exert extensional forces more than shear forces, EME's succeed in breaking the droplets into small fractions, thereby leading to the formation of the droplet morphology.

On the contrary in the case of PP/LCP composites, the trends are seen to reverse and now EME's are found to give better properties as compared to KB. A plausible explanation for the same is that the EME's break the particles into smaller domains and tends to offer better dispersive and dissipative mixing. However a more quantitative study needs to be performed in the future to prove the above hypothesis. The average length of glass fibers in the both blends and composites were found to be similar for all the different mixing elements post extrusion, confirming the fact that morphology is the reason for difference in mechanical properties.

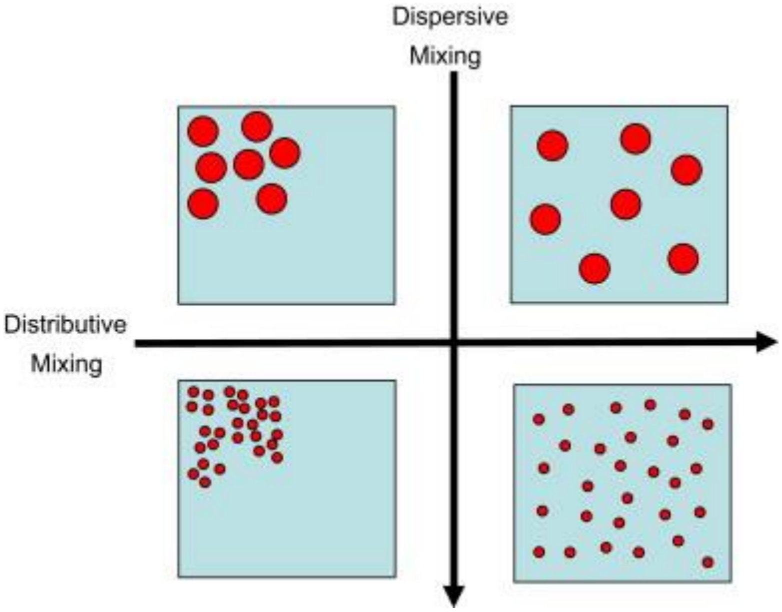


Figure 2.1 – Dispersive and Distributive Mixing

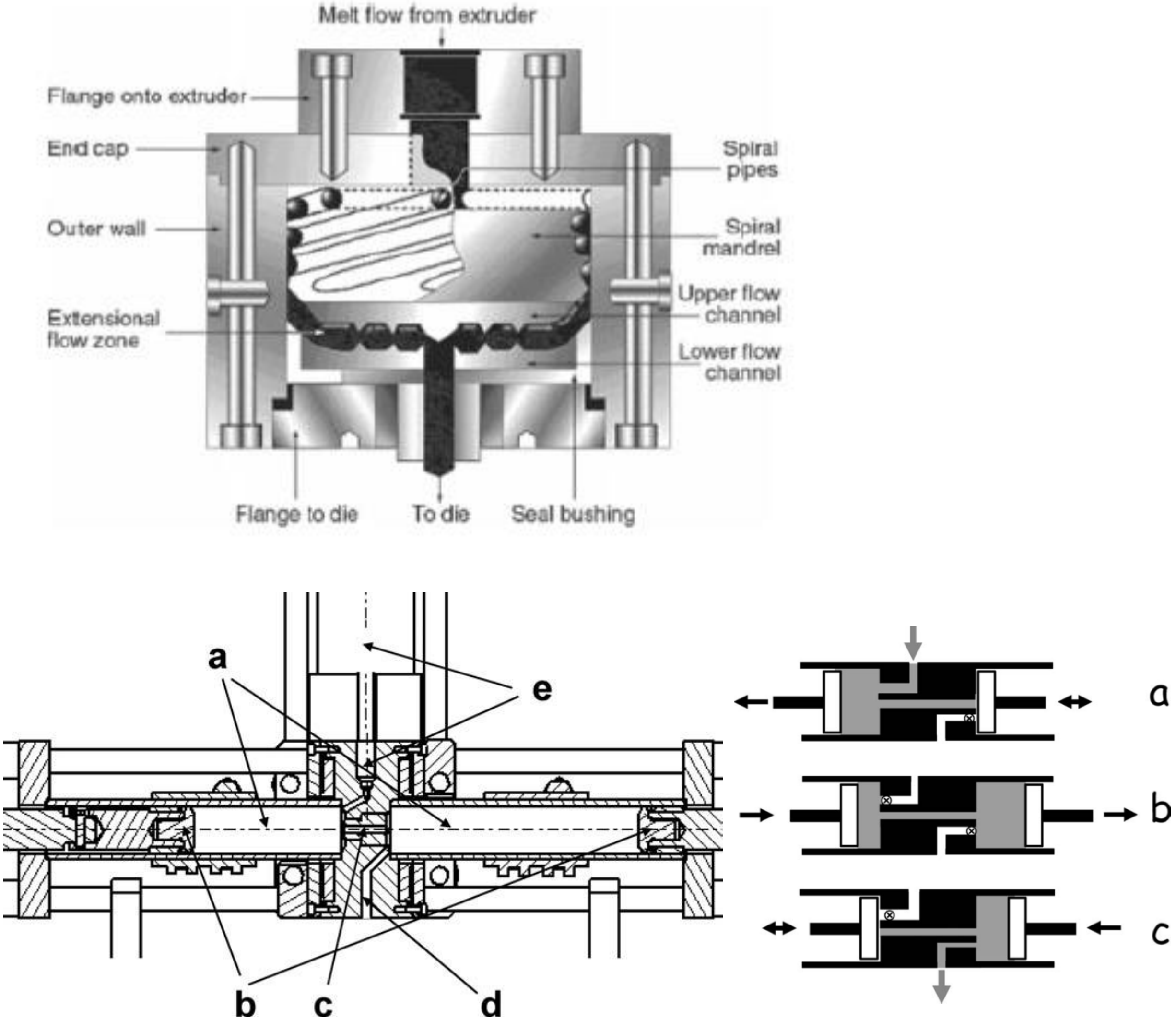


Figure 2.2 – Top – Extensional Flow mixer (EFM). Bottom – Elongational Flow Reactor and Mixer (RMX)

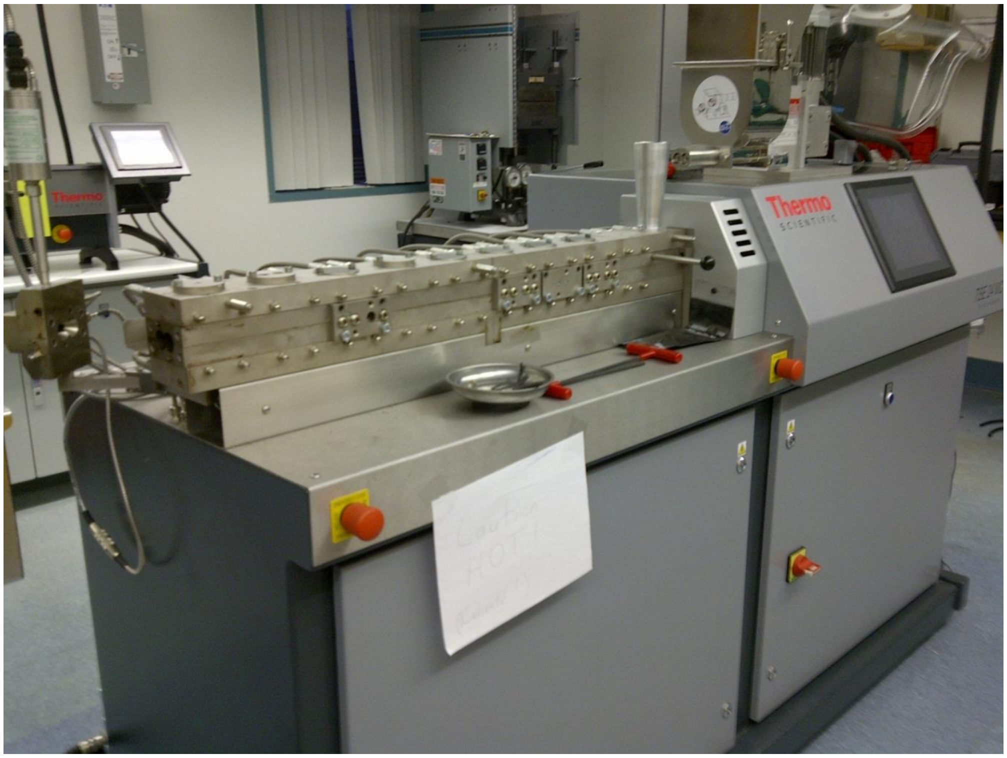


Figure 2.3 – Co-rotating twin screw extruder on which all the extrusions were carried out.

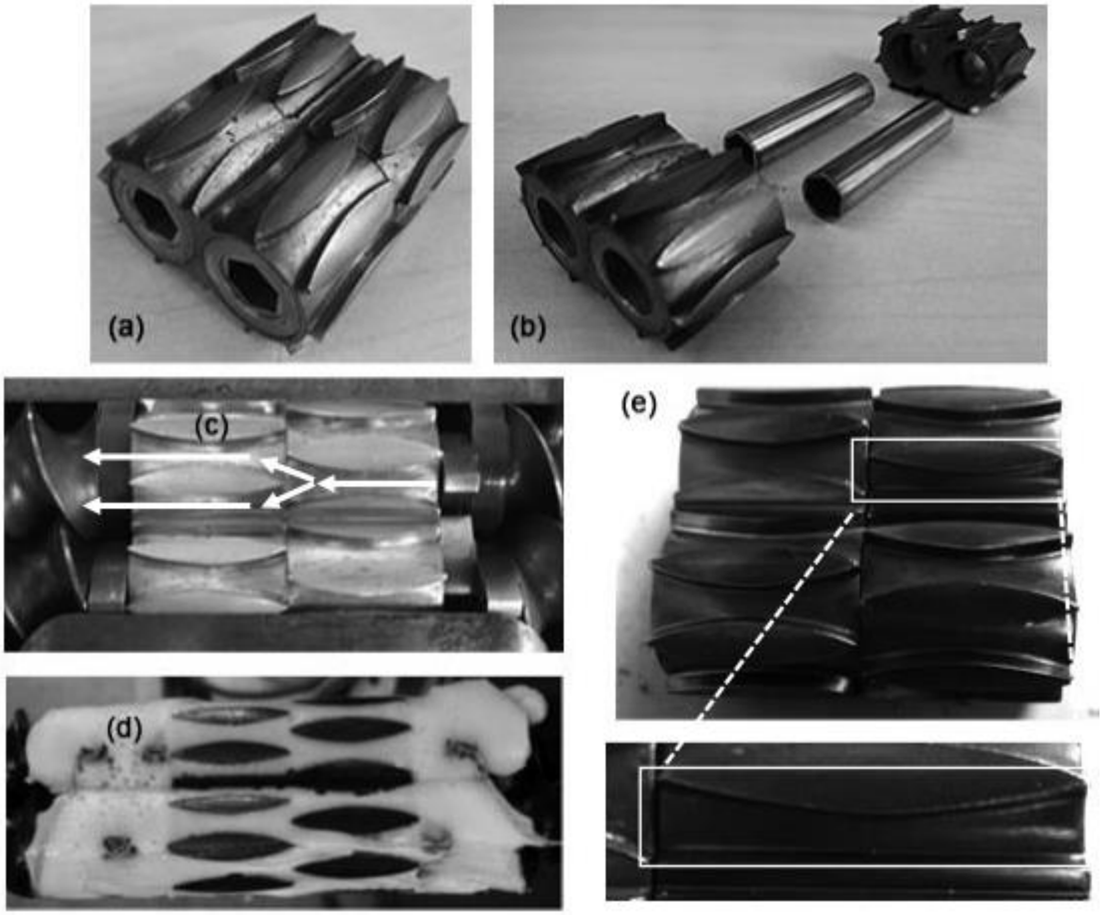


Figure 2.4 – (a) Extensional Mixing element (L2). (b) L2 along with the internal shaft to show construction. (c) L2 assembled in the TSE. (d) Elements filled with material. (e) Magnified view of the contraction-expansion channel in L2.

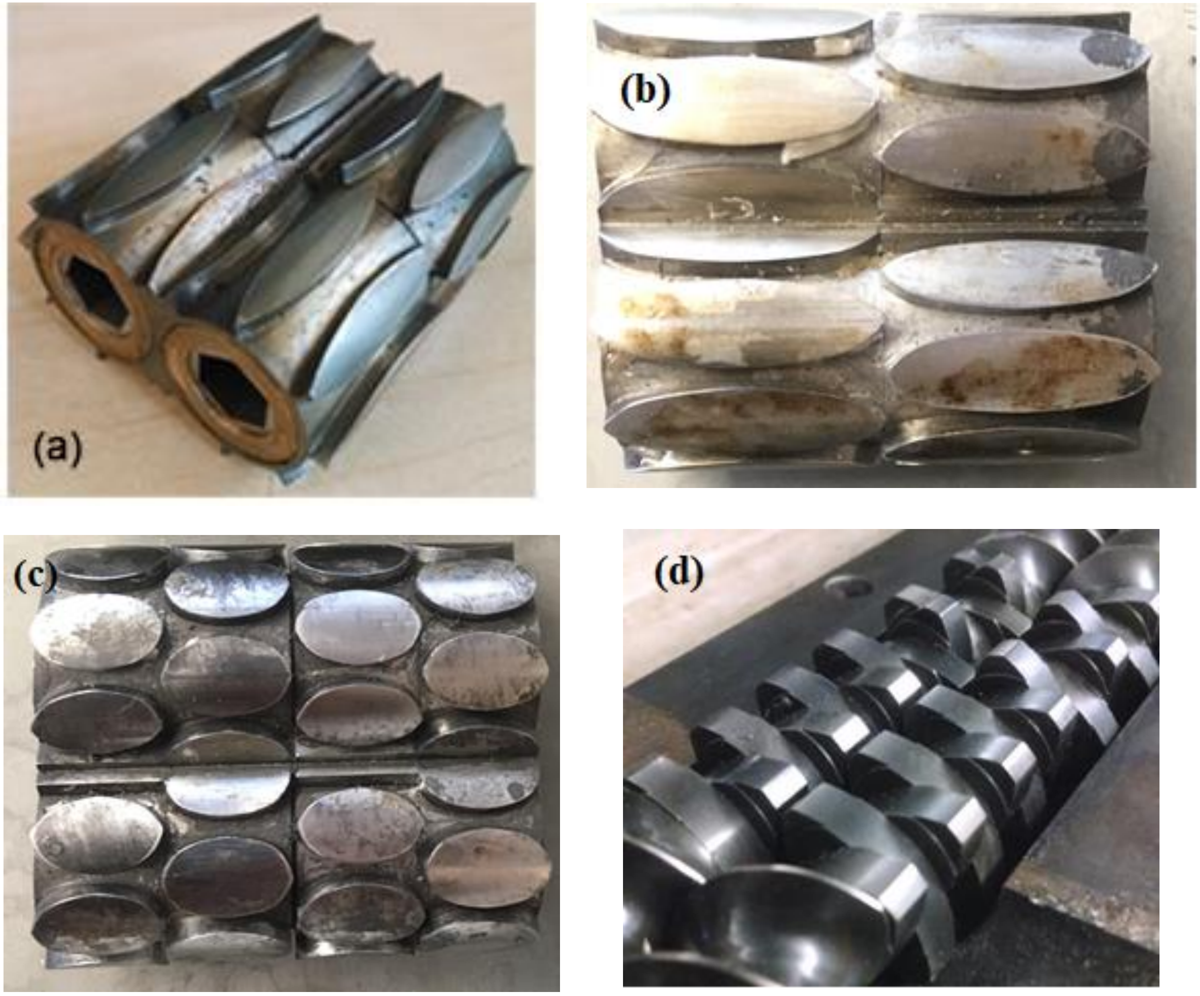


Figure 2.5 – Differenent mixing elements. (a) Extensional Mixing Element (L2). (b) Extensional Mixing Element (L4). (c) Extensional Mixing Element (S4). (d) Kneading Blocks (KB)

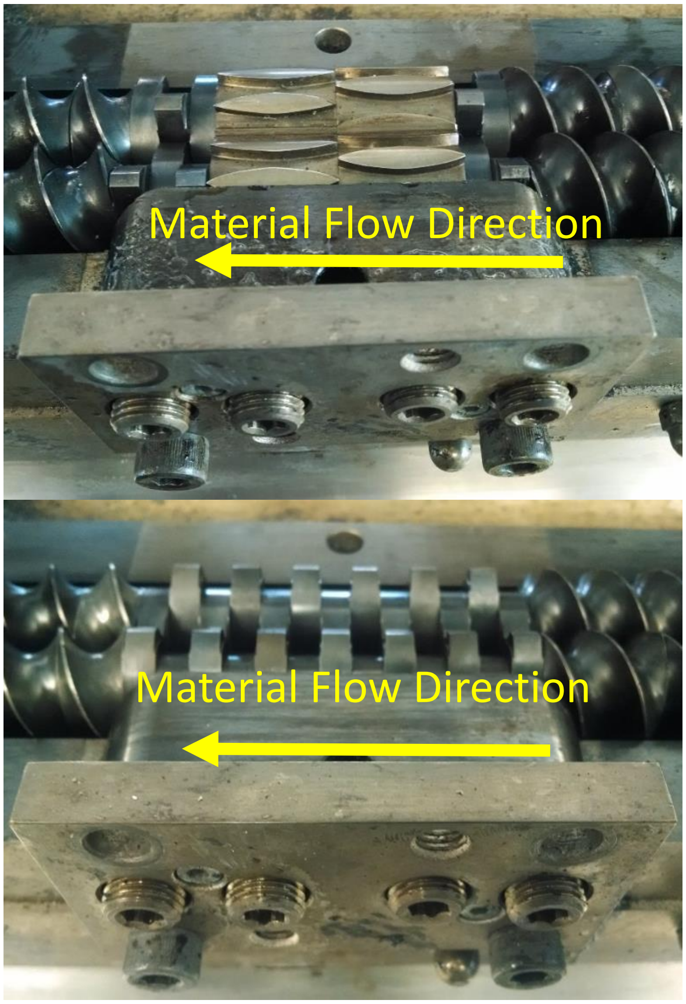


Figure 2.6 – Mixing section in the twin screw extruder. Top – Screw Configuration with the extensional mixing elements (L2). Bottom – Screw Configuration with Kneading Blocks.

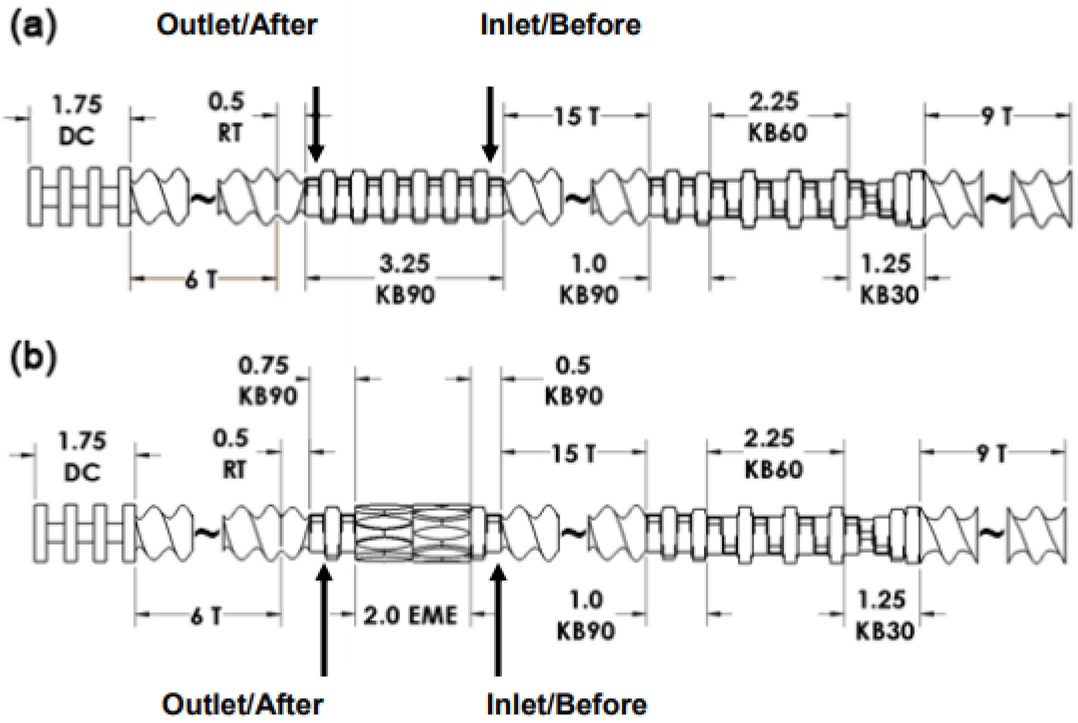


Figure 2.7 - Screw Configurations used for the extrusion of PP/LCP blends and composites. (a). Screw configuration with Kneading blocks. (b). Screw Configuration with Extensional Mixing Elements (L2, L4, S4).

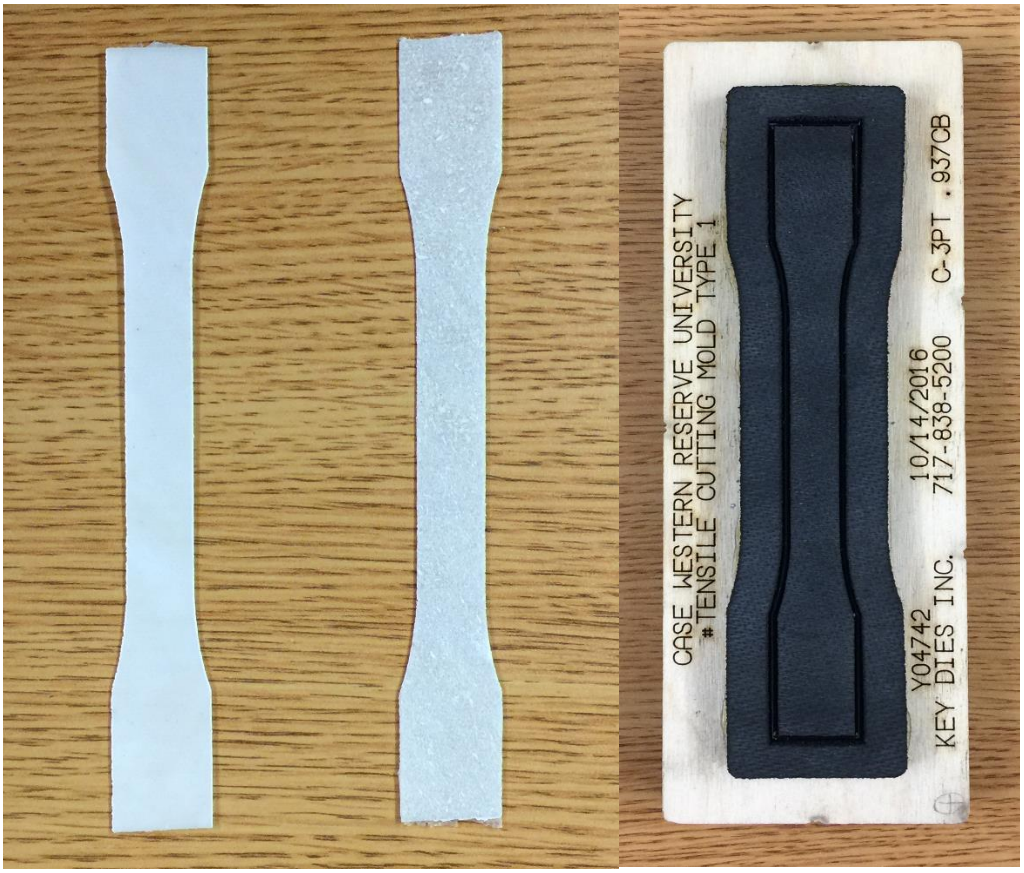


Figure 2.8 – Left – The sample on the left is PP/LCP blend while the sample on the right is PP/LCP composite. Right – The mold from while the samples were cut.

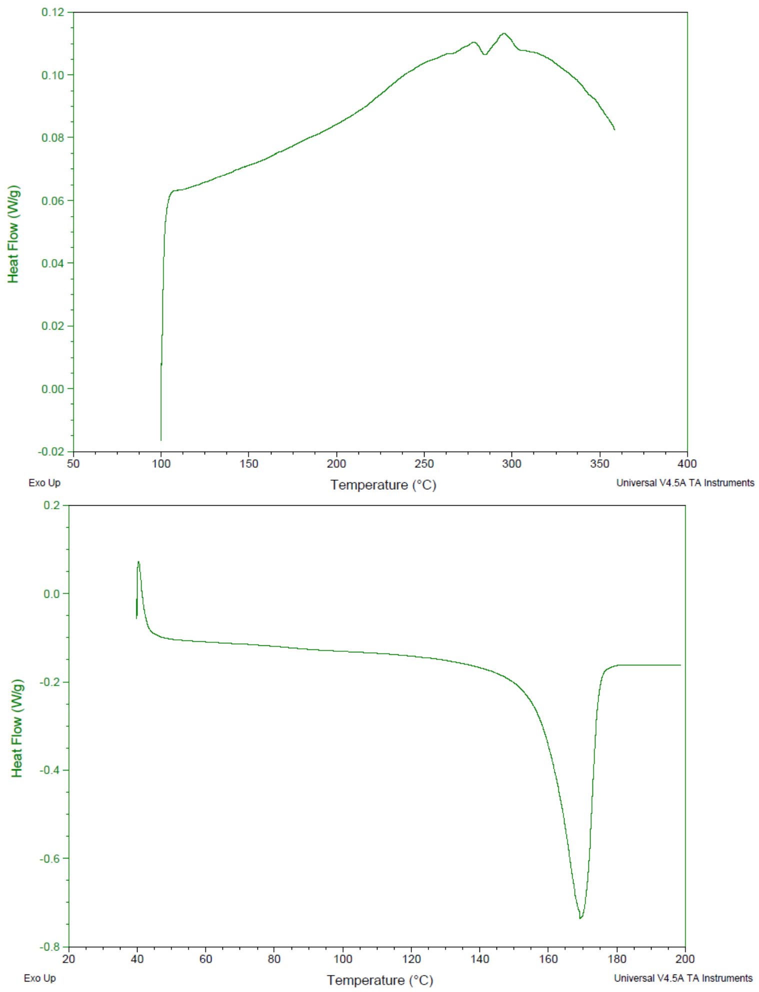


Figure 2.9 – The DSC curves of the raw materials PP and LCP give the melting points to be around 170 ^{0}C and 280 ^{0}C respectively.

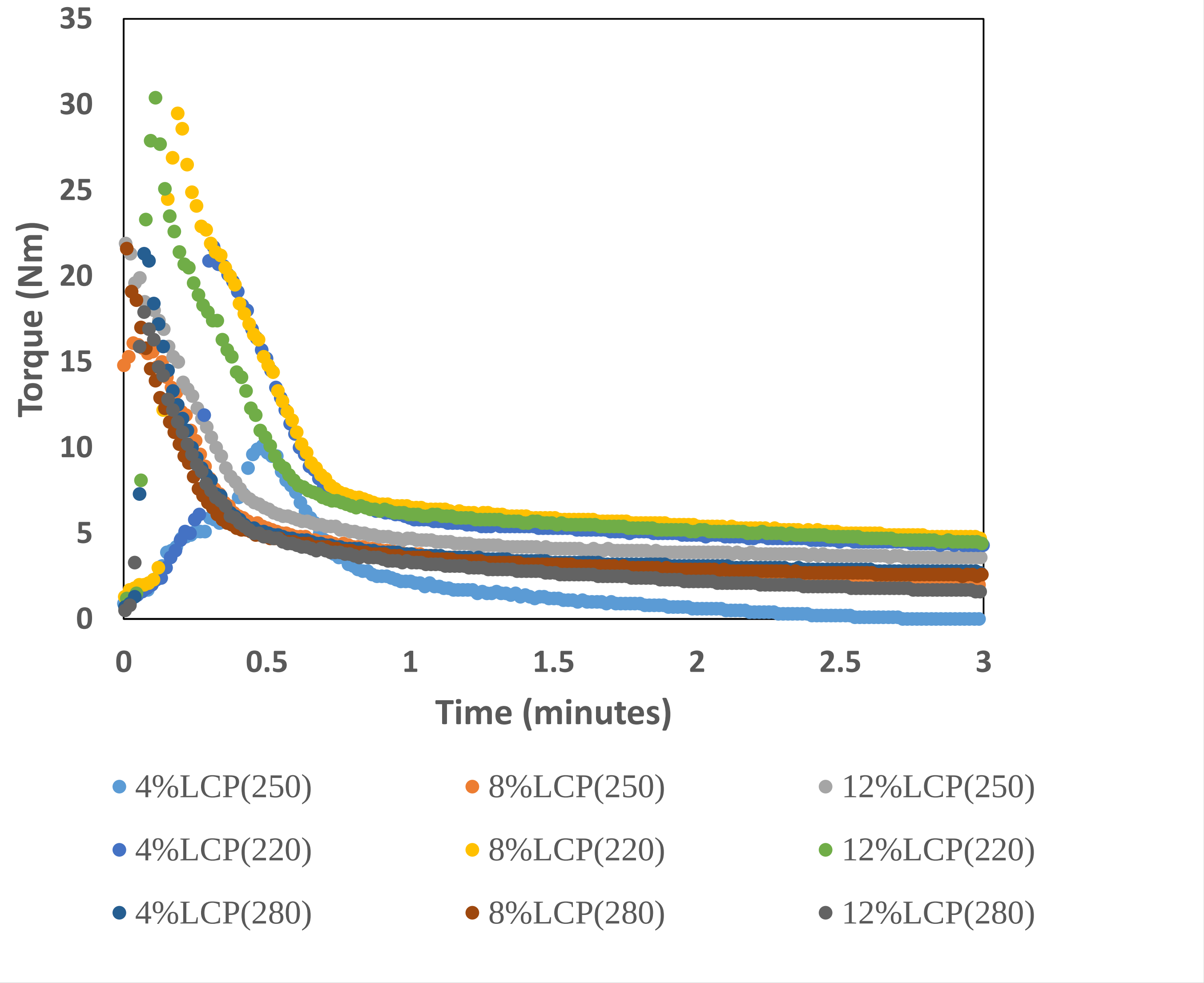


Figure 2.10 – Batch mixer results for PP/LCP blends and composites having same amount of EAA (5%) but different amounts of LCP (indicated in the legend by the number to the left of LCP). The batch mixer was run at different temperatures (indicated in the legend, by the number in the bracket).

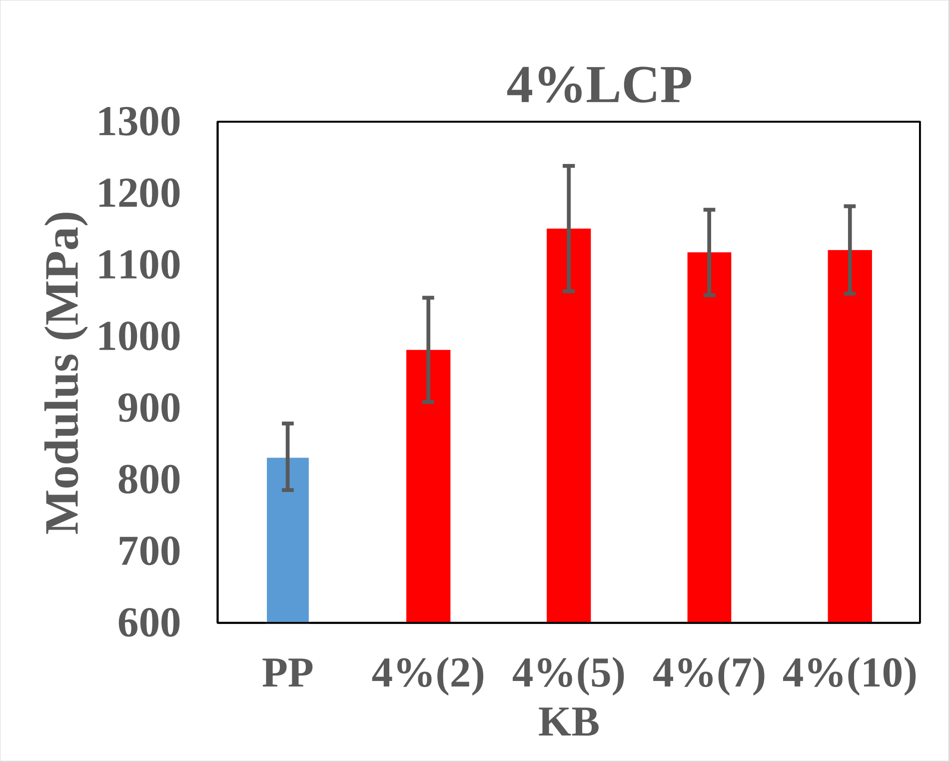


Figure 2.11 Mechanical properties of PP/LCP blends with the same amount of LCP (4%) but varying amounts of compatibilizer. The number in the bracket reflects the amount (in %) of compatibilizer (EAA), while the number outside the bracket is the amount (in %) of LCP. These blends were processed at 285-295 ^{0}C, using the kneading blocks (KB) screw configuration.

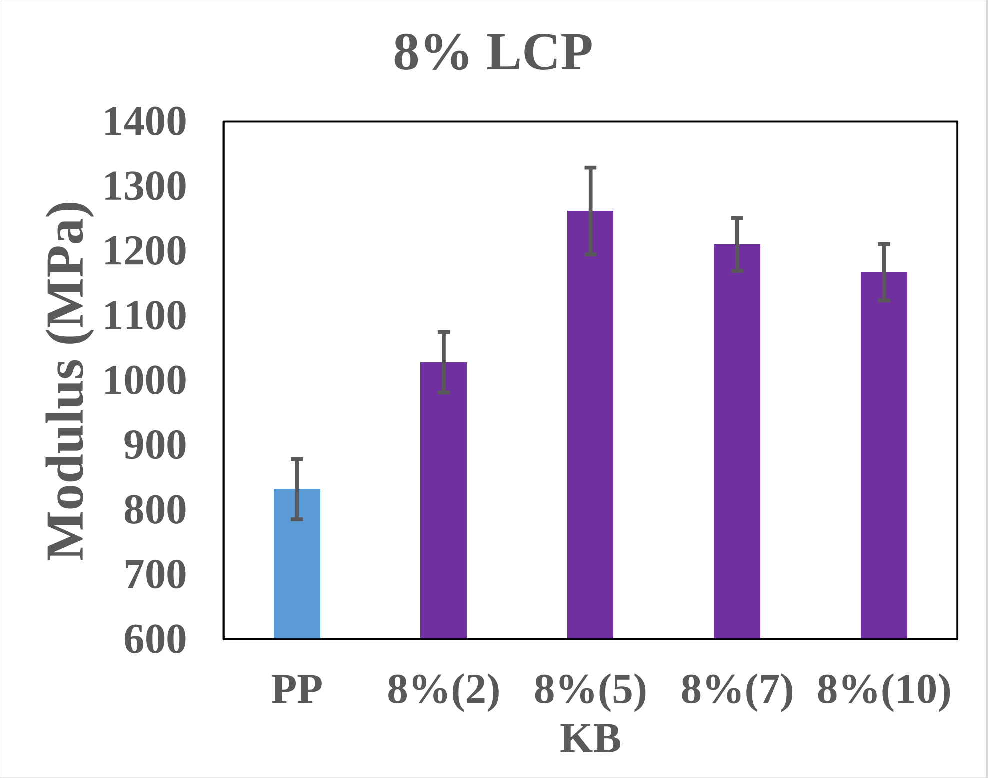


Figure 2.12 - Mechanical properties of PP/LCP blends with the same amount of LCP (8%) but varying amounts of compatibilizer. The number in the bracket reflects the amount (in %) of compatibilizer (EAA), while the number outside the bracket is the amount (in %) of LCP. These blends were processed at 285-295 ^{0}C, using the kneading blocks (KB) screw configuration.

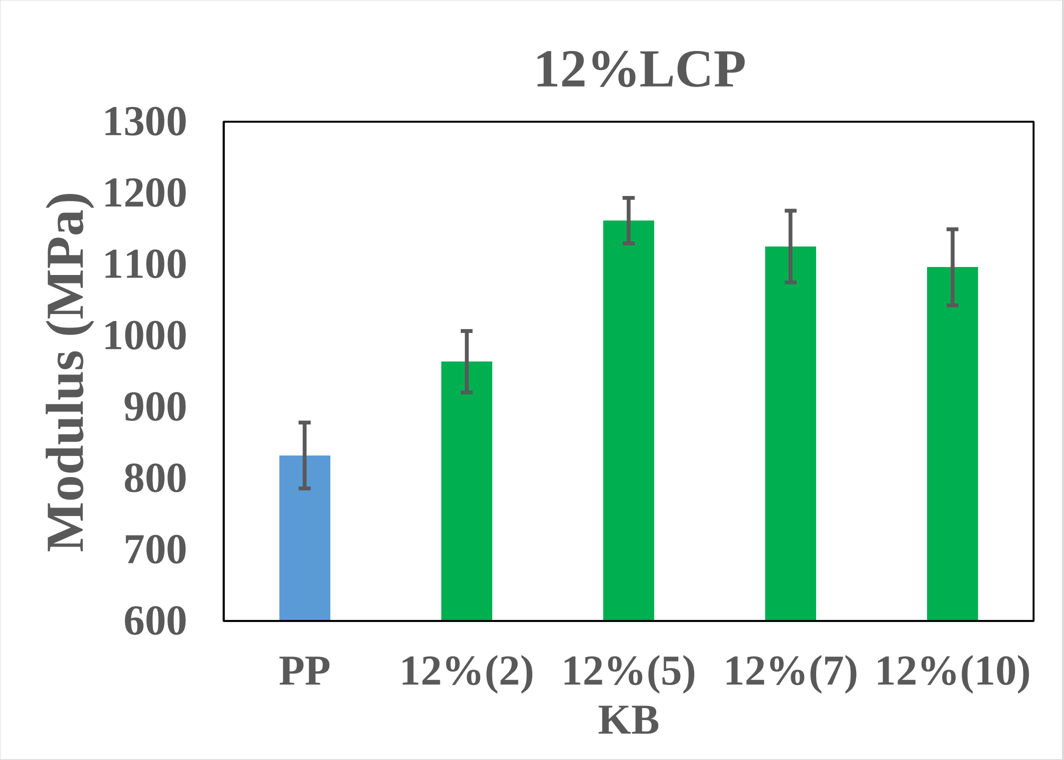


Figure 2.13 - Mechanical properties of PP/LCP blends with the same amount of LCP (12%) but varying amounts of compatibilizer. The number in the bracket reflects the amount (in %) of compatibilizer (EAA), while the number outside the bracket is the amount (in %) of LCP. These blends were processed at 285-295 ^{0}C, using the kneading blocks (KB) screw configuration.

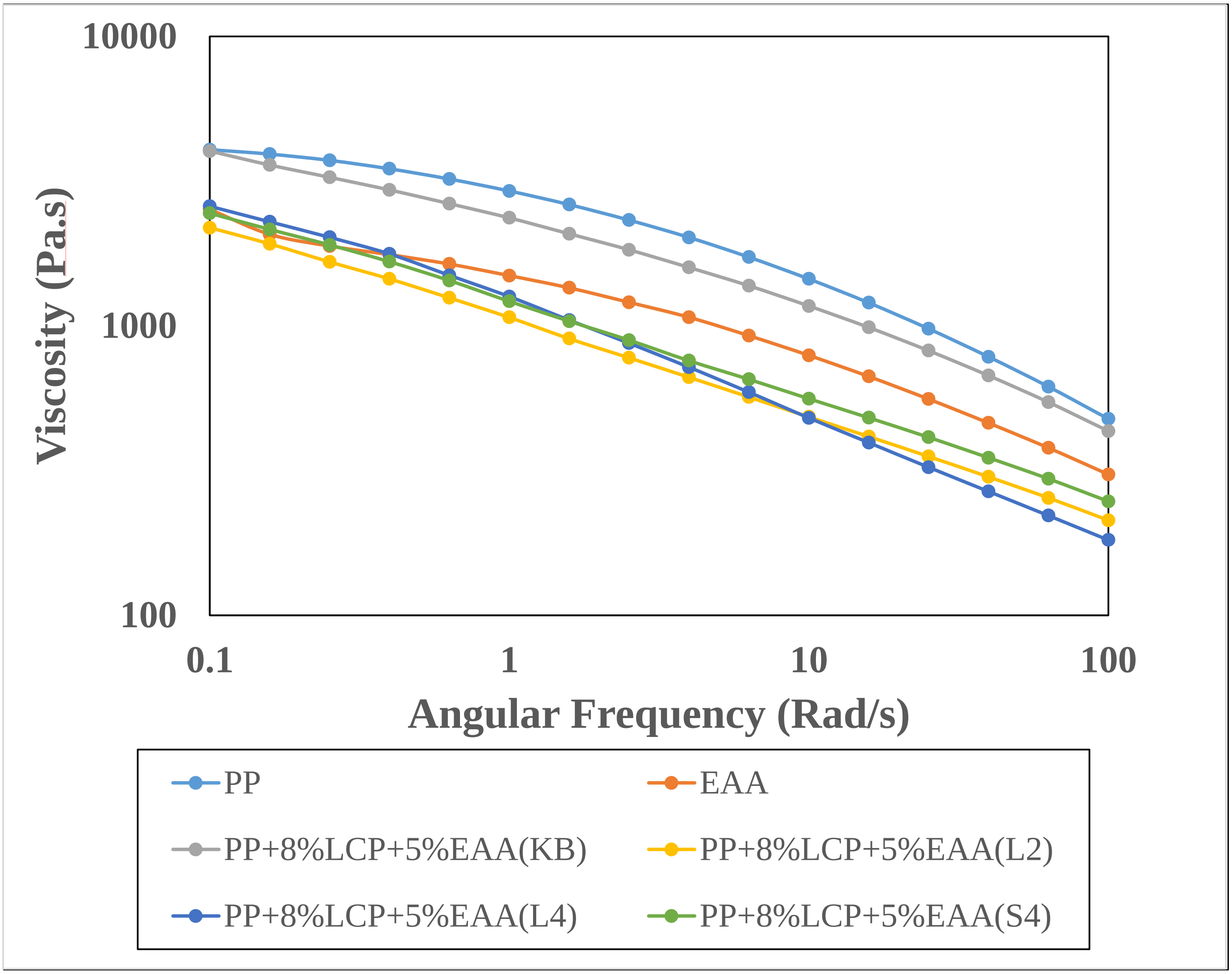


Figure 2.14 - Frequency Sweep of PP, EAA and the PP/LCP blends having the same composition (i.e. the same amount of PP, LCP and EAA in each sample). PP/LCP blends have been extruded using different screw configurations, which have been indicated in the brackets.

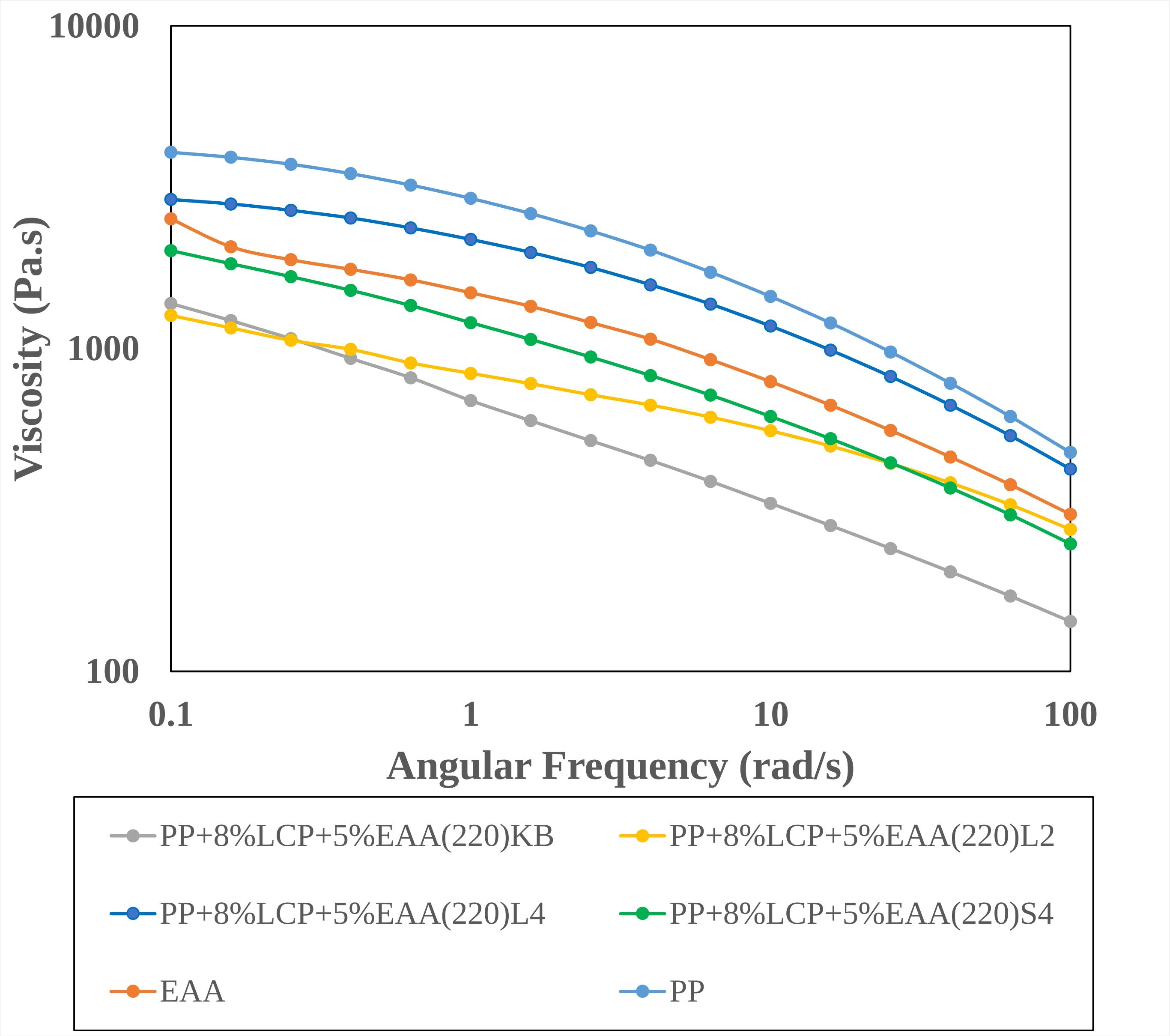


Figure 2.15 - Frequency Sweep of PP, EAA and the PP/LCP composites having the same composition (i.e. the same amount of PP, LCP and EAA in each sample). PP/LCP composites have been extruded using different screw configurations at 220 ^{0}C.

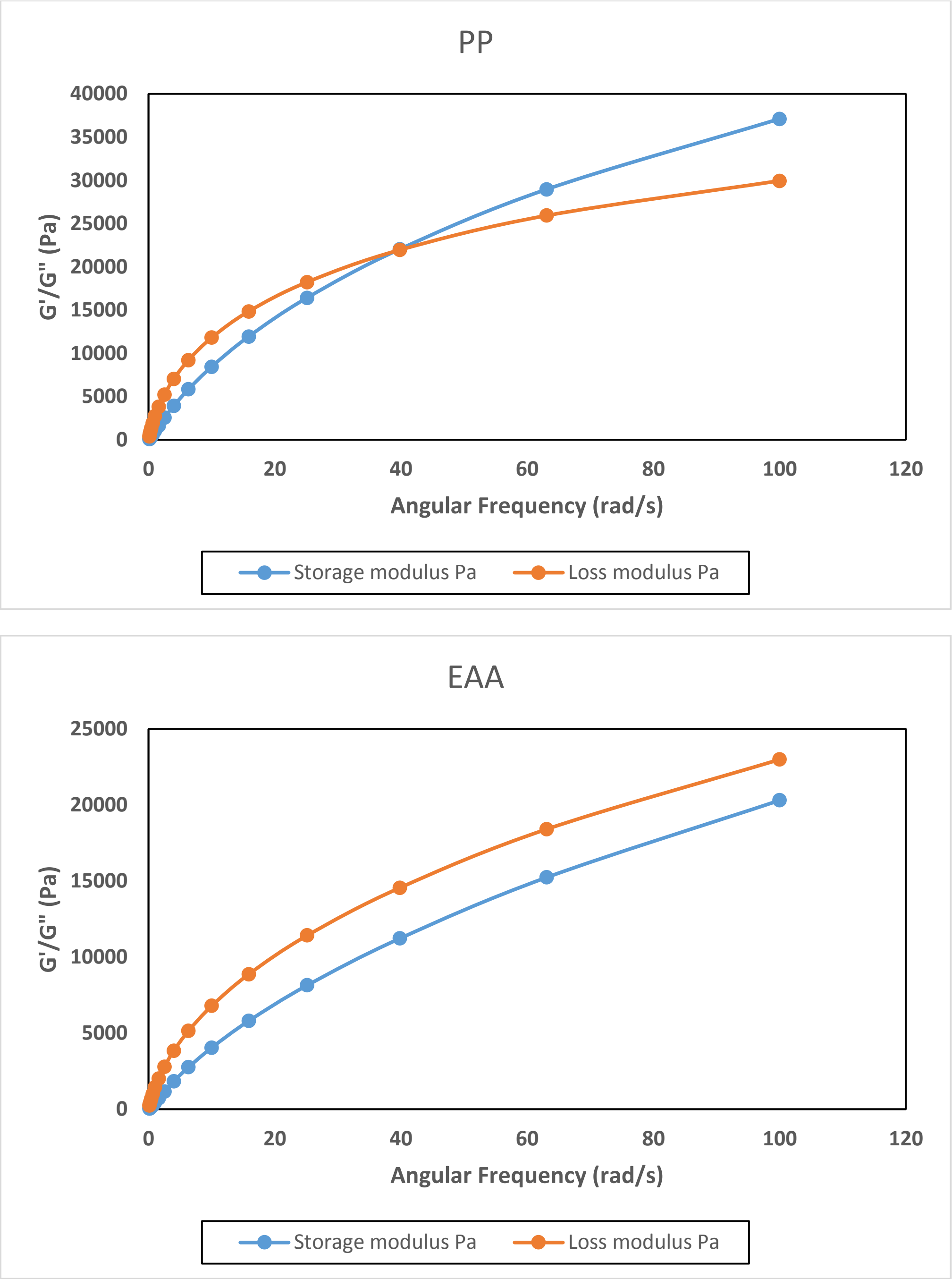
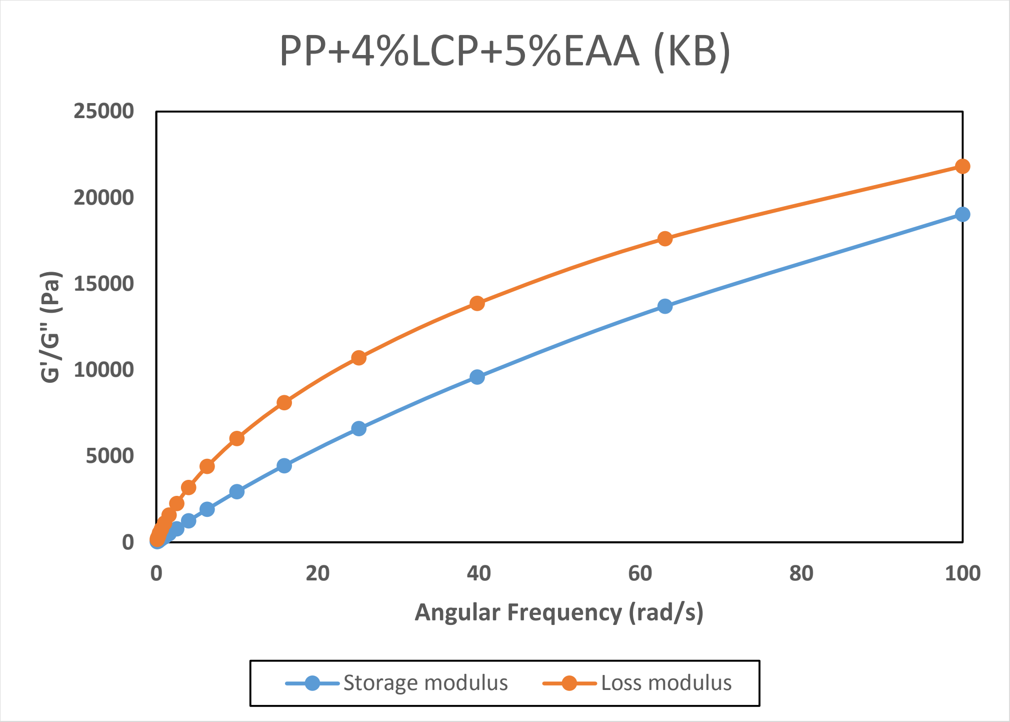


Figure 2.16 – Storage/Loss modulus of raw materials PP and EAA.



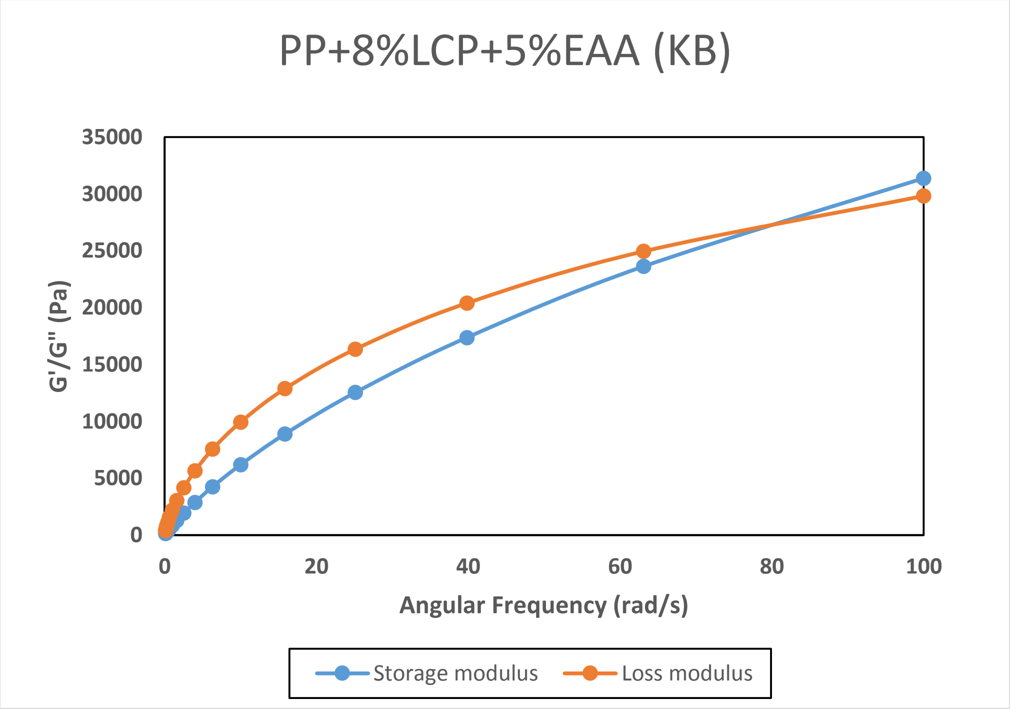


Figure 2.17 – Storage/Loss modulus of PP/LCP systems processed at 285 to 295 ^{0}C using same screw configuration.

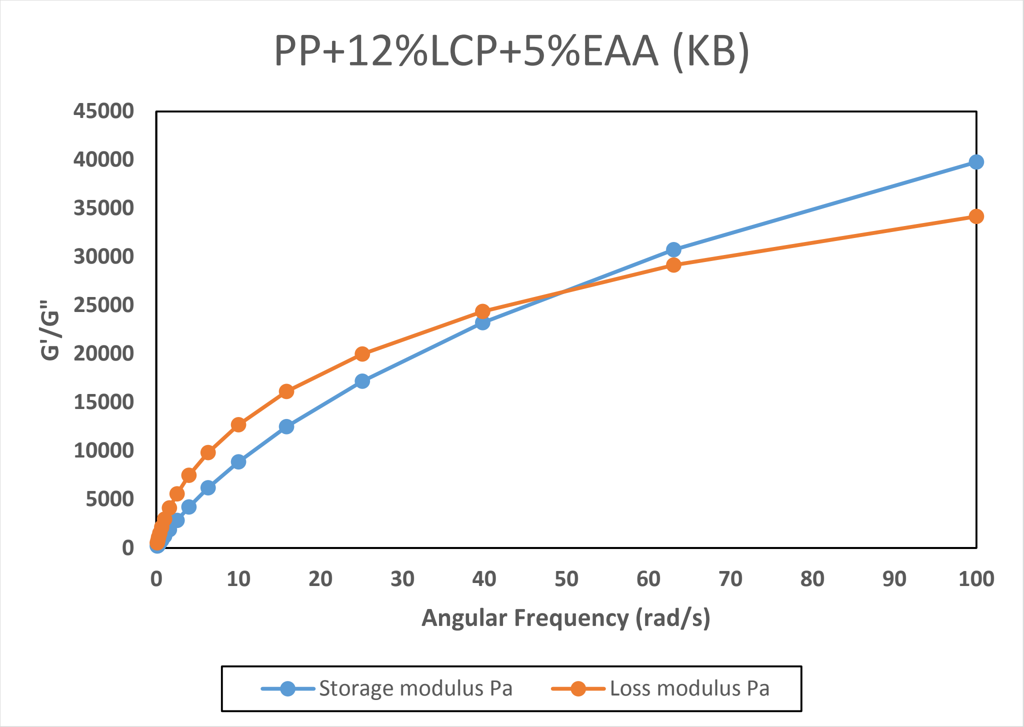
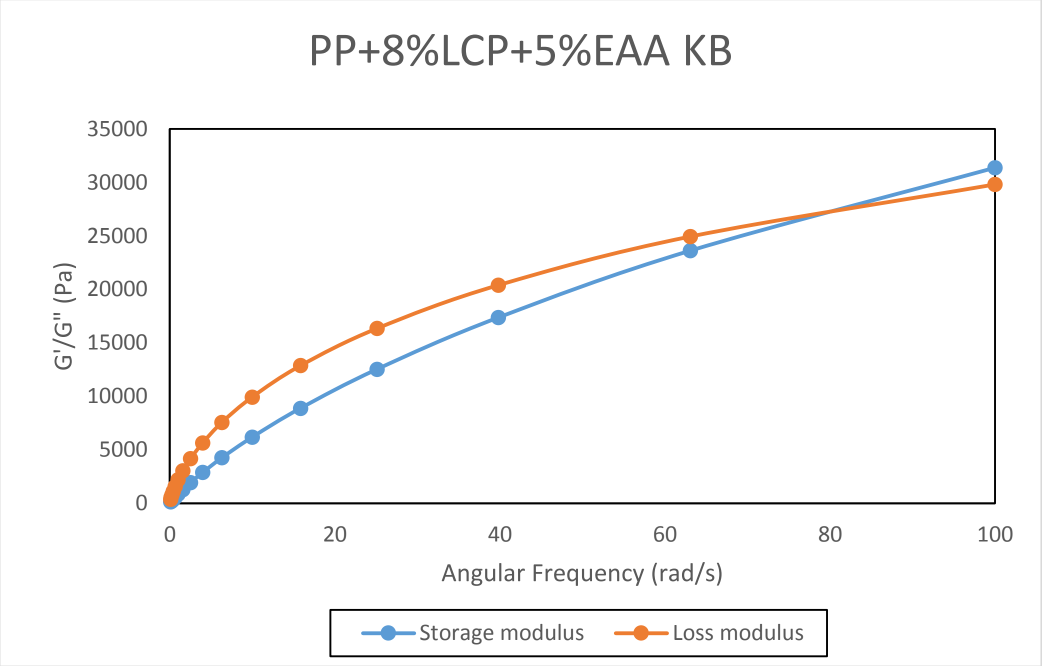


Figure 2.18 – Storage/Loss modulus of PP/LCP system processed at 285 to 295 ^{0}C using same screw configuration.



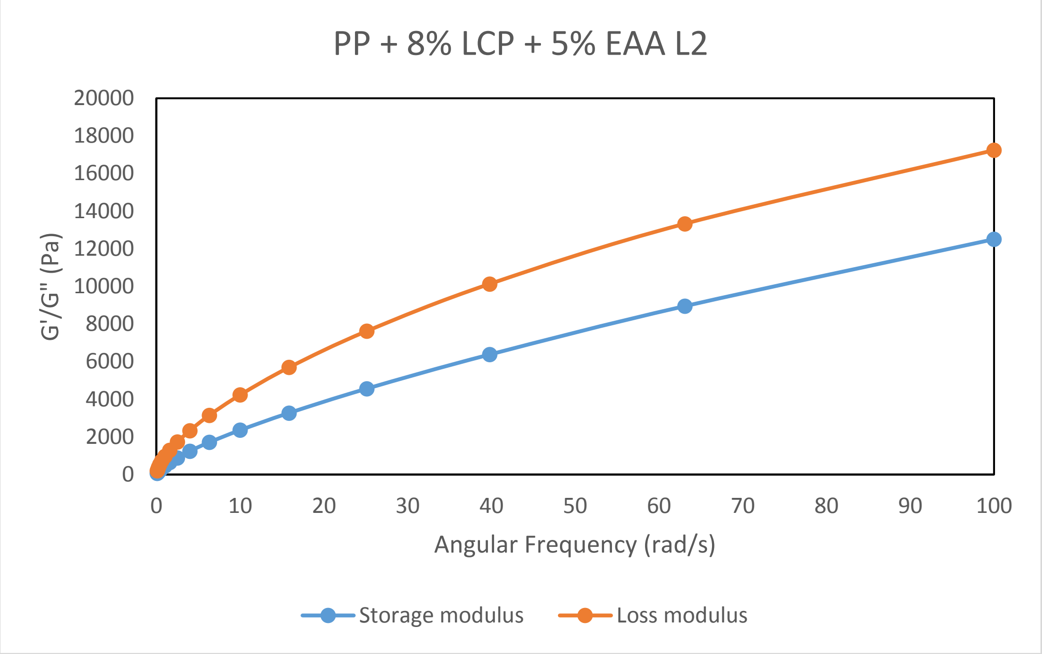
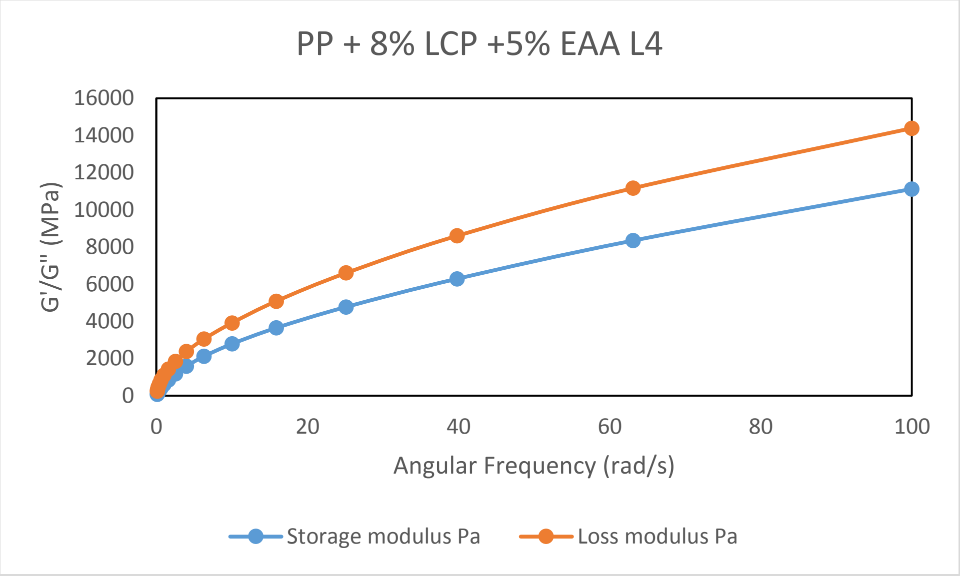


Figure 2.19 – Storage/Loss modulus of PP/LCP systems processed at 285 to 295 ^{0}C using different screw configurations.



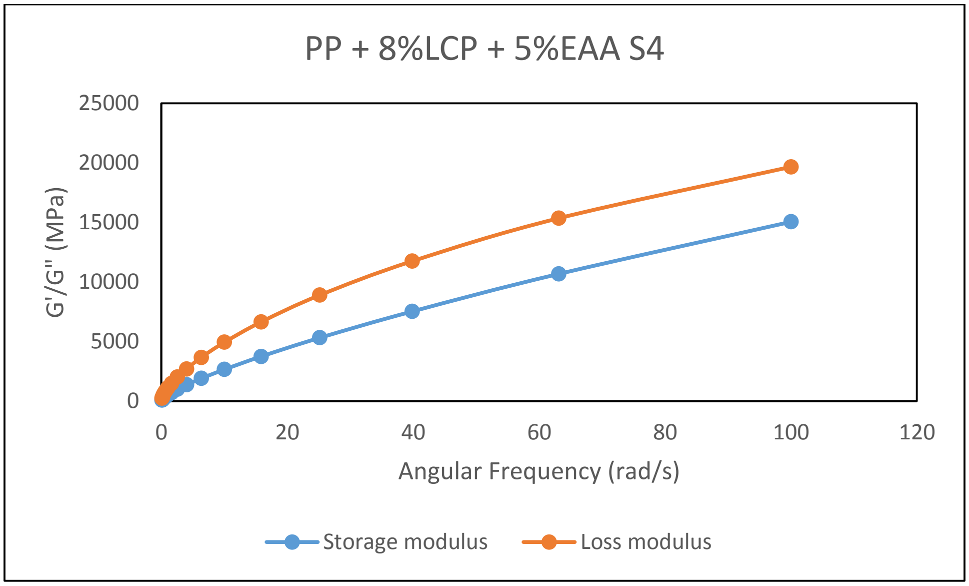


Figure 2.20 – Storage/Loss modulus of PP/LCP systems processed at 285 to 295 ^{0}C using different screw configurations.

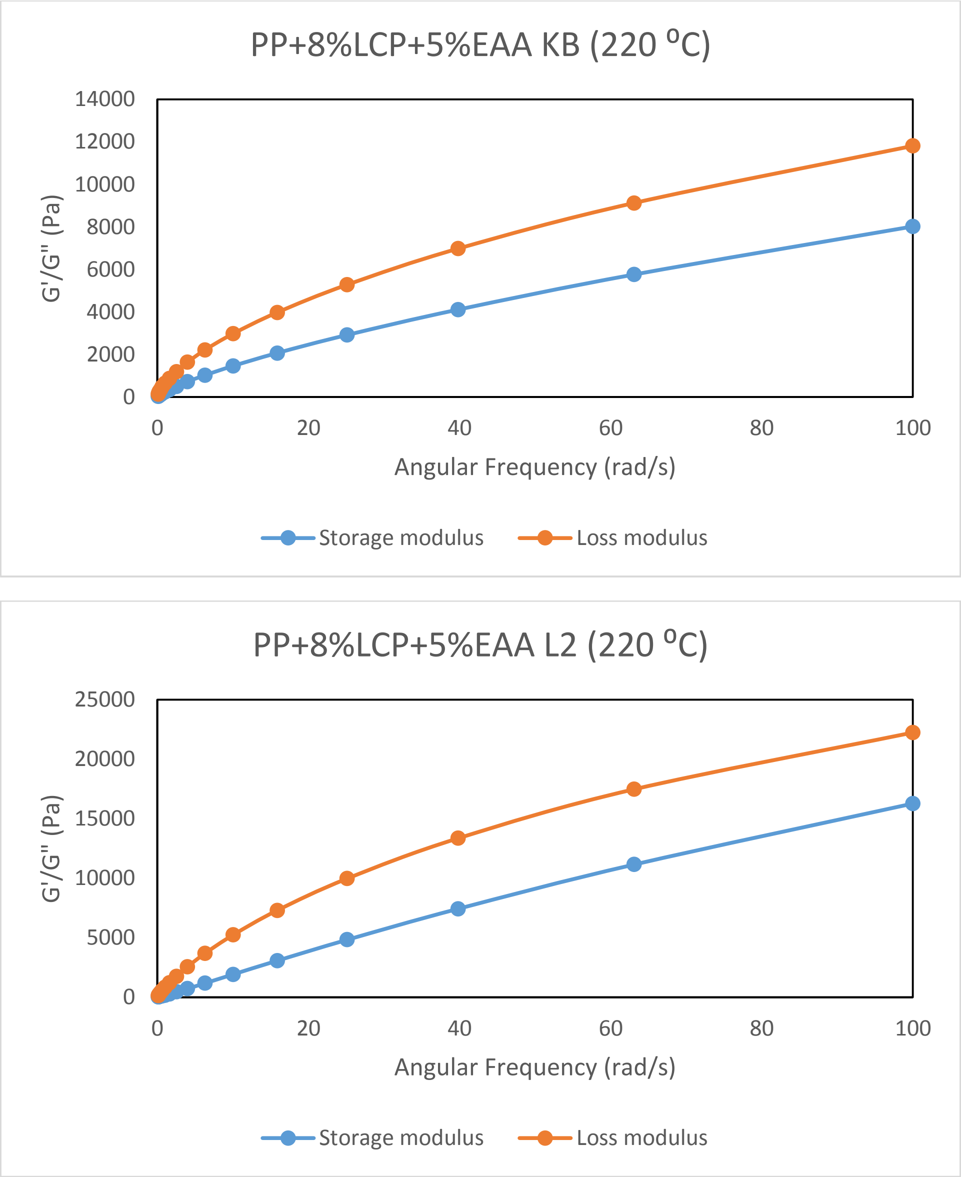
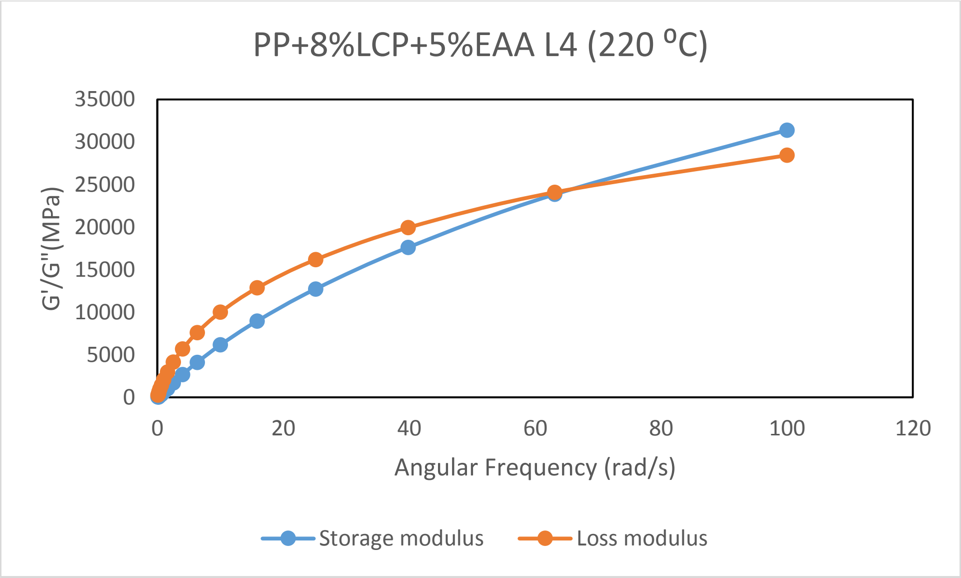


Figure 2.21 – Storage/Loss modulus of PP/LCP systems processed at 220 to 230 ^{0}C using different screw configurations.



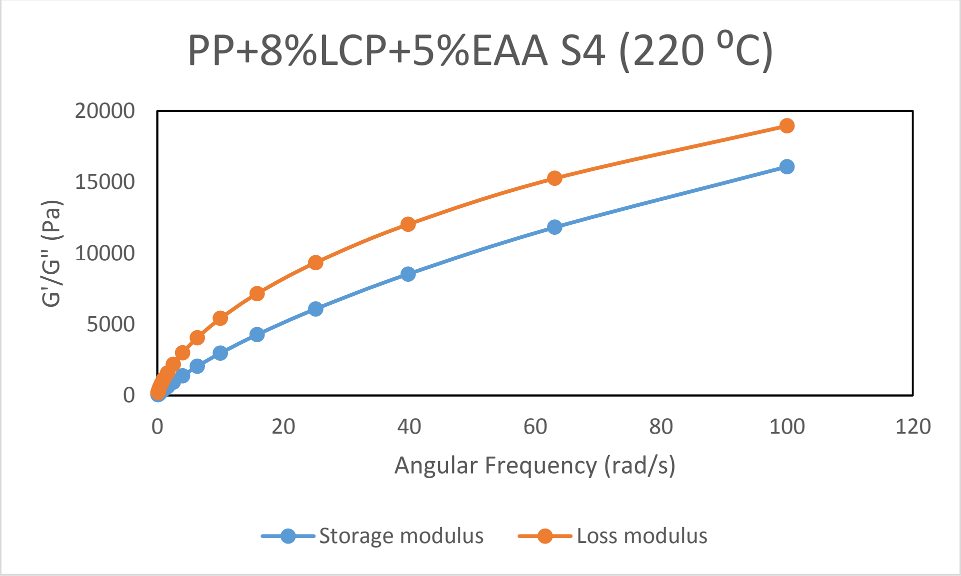


Figure 2.22 – Storage/Loss modulus of PP/LCP systems processed at 220 to 230^{0}C using different screw configurations.

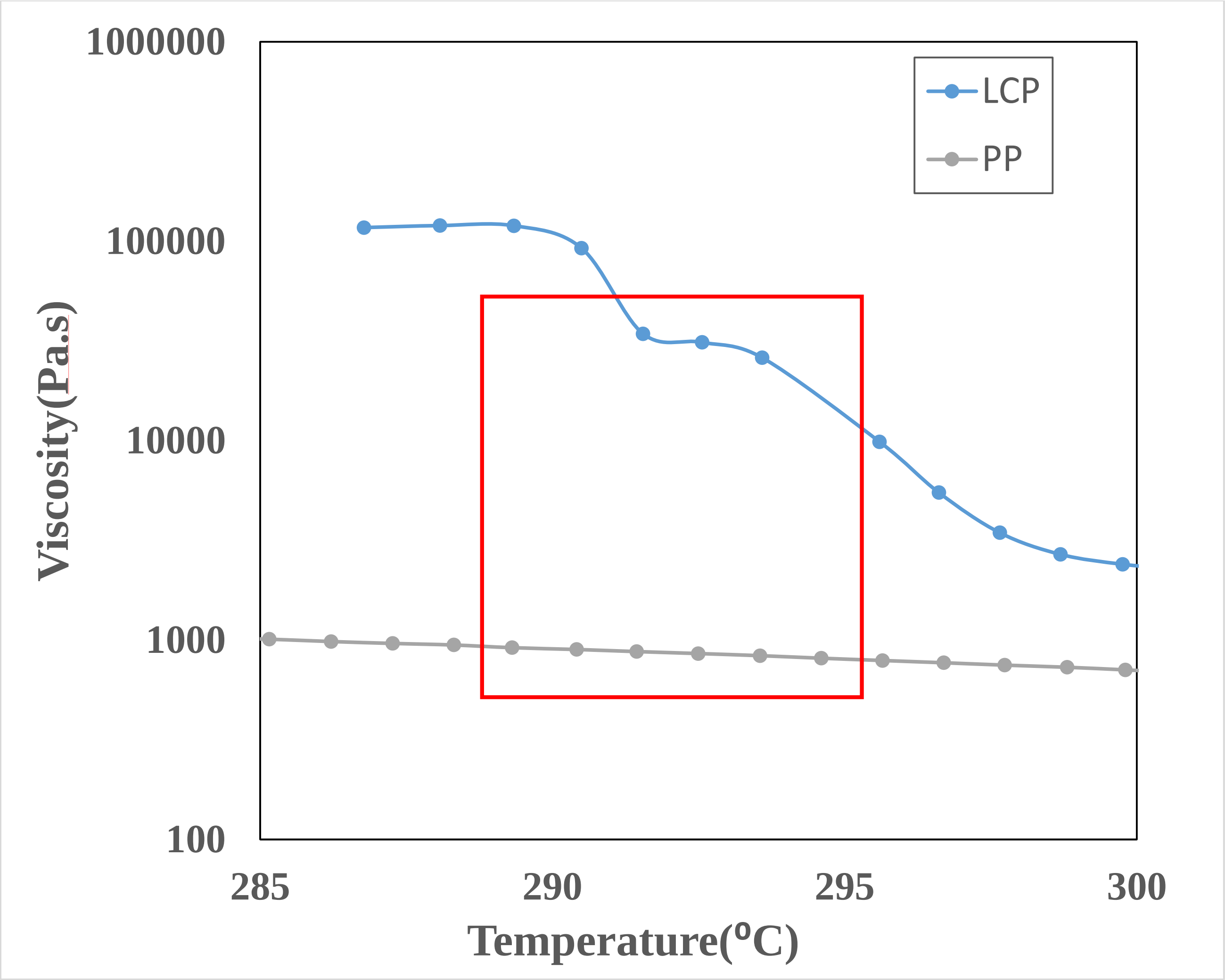


Figure 2.23 - Temperature Ramp of the raw materials PP and LCP, gives the viscosity ratio. The red box highlights the temperature range of the extrusion.

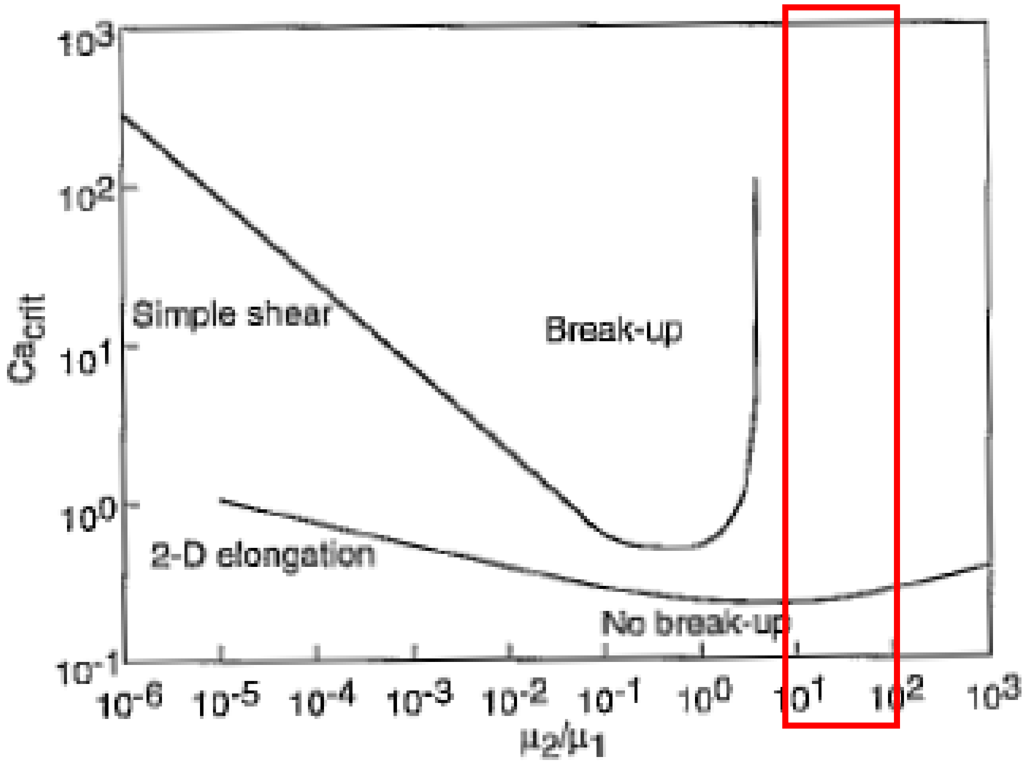


Figure 2.24 – Grace plot with the highlighted viscosity ratio range.

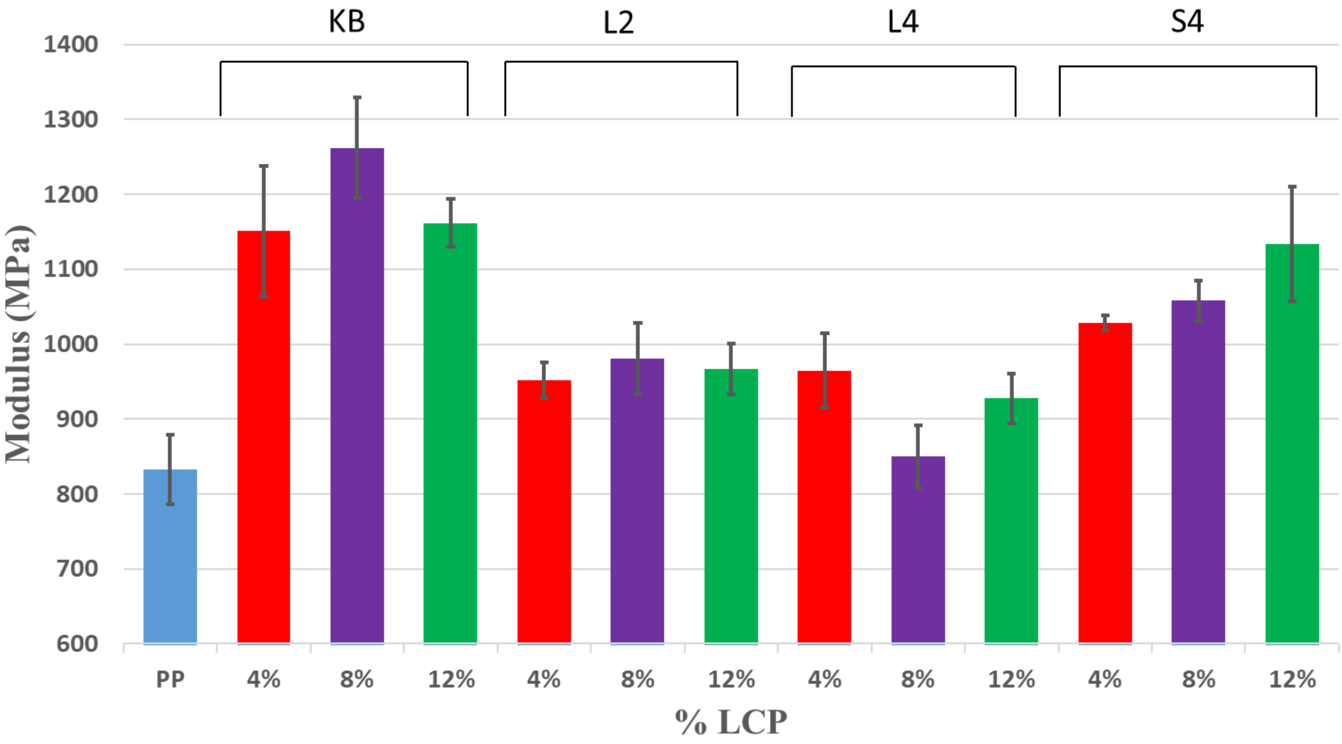


Figure 2.25 – Summary of the mechanical properties of PP/LCP blends with three different amounts of LCP (4%, 8% and 12%) for the same amount of EAA (5%) using different screw configurations.

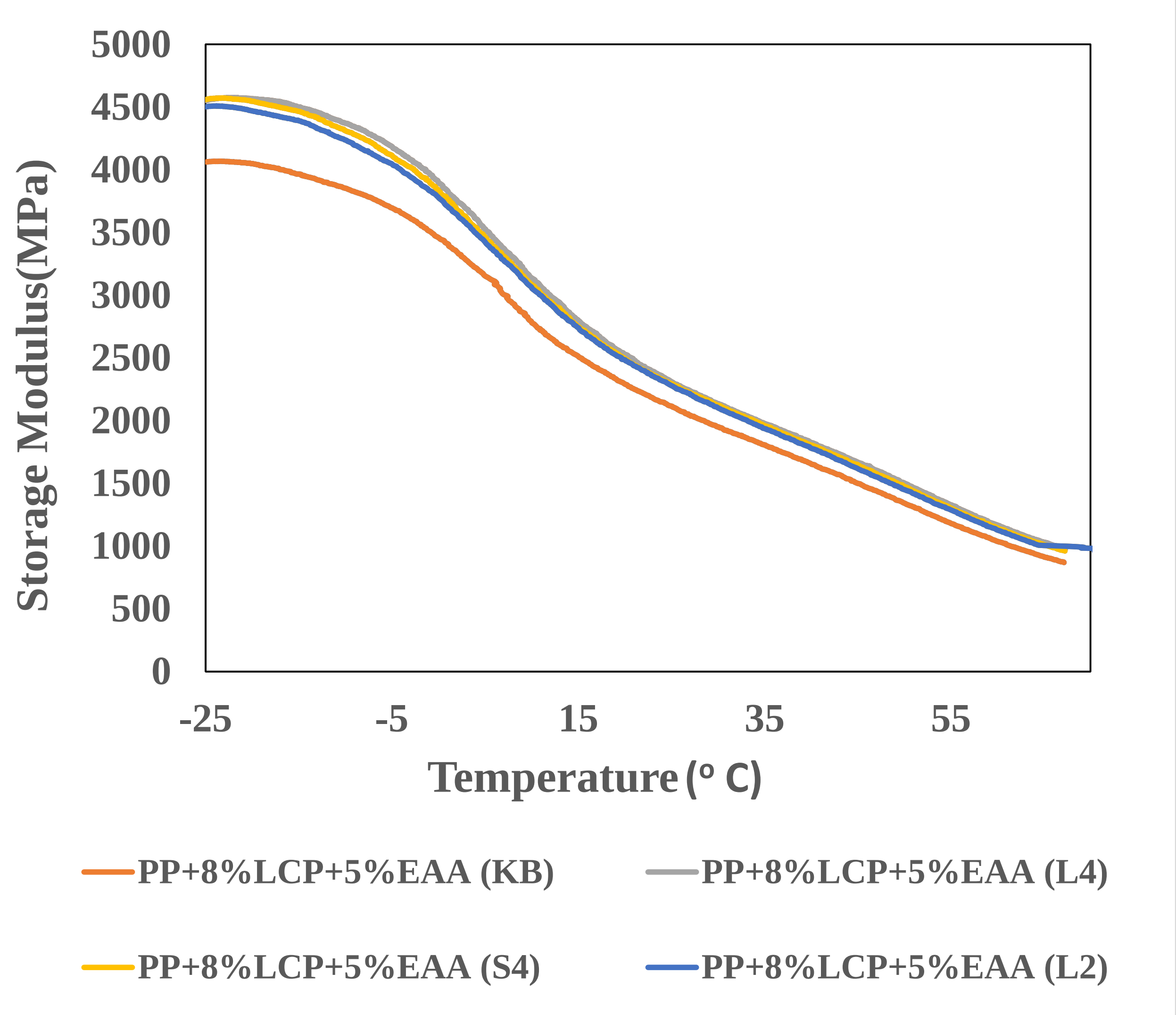


Figure 2.26 – DMA results for PP/LCP composites having the same composition, processed at 220-230 ^{0}C using different screw configurations.

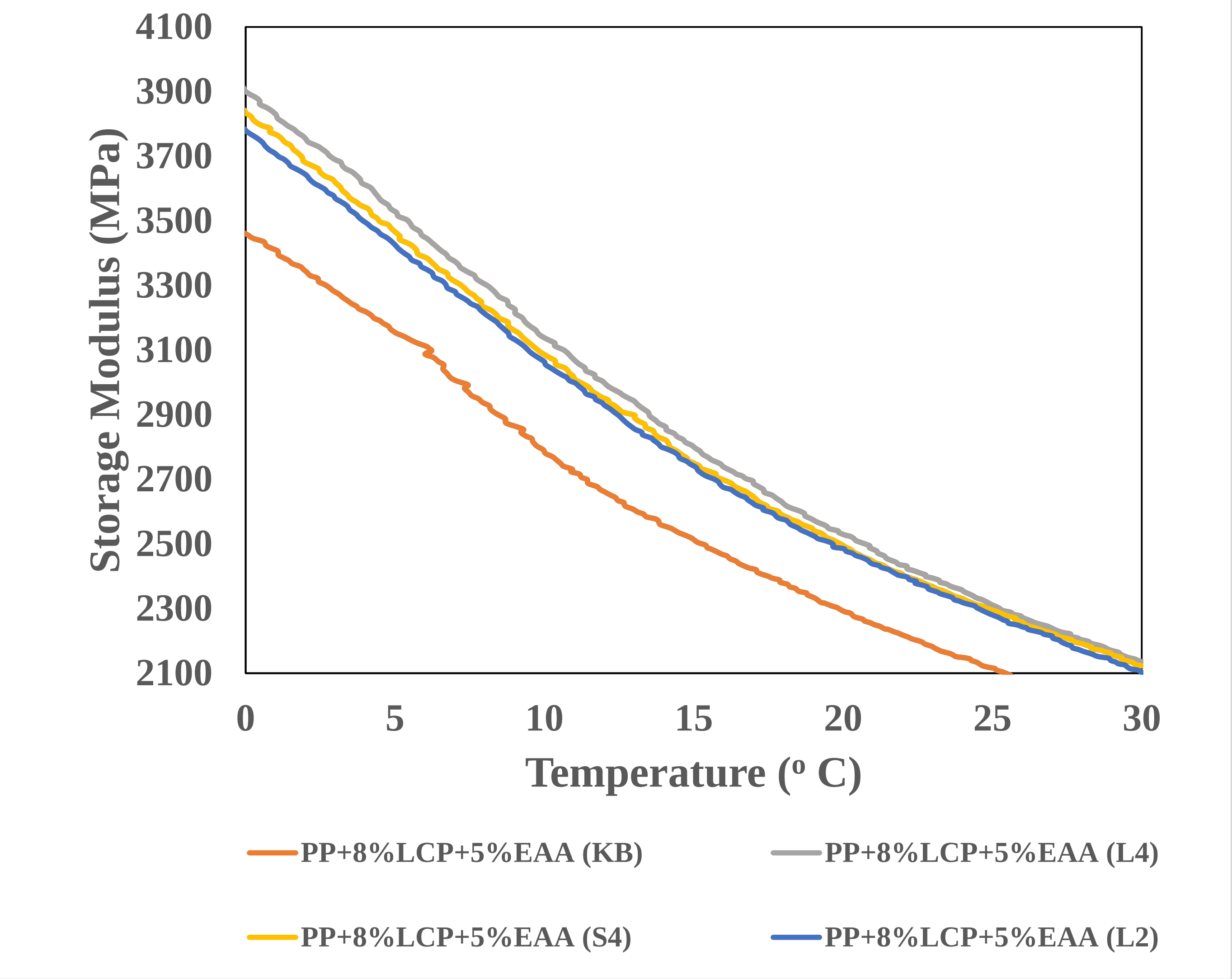
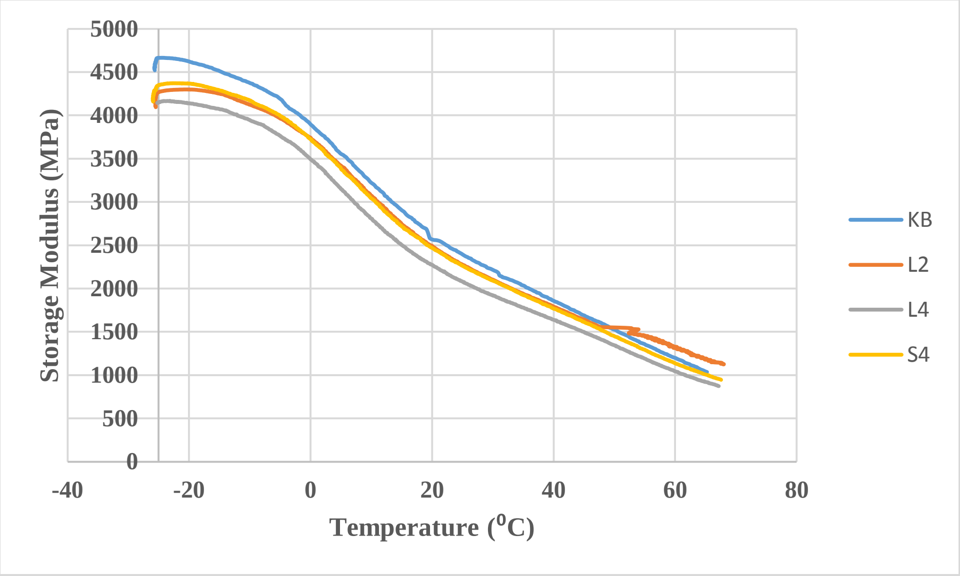


Figure 2.27 – Room temperature DMA results for PP/LCP composites having the same composition, processed at 220-230 ^{0}C using different screw configurations.



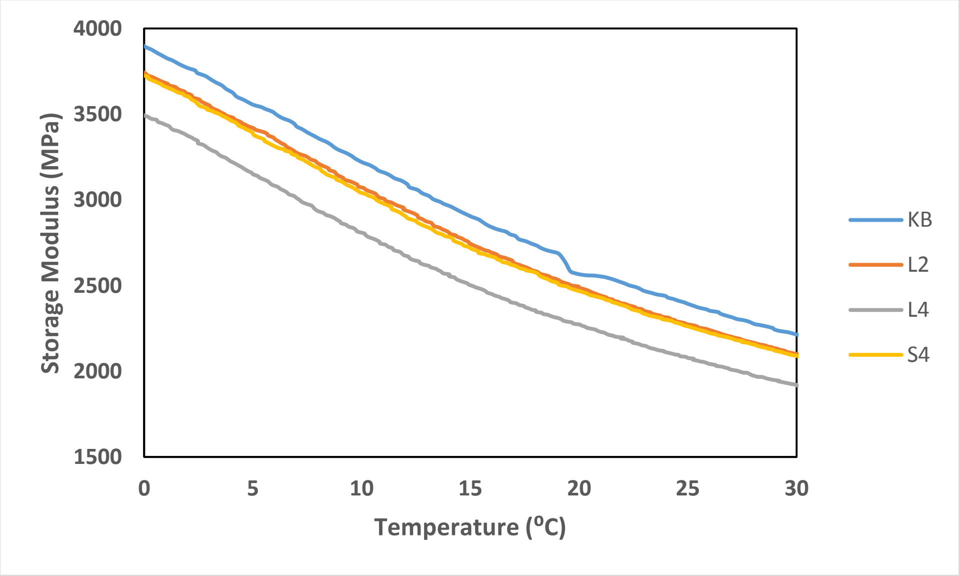


Figure 2.28 – Top - DMA results of PP/LCP Blends. Bottom – Room Temperature DMA results of PP/LCP Blends.

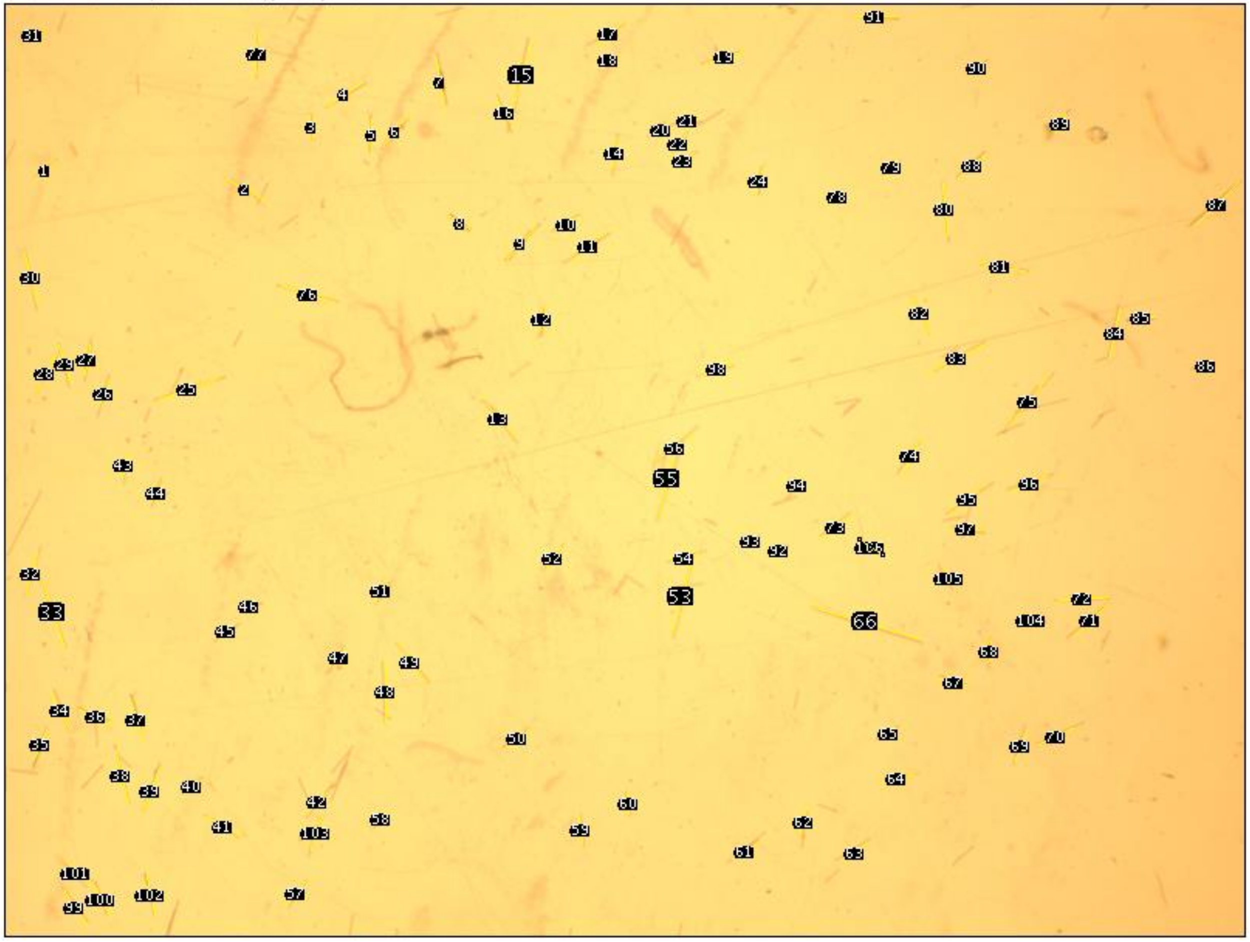


Figure 2.29 – A screenshot of measuring the lengths of glass fibers using Image J.

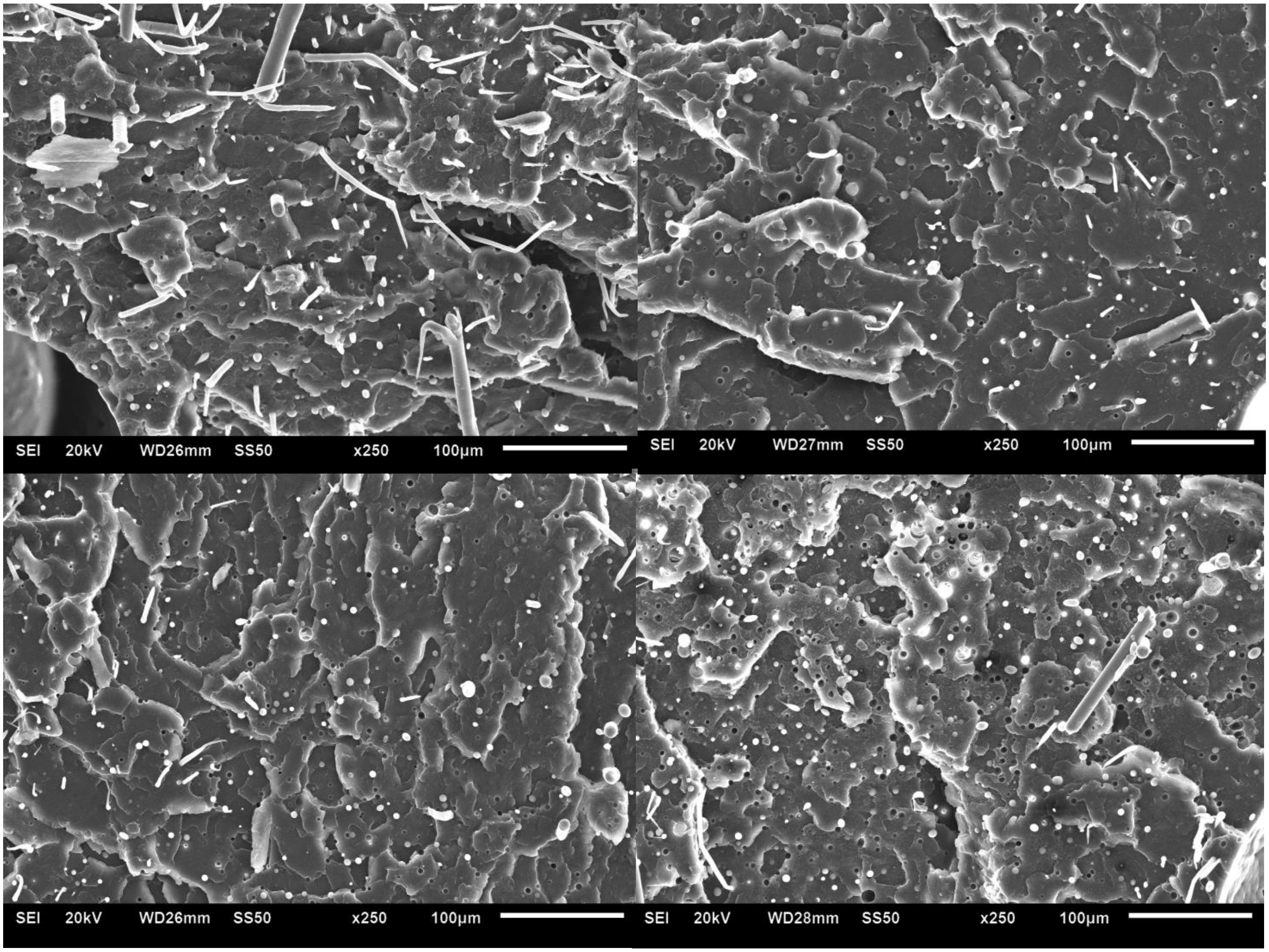


Figure 2.30 – SEM of PP/LCP blends having the same composition (PP+8%LCP+5%EAA), processed at 285-295 ^{0}C with different screw configurations. Top left – Screw configuration used KB. Top Right – Screw Configuration used L2. Bottom Left – Screw Configuration used L4. Bottom right – Screw Configuration used – S4.

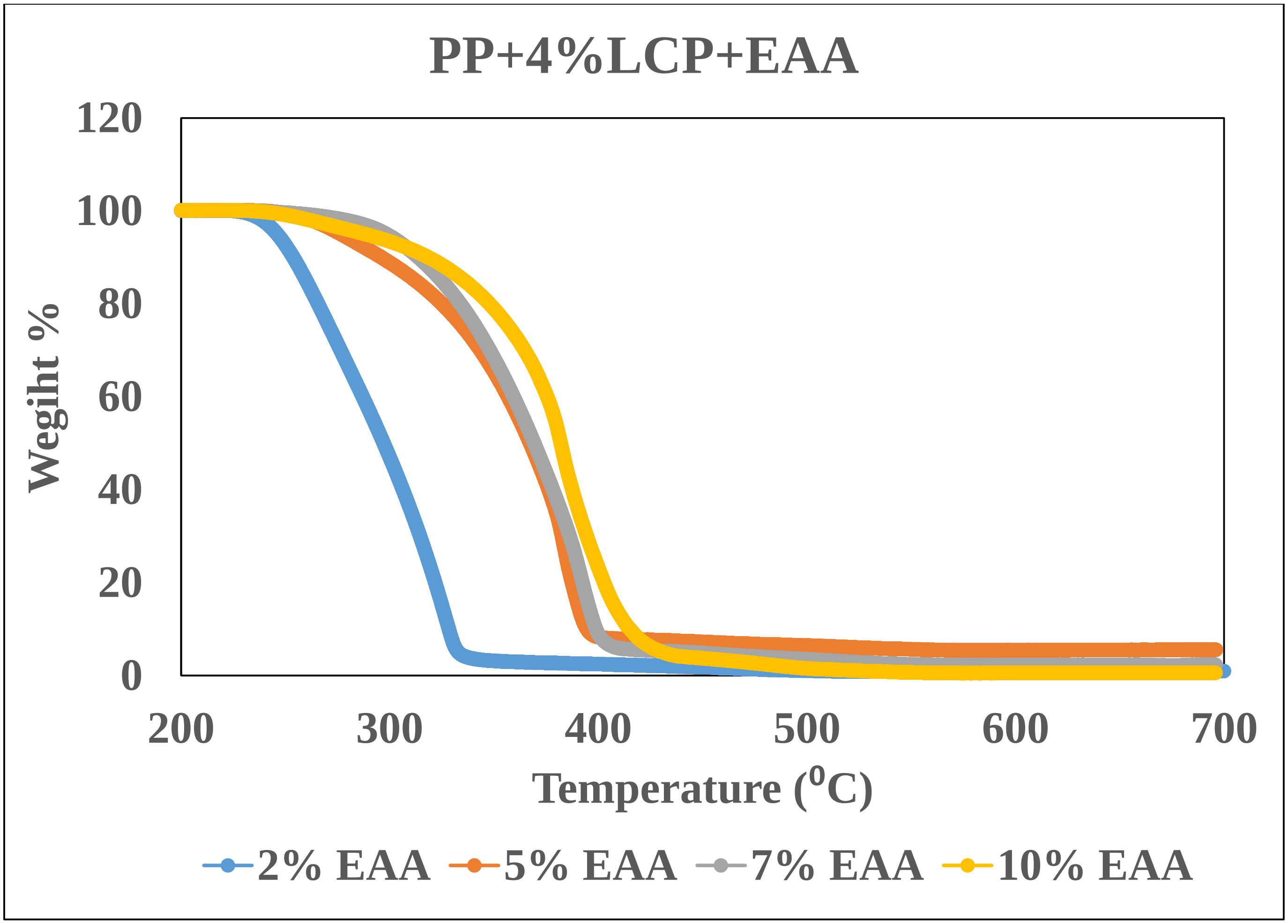


Figure 2.31 - TGA results of PP/LCP blends with the same amount of LCP (4%) but varying amounts of compatibilizer. These blends were processed at 285-295 ⁰C, using the kneading blocks (KB) screw configuration.

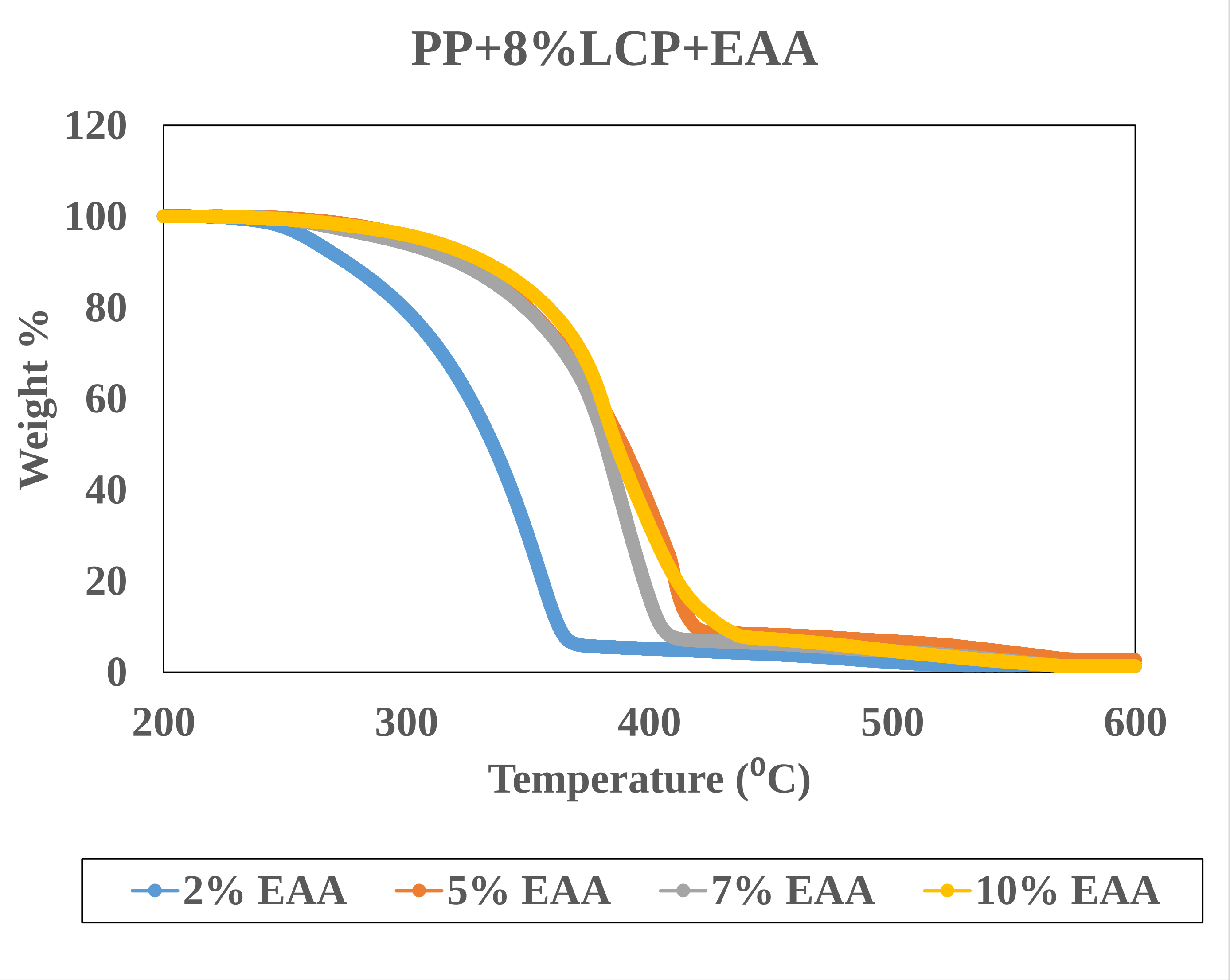


Figure 2.32 - TGA results of PP/LCP blends with the same amount of LCP (8%) but varying amounts of compatibilizer. These blends were processed at 285-295 ^{0}C, using the kneading blocks (KB) screw configuration.

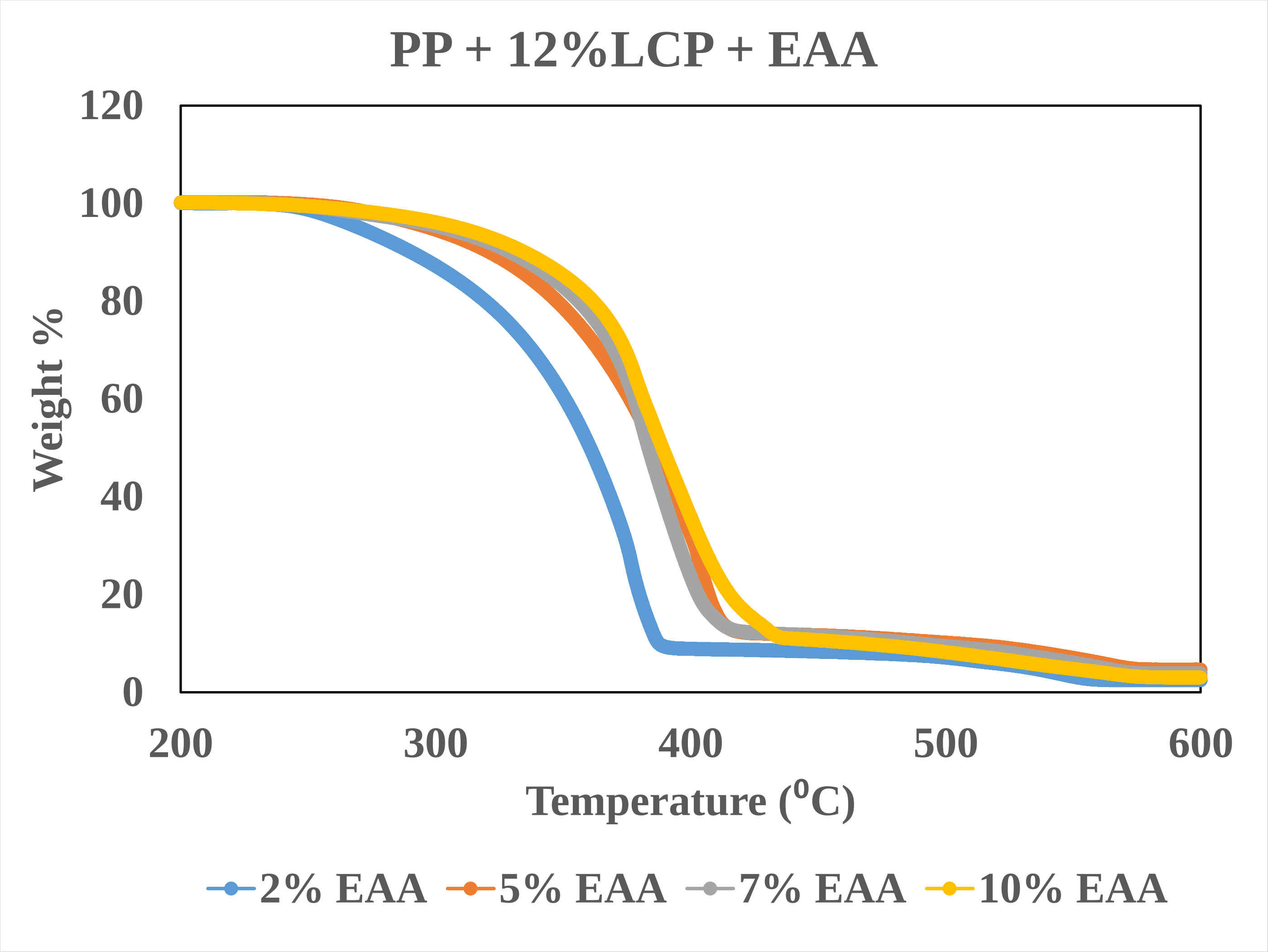


Figure 2.33 - TGA results of PP/LCP blends with the same amount of LCP (12%) but varying amounts of compatibilizer. These blends were processed at 285-295 °C, using the kneading blocks (KB) screw configuration.

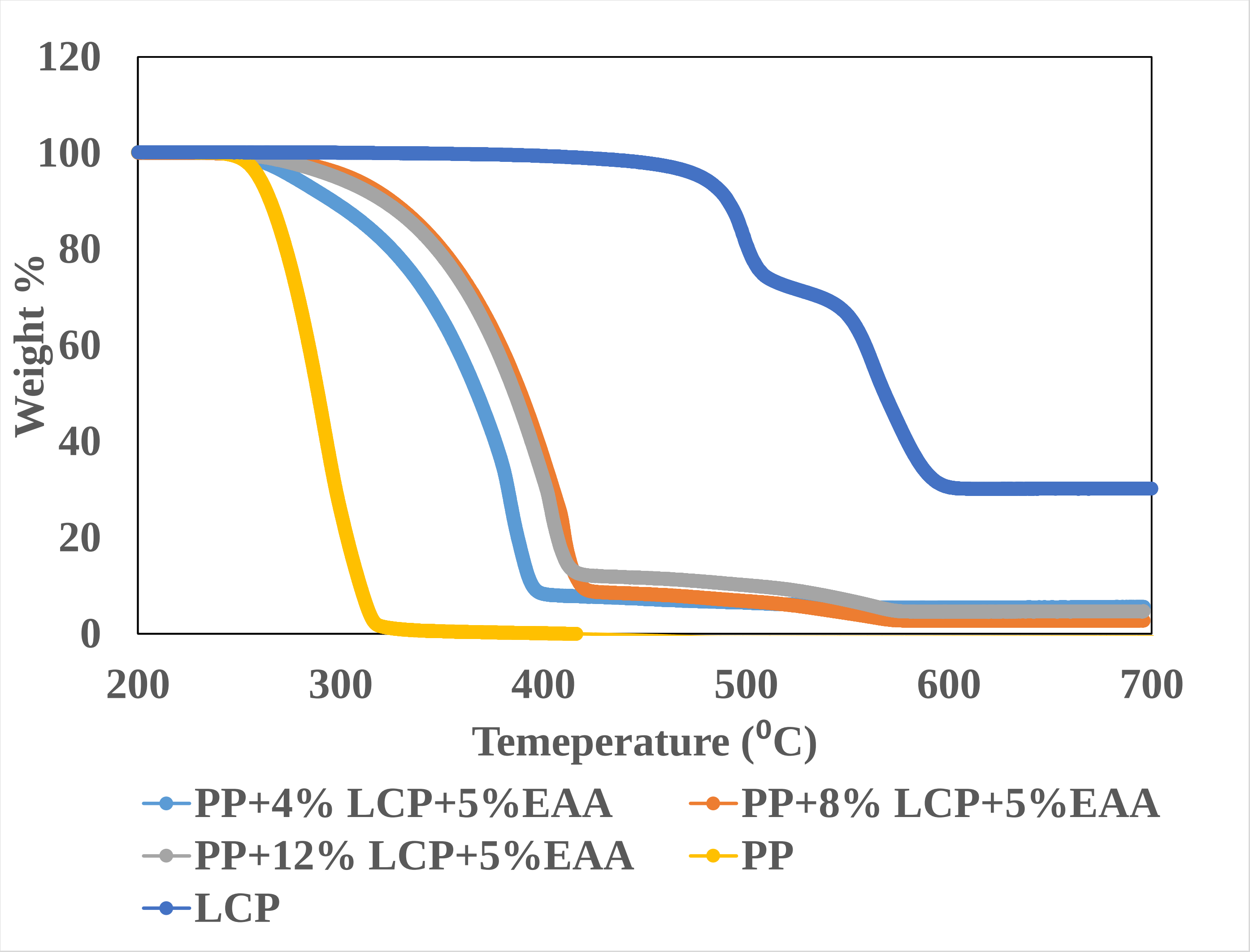


Figure 2.34 – Summary of the thermal properties of PP/LCP blends, having same amount of compatibilizer (5%) but different amounts of LCP (4%, 8% and 12%). These blends were processed at 285-295 ⁰C, using the kneading blocks (KB) screw configuration.

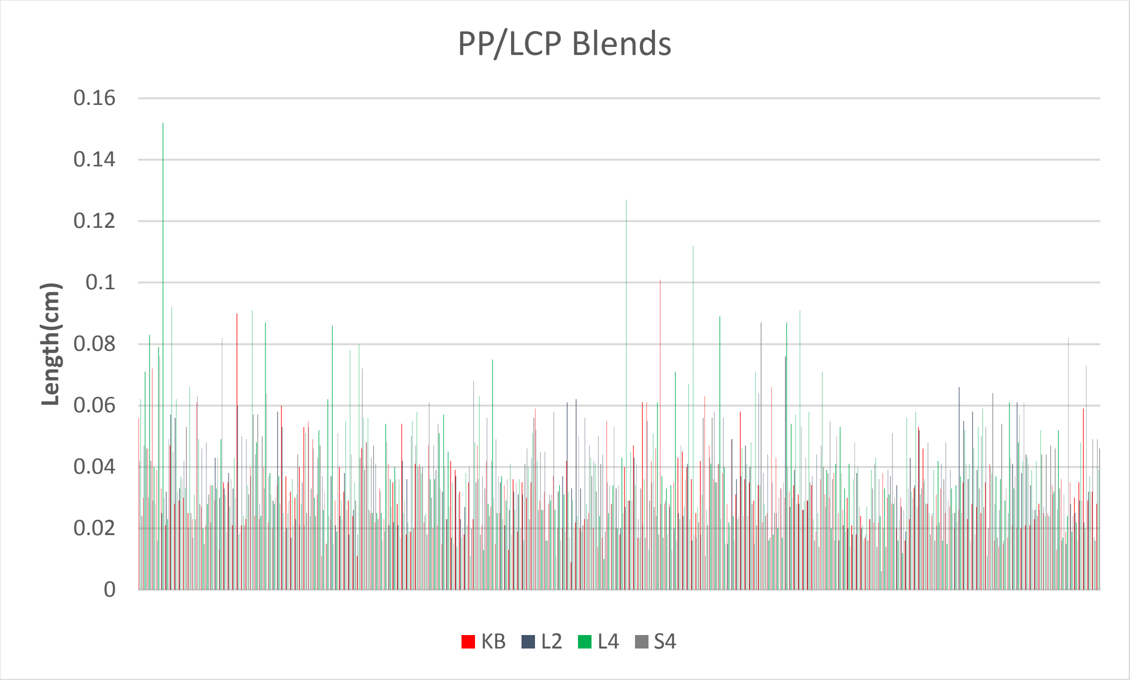


Figure 2.35 – Glass Fiber length of PP/LCP Blends after extrusion.

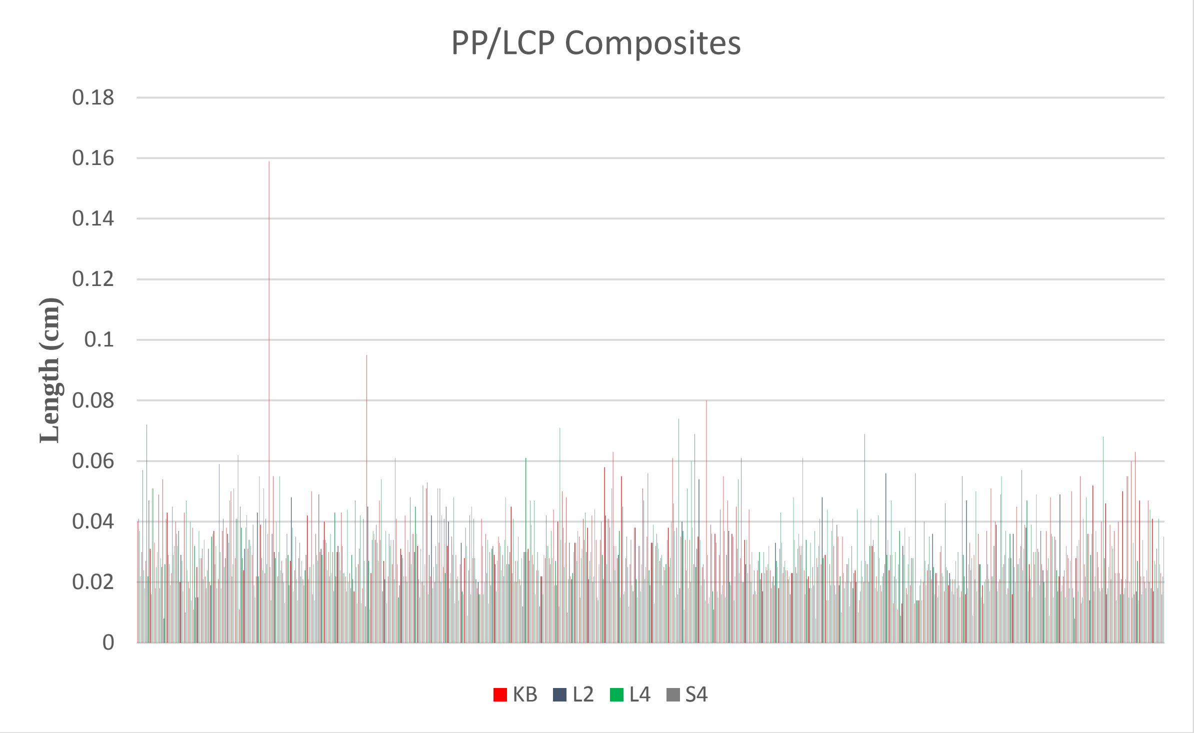


Figure 2.36 – Glass Fiber length of PP/LCP Composites after extrusion.

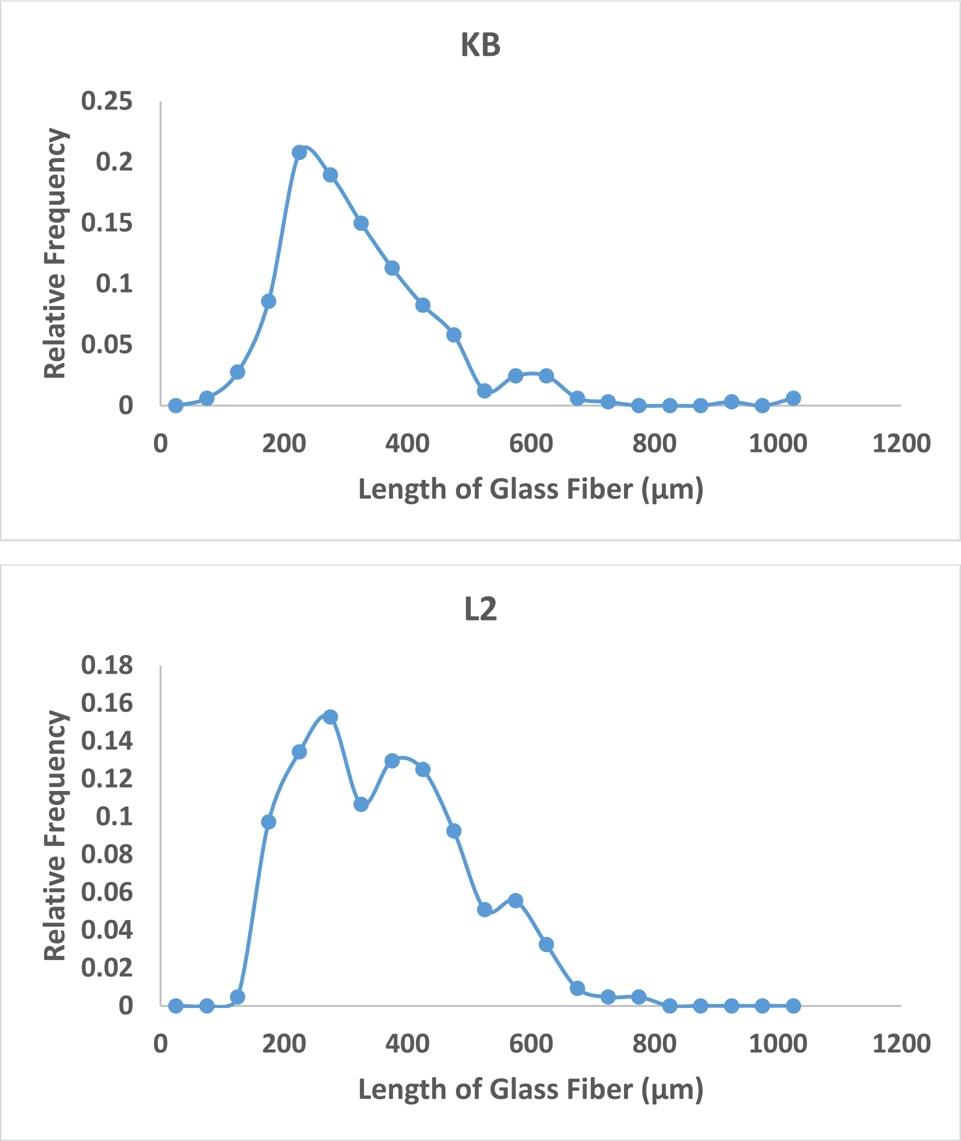


Figure 2.37 – Glass Fiber length distribution of PP/LCP Blends after extrusion using KB and L2.

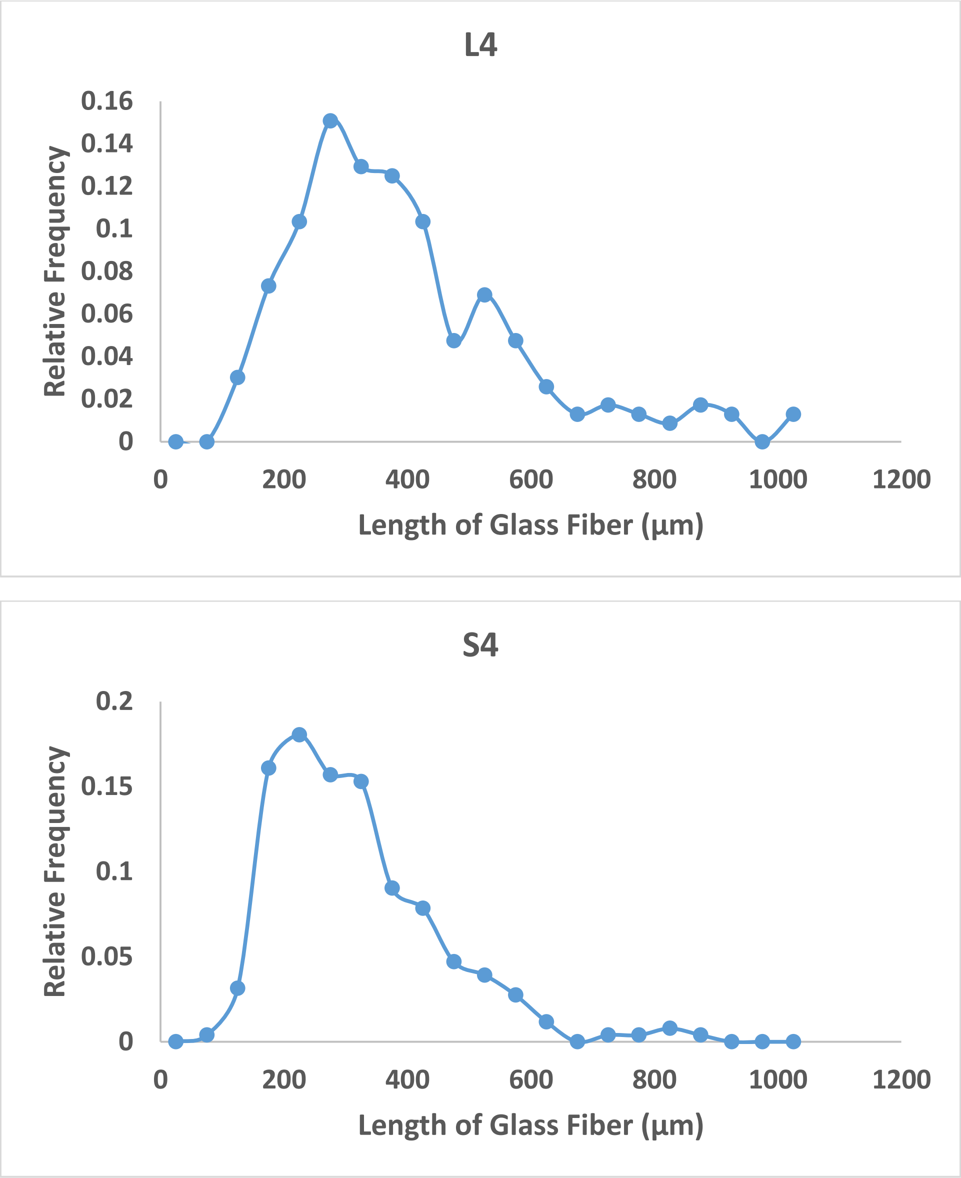


Figure 2.38 – Glass Fiber length distribution of PP/LCP Blends after extrusion using L4 and S4.

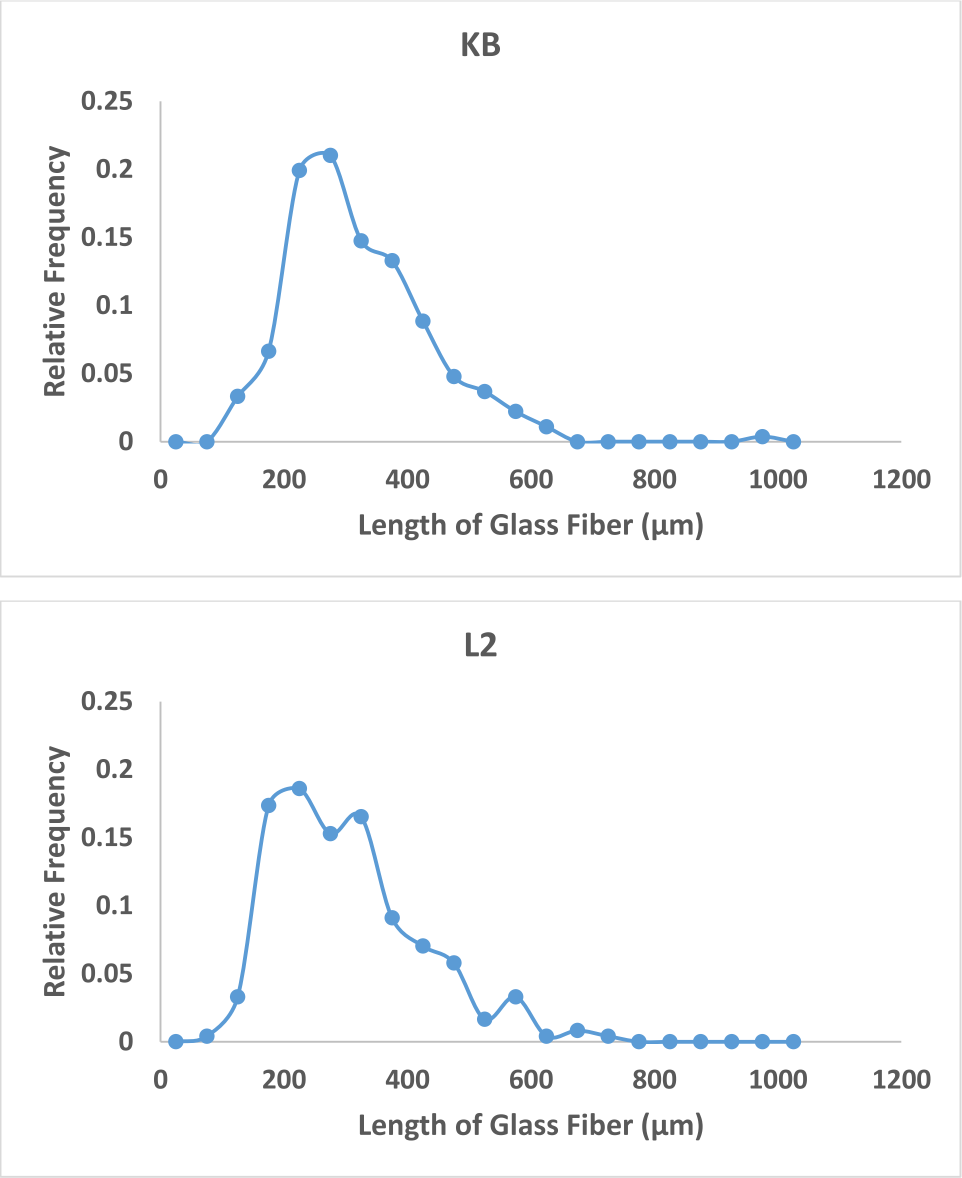


Figure 2.39 – Glass Fiber length distribution of PP/LCP Composites after extrusion using KB and L2.

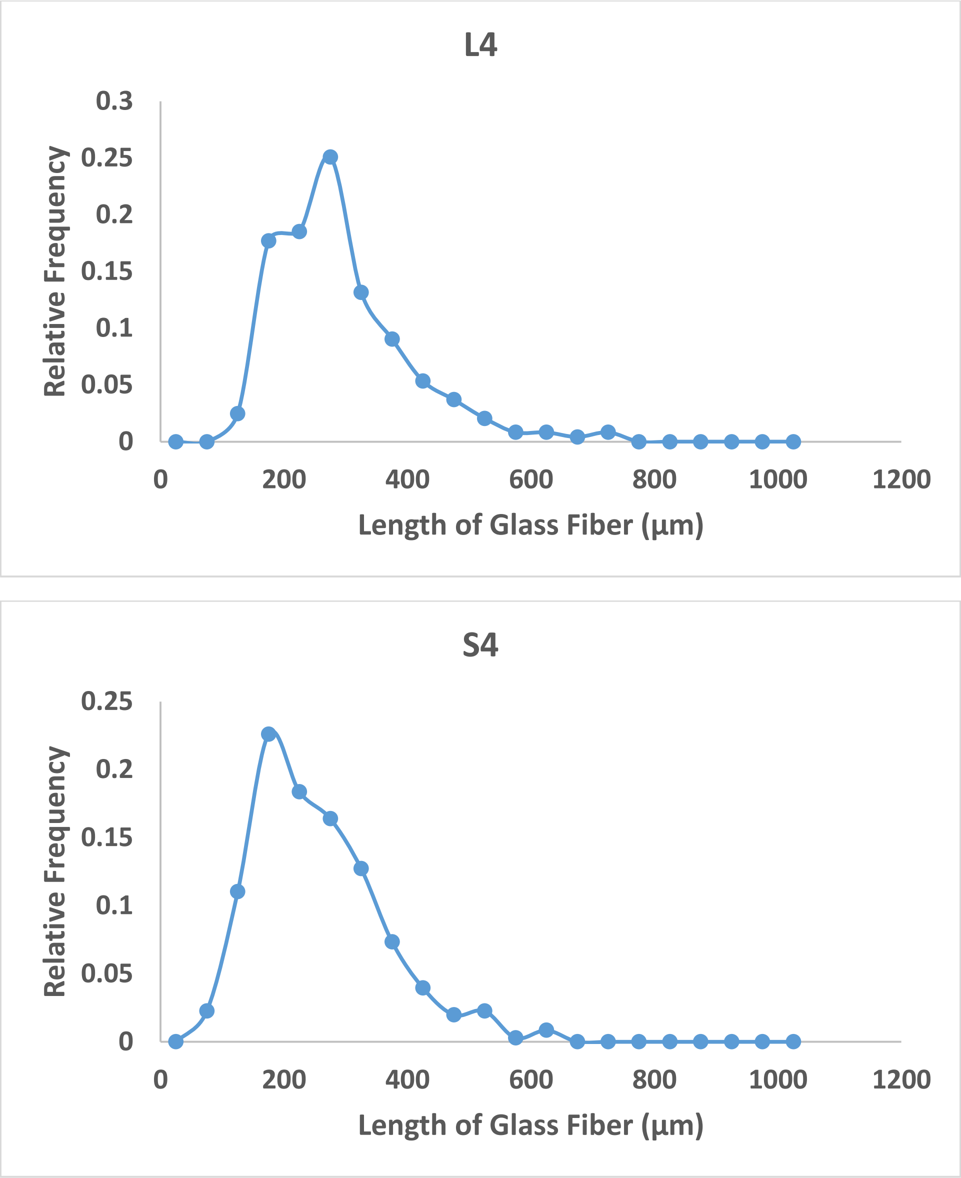


Figure 2.40 – Glass Fiber length distribution of PP/LCP composites after extrusion, using L4 and S4.

Table 2.1 – Quantities (in %) of PP, LCP and EAA mixed together before extruding for compatibilizer optimization.

PP (%)	LCP (%)	EAA(% of mixture of PP + LCP)	Screw Configuration	Temperature of Processing (^{0}C)
96	4	2	Kneading Blocks (KB)	285-295
96	4	5	Kneading Blocks (KB)	285-295
96	4	7	Kneading Blocks (KB)	285-295
96	4	10	Kneading Blocks (KB)	285-295
92	8	2	Kneading Blocks (KB)	285-295
92	8	5	Kneading Blocks (KB)	285-295
92	8	7	Kneading Blocks (KB)	285-295
92	8	10	Kneading Blocks (KB)	285-295
88	12	2	Kneading Blocks (KB)	285-295
88	12	5	Kneading Blocks (KB)	285-295
88	12	7	Kneading Blocks (KB)	285-295
88	12	10	Kneading Blocks (KB)	285-295

Table 2.2 – Actual Quantities (in g) of PP, LCP and EAA mixed together before extruding for compatibilizer optimization in the case of PP/LCP blends.

Blend	PP (g)	LCP (g)	EAA (g)	Screw Configuration	Temperature of Processing (ºC)
PP+4%LCP+2%EAA	672	28	14	Kneading Blocks (KB)	285-295
PP+4%LCP+5%EAA	672	28	35	Kneading Blocks (KB)	285-295
PP+4%LCP+7%EAA	672	28	49	Kneading Blocks (KB)	285-295
PP+4%LCP+10%EAA	672	28	70	Kneading Blocks (KB)	285-295
PP+8%LCP+2%EAA	644	56	14	Kneading Blocks (KB)	285-295
PP+8%LCP+5%EAA	644	56	35	Kneading Blocks (KB)	285-295
PP+8%LCP+7%EAA	644	56	49	Kneading Blocks (KB)	285-295
PP+8%LCP+10%EAA	644	56	70	Kneading Blocks (KB)	285-295
PP+12%LCP+2%EAA	616	84	14	Kneading Blocks (KB)	285-295
PP+12%LCP+5%EAA	616	84	35	Kneading Blocks (KB)	285-295
PP+12%LCP+7%EAA	616	84	49	Kneading Blocks (KB)	285-295
PP+12%LCP+10%EAA	616	84	70	Kneading Blocks (KB)	285-295

Table 2.3 - Actual Quantities (in g) of PP, LCP and EAA mixed together before extruding in the case of PP/LCP blends at a fixed % of EAA, using different screw configurations.

Blend	PP (g)	LCP (g)	EAA (g)	Screw Configuration	Temperature of Processing (^{o}C)
PP+4%LCP+5%EAA	672	28	35	Kneading Blocks (KB)	285-295
PP+8%LCP+5%EAA	672	28	35	Kneading Blocks (KB)	285-295
PP+12%LCP+5%EAA	616	84	35	Kneading Blocks (KB)	285-295
PP+4%LCP+5%EAA	672	28	35	Extensional Mixing Elements (L2)	285-295
PP+8%LCP+5%EAA	644	56	35	Extensional Mixing Elements (L2)	285-295
PP+12%LCP+5%EAA	616	84	35	Extensional Mixing Elements (L2)	285-295
PP+4%LCP+5%EAA	672	28	35	Extensional Mixing Elements (L4)	285-295
PP+8%LCP+5%EAA	644	56	35	Extensional Mixing Elements (L4)	285-295
PP+12%LCP+5%EAA	616	84	35	Extensional Mixing Elements (L4)	285-295
PP+4%LCP+5%EAA	672	28	35	Extensional Mixing Elements (S4)	285-295
PP+8%LCP+5%EAA	644	56	35	Extensional Mixing Elements (S4)	285-295
PP+12%LCP+5%EAA	616	84	35	Extensional Mixing Elements (S4)	285-295

Table 2.4 - Actual Quantities (in g) of PP, LCP and EAA mixed together before extruding in the case of PP/LCP composites at a fixed % of EAA, using different screw configurations.

Blend	PP (g)	LCP (g)	EAA (g)	Screw Configuration	Temperature of Processing (°C)
PP+4%LCP+5%EAA	576	24	30	Kneading Blocks (KB)	220-230
PP+8%LCP+5%EAA	552	48	30	Kneading Blocks (KB)	220-230
PP+12%LCP+5%EAA	528	72	30	Kneading Blocks (KB)	220-230
PP+4%LCP+5%EAA	576	24	30	Extensional Mixing Elements (L2)	220-230
PP+8%LCP+5%EAA	552	48	30	Extensional Mixing Elements (L2)	220-230
PP+12%LCP+5%EAA	528	72	30	Extensional Mixing Elements (L2)	220-230
PP+4%LCP+5%EAA	576	24	30	Extensional Mixing Elements (L4)	220-230
PP+8%LCP+5%EAA	552	48	30	Extensional Mixing Elements (L4)	220-230
PP+12%LCP+5%EAA	528	72	30	Extensional Mixing Elements (L4)	220-230
PP+4%LCP+5%EAA	576	24	30	Extensional Mixing Elements (S4)	220-230
PP+8%LCP+5%EAA	552	48	30	Extensional Mixing Elements (S4)	220-230
PP+12%LCP+5%EAA	528	72	30	Extensional Mixing Elements (S4)	220-230

Table 2.5 - The average length of glass fibers (based on a sample size of approximately 250), of PP/LCP blends processed at 285-295 (^{0}C) using different mixing elements.

KB (µm)	L2 (µm)	L4 (µm)	S4 (µm)
324 ± 132	367 ± 134	394 ± 202	310 ± 134

Table 2.6 - The length of glass fibers (based on a sample size of approximately 250), of PP/LCP composties processed at 220-230 (^{0}C) using different mixing elements.

KB (µm)	L2 (µm)	L4 (µm)	S4 (µm)
321 ± 138	298 ± 119	286 ± 110	251 ± 103

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Chapter 3

Simulation of Pressure Drops

The goal of simulating the pressure drops was to get an approximate idea of the range, as this was the first time that the Extensional Mixing Elements were going to be used. The idea of this exercise was to ensure that on extrusion of the PP/LCP system using the EME's as the mixing elements, will not over torque the instrument.

Experimental

A sample of PP + 8% LCP + 5% EAA was prepared and extruded through the 24 mm twin screw extruder. This was the same equipment on which all the future experiments were carried out. While the extrusion was being carried out, a portion of sample was extracted by opening the port just before the extensional mixing elements. The sample was collected in cold water.

Rheological Characterization

The material was compression molded into discs of 25 mm in diameter and 1 mm in thickness, using a CAVER press at a temperature of 210 ºC. A pressure of 10 metric tons was applied during the compression molding stage and then released. This cycle was repeated three times and then the discs were cooled using running cold water.

A frequency sweep was carried out using ARES G2. The curve of viscosity versus shear rate was obtained at 285 ºC. This data was then exported to excel, which was then eventually imported to IRIS. Using this information, the closest fit to Cross model was found (Figure 3) and the parameters were noted.

Simulation Method

All the simulations were carried out on ANSYS POLYFLOW, assuming that the material cannot be compressed and the flow is isothermal. There are several fundamental equations on which the calculations are based upon [1][2]. One of them is incompressibility equation,

$$\nabla \cdot \mathbf{v} = 0$$

Second is the equation of momentum.

$$-\nabla p + \nabla \cdot \mathbf{T} + \mathbf{f} = \rho \mathbf{a}$$

Here, p refers to the Pressure, a represents acceleration, v gives the velocity vector. Furthermore, there is stress tensor represented by T which is actually the total stress tensor as explained by the constitutive equations governing the rheological behavior of the fluid. Newtonian Fluid was chosen as the constitutive model. The shear dependency of the same was determined by using the Cross Model. For the case of a generalized Newtonian Fluid, the total stress tensor T, is mathematically show as the following[3][4]:

$$\mathbf{T} = 2\, \eta\, D$$

The viscosity as we know depends of the shear rate as shown,

$$\dot{\gamma} = \sqrt{2trD^2}$$

The dependence of viscosity on shear rate for the cross model is given as follows:

$$\eta(x) = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^{1-n}}$$

In the above equation, η stands for the power law index, η_0 gives the zero shear viscosity. For the current PP/LCP system the value of η_0 was 300 Pa.s. λ, is defined as the inverse of shear rate.

The value of λ used in the current simulation is 0.6. In the above equation, n is the power-law index, the value of which was taken as 0.4. Furthermore, the number of nodes were taken to be approximately 400,000.

Results and Discussion

The results of the simulations were tabulated below (Table 3.1). As expected, the pressure drops were found to increase as the aggressiveness of the extensional mixing elements increased, i.e. from L2 to S4. These pressure drops were however, found to be within acceptable range to run on the extruder.

It is important to bear in mind that the simulated pressure drops were only a very rough approximation. For accurate simulation values, simulation using the PTT model is recommended. The Cross model which has been currently used, is an inelastic model. On the other hand, the PTT model assumes elasticity. Since this was supposed to be a rough estimate, the real pressure drops were found to be different than the simulated ones (Table 3.2)

Conclusion

Based on simulation, rough pressure drops were calculated for the extensional mixing elements using the inelastic Cross model. As expected, the simulated values indicated that the pressure drops increase from L2 to S4.

However, the pressure drops were found to be within the acceptable range for running in the twin screw extruder.

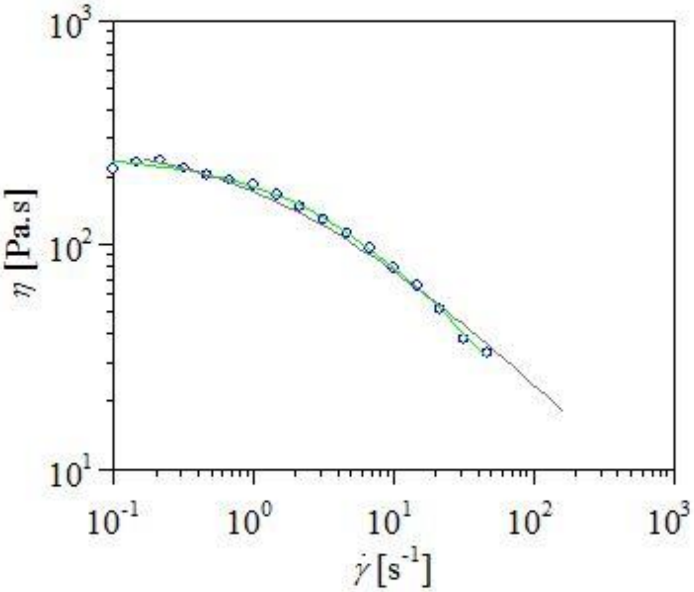

Figure 3 – Curve fitting using IRIS.

Table 3.1 – Simulated Pressure Drops for PP/LCP blends processed at 285-295 ^{o}C

System	L2 (PSI)	L4 (PSI)	S4 (PSI)
PP+8%LCP+5%EAA	67	122.4	140

Table 3.2 Pressure Drops for PP/LCP blends processed at 285-295 ^{o}C using different screw configurations.

System	KB (PSI)	L2 (PSI)	L4 (PSI)	S4 (PSI)
PP+4%LCP+5%EAA	20	110	240-250	260-290
PP+8%LCP+5%EAA	30	100	230-240	230-250
PP+12%LCP+5%EAA	20	100	220-240	230-250

Table 3.3 Pressure Drops for PP/LCP composites processed at 220-230 ^{o}C using different screw configurations.

System	L2 (PSI)	L4 (PSI)	S4 (PSI)
PP+4%LCP+5%EAA	270-280	320	400-410
PP+8%LCP+5%EAA	270-280	330-340	400-410
PP+12%LCP+5%EAA	280-290	330-350	400-420

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