Development of Biodegradable Polymer-Leather Composite by Incorporation of Leather Buffing Waste in Poly-ε-Caprolactone Matrix.

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Submitted by

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CERTIFICATE

This is to certify that the M.Tech major project entitled **"Development of Biodegradable Polymer-Leather Composite by Incorporation of Leather Buffing Waste in Poly-ε-Caprolactone Matrix"**, submitted by **Abhijit Salvekar**, for the award of the degree of **"Master of Technology in Polymer Technology"** is a record of bonafide work carried out by him. Abhijit Salekar has worked under our guidance and supervision and has fulfilled the requirements for the submission of the dissertation. The project work has been carried out during the session 2012-2013.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

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ABSTRACT

The leather processing industry produces large volumes of leather buff during the leather cleaning process. The buff is a fluffy material of low bulk density and is made up of micron diameter fibers and particles. Currently, it is land-filled and this raises severe environmental concerns, particularly if the leather is chrome-tanned. This project envisages the use of the leather buff as a filler into Poly-ε-Caprolactone matrix with the aim of producing low cost, biodegradable leather-like polymer-leather composites.

Waste leather buff was incorporated into polycaprolactone polymer in different weight proportion from 2 to 40 wt%. The blends were prepared by melt mixing process using a DSM micro-compounder. The components of the composites were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and Fourier transform infrared spectroscopy (FTIR). Effect of leather contents on mechanical properties of composites is investigated by tensile testing.

PCL grafted with maleic anhydride was synthesized and its use as compatiblizer for PCL-Leather composite was investigated.

CHAPTER 1

INTRODUCTION

1.1 NATURAL FIBER COMPOSITES

Natural fibers can be classified according to their origin: vegetable, animal or mineral. Vegetable fibers include wood flour (or sawdust) from a huge variety of softwood and hardwood specimens and plant fibers, such as hemp, kenaf, curaua, coir, jute, sisal, bamboo, among others. Animal fibers include silk and leather. The most well-known mineral fibers are glass, boron and asbestos; the latter in disuse nowadays as it has been found to be harmful to humans.

Over the past years sustainable eco-efficient practices and products have gained increasing attention and the use of natural fibers as reinforcement for polymers has been rapidly expanding.

Advantages of biofibers over synthetic ones include the fact that they are renewable and biodegradable, present low cost, light weight, low energy consumption, carbon dioxide sequestration, low abrasiveness and excellent strength to weight ratio [1].

Limitations of biofibers as reinforcement in polymers are: difficulties in maintaining homogenization of fiber properties; processing temperature, which should not exceed the degradation temperature of these fibers of around 200°C; and high moisture absorption, which may impair mechanical properties as well as facilitate fungus growth [2]. Typical thermoplastic polymers that can be easily processed at temperatures up to 200-220°C, and thus may be used as matrix, include: polypropylene (PP), polyethylene (PE), polystyrene (PS) acrylonitrile-butadiene-styrene (ABS), PVC and more recently polyvinyl butyral (PVB).

Incorporation of natural fibers into polymers will result in composites with adequate properties only when a set of factors are judiciously controlled in their manufacture, such as moisture and particle size which may adversely affect composite properties. Fiber moisture should not exceed the 1 to 2% range, since excessive moisture can cause internal bubbles in the composites and fiber degradation. On the other hand if the fiber is completely dried, firing explosions can be caused during transport and feeding processing operations. Particle size studies indicate that very small particles may burn during processing, leading to degradation of the thermoplastic composites. Another important factor in the manufacture of these composites is that mixing of the polymer and the fibers should preferably be carried out in twin-screw extruders, which provide high level of mixing and homogeneity resulting in the production of high performance materials. A smooth screw elements profile, a high enough length to diameter ratio (L/D) and degassing zones are factors that must be accounted for. The feed process may also be a problem since the non-homogeneity of fiber surface topography may cause bridging in hoppers. In addition to temperature during extrusion and injection molding, other processing conditions must be carefully chosen to avoid excessive shearing of the fiber: low screw speed, flow rates and back pressure levels. Tools (molds and dies) should also be correctly designed to avoid excessive shear and stagnation regions. Excessive shearing will cause shear heating which consequently can cause fiber degradation.

It is necessary to create an adequate interface between the polymer matrix and the fibers, as in all composites, to generate good stress transfer during loading. Chemical polarity of the matrix will favor interaction with the fibers, since cellulose has a large number of –OH groups on the surface. When the polymer is non polar, such as PP and PE, compatibilizers and coupling agents must be used to improve adhesion between matrix and fibers. They are bifunctional molecules that can interact or even react with both the non polar matrix and with the very polar fiber. Another alternative is to promote chemical attack of the fiber surface, rendering it more irregular to facilitate adhesion to the polymer matrix. Among these the use of compatibilizer has shown to be more efficient in improving interface adhesion.

It should be pointed out that the polymer and the fibers are not the only components in the formulation of these composites. Depending on the final application and the composite, different levels of additives are incorporated: compatibilizers or coupling agents, internal and external lubricants, UV stabilizers, antioxidants, mineral fillers (such as talc, calcium carbonate and mica), flame retardants and smoke suppressants, biocides, acid scavengers, blowing agents, among others [3-4].

1.2 WASTE LEATHER FIBRES

Among natural fibers, leather residues are superior because collagen is the main component of the fibers [5]. The treatment of leather with products made of heavy metals such as chromium (chromium oxide) and other additives such as caustic soda, fat liquors, dyes, and other types of salts is still allowed in several countries. Leather treated with chromium oxide during the tanning process is used on a large scale in the footwear, automotive, garment, and personal protective equipment (PPE) industries, generating a large amount of residue.

Chrome leather wastes, leather scraps, or chrome shavings are produced in post-tanning operations such as trimming, splitting, and shaving. Processing of one ton wet salted hide yields only 200 Kgs of leather and produce over 600 Kgs as a rejected wastes [6].

Residue management has become a major problem in modern society, especially solid residue with potential toxic effects [7]. The search for innovative solutions for the reuse of solid residue increased in the late 20th century and has intensified with growing urgency for environmental preservation. Many residue management solutions aim to add value to residue through the development of new materials and processes.

However, there are many residue materials generated in great quantities for which no large-scale application has yet been found, such as chromium-treated leather. Very interestingly, leather scraps after chromium tanning represents a huge source of waste. In fact, in 1996 approximately 45% of footwear made worldwide was leather, which equates to 4.150 million pair of shoes. To make these goods, an estimate of 6.750 million $ft^2$of leather was processed. Assuming an average of 30% scrap, this gives 2.025 million $ft^2$of leather wastes in 1996. The above calculation suggests around 400,000 tonnes of waste which may seem small compared to that produced by the tanning industry [8]. In addition, these sources of scrap can have potential contribution to environmental pollution, taking into account that chromium treated products are classified in the first category of hazardous waste.

About 90% of the total waste leather is chromium tanned and, more specifically, consists of:

- Leather scraps containing up to 12.5% nitrogen, 2% fat, 3.5–5% chromium (III) and a minimum of 30% moisture.

- Tanning solid wastes, derived from trimming and splitting, with the same as above composition with the exception of higher water content (up to 70%).

Leather deposition in the environment is a serious matter because, under certain pH and temperature conditions, the chromium used during the tanning process can undergo valence changes, going from trivalent chromium (Cr^{+3}) to hexavalent chromium (Cr^{+6}), a highly toxic and carcinogenic metal. Thus, if leather residue is dispersed in nature, it can contaminate rivers, lakes, and groundwater and, consequently, animals and plants [9].

An alternative solution for these residues is recycling (reuse), which can focus on the same sectors that generate the residue. Various processes have been proposed for the hydrolysis of leather waste and preparation of fertilizers, specified for different agricultural applications. Another way to utilize leather residue is to incorporate the leather as filler in thermosetting and thermoplastic polymers using batch equipment such as Banbury internal mixers or continuous feed extruders [5, 7, 10–16]. The advantage of a continuous process such as extrusion is that the components can be shaped into a final product just off the extruder, making this process highly productive.

1.3 LEATHER-POLYMER COMPOSITES

There are some studies in the literature on thermoplastic composites containing leather fibers as filler into appropriately selected polymer matrix with the aim of producing low grade leather-like polymer-leather composites for potential applications in upper shoe sole and other leather-like personal goods.

These composites are expected to combine the properties of plastic and leather and therefore, to be of potential use in the shoe industry as a substitute for the pure raw materials. Furthermore, applications such as floorings etc. could be possible provided that some critical properties, Ex- wear resistance, are acceptable.

Matrices include highly plasticized PVC (pPVC) [5], acrylonitrile-butadiene-styreneterpolymer (ABS) [16] and poly(methyl methacrylate) (PMMA) [10], where the elastic modulus has shown different behavior. While ABS/leather and PMMA/leather composites exhibit decrease in elastic modulus or a slight increase as leather fiber content increases, p-PVC/leather composites show similar behavior to PVB/leather composites, i.e., the elastic modulus is strongly influenced by fiber content, especially at compositions exceeding 30 wt% leather fibers. It should be pointed out that both polymer/leather composites where the elastic modulus increases considerably with increasing amounts of leather fiber, had plasticized thermoplastic matrices, i.e., p-PVC and PVB used in this study. The reduction in tensile strain of the PVB/leather composites may be attributed to a reduction in the deformation ability of the matrix due to the concentration of leather fiber agglomerates [17].

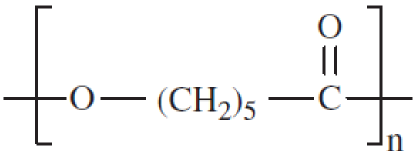
It should be mentioned that, despite the fact that the mechanical properties of this composite did not show great improvement, this material has presented all the adequate standard properties for its use in shoe soles and insoles: abrasion resistance, hardness, tear resistance, adhesion to commercial glues, flexibility or folding ability, appearance etc. and is currently being tested in shoe factories with success. By means of a simple and cheap processing technique, i.e., a harvest feed extrusion equipped with a Maillefer single screw, composites were manufactured with suitable properties for use as shoe soles, to be returned as a raw material to the shoe industry chain, facilitating approval of the recycled products by the regulatory agencies

CHAPTER 2

LITERATURE REVIEW

2.1 POLYCAPROLACTONE (PCL)

Poly(ε-caprolactone) (PCL) is a linear polyester manufactured by ring-opening polymerization of a seven-membered lactone, ε-caprolactone.



$$\left[-O-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}- \right]_n$$

Fig.1: Structure of PCL

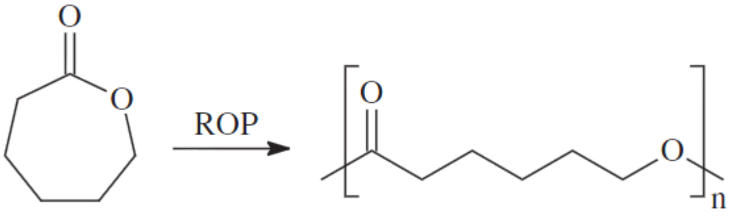


Fig.2: Ring opening polymerization of caprolactone

PCL is a semi crystalline aliphatic polyester and is of great interest as it can be obtained by ROP of a relatively cheap monomeric unit “ε -caprolactone” and is known for its extremely low Tg (- 60^{o}C) and long-term degradation properties (>24 months to lose total mass). The low melting-point makes the material suited for composting as a means of disposal, due to the temperature obtained during composting routinely exceeding 60^{o}C [38]. PCL is an attractive polymer to use based on its elastomeric properties and high elongation [39]. For biomedical applications, PCL has been approved for use by the FDA since the 1970s and can be found in many common sutures and suture components. In the recent past, PCL has been used more and more by tissue engineers. Specifically with PCL, some of its attractive qualities are its enhanced solubility in organic solvents, ability to be processed at low temperatures, and its non-toxic degradation byproducts. One of its most attractive qualities for use in biomedical applications is its slow rate of degradation. PCL degrades by hydrolysis and will lose about 50% of its strength in 8 weeks using an *in vitro* degradation test [40]. Because of its attractive mechanical properties and ability to blend easily, many researchers have turned to using co-polymerizations of PCL with various starches to reduce production costs and to also encourage cell growth with the presence of a natural biopolymer. When blended with starch, the non-isothermal crystallization rate of PCL is increased. This reinforced PCL and its damping properties, provide attractive qualities for biomedical applications that undergo extensive mechanical strain, such as orthopaedic implants [40]. PCL has also been blended with higher amounts of starch to increase its degradation rate. With higher starch content, PCL is more susceptible to enzymatic degradation by proteinase K49 [41]. PCL has been blended with several other polymers, including PEO, PLA, and PGA in the past and has been used in many studies relating to biomedical applications.

Tradename	Supplier	Origin	Website
Tone	Union Carbide	USA	www.unioncarbide.com
CAPA	Solvay	Belgium	www.solvay.com
Placcel	Daicel Chemical Indus.	Japan	www.daicel.co.jp/english/kinouhin/ category/capro.html

Table 1: Polycaprolactone manufacturers

Properties

Polycaprolactone (PCL) was developed as a biodegradable plastic of aliphatic polyester typederived from the chemical synthesis of crude petroleum. It has a low melting point (60°C), low viscosity of its melt and it is easy to process. PCL has good water, oil and chlorine resistance. The PCL chain is flexible and exhibits high elongation at break and low modulus. The elongation at break and tensile strength of PCL films have been reported to be between 450 and 1100% and 25 and 33 MPa, respectively. These values are quite high as compared with the elongation at break, 500–725%, and tensile strength, 9.7–17.2 MPa, of low density polyethylene. The main drawback of PCL is its low melting point which can be overcome by blending it with other polymers or by radiation crosslinking processes resulting in enhanced properties for a wide range of applications.

Processing

PCL can be processed by the usual thermoplastic processing techniques, including blows and slot cast film extrusion, sheet extrusion, and injection moulding. The low melting point of PCL polymers requires lower temperatures than polyethylene and other polyolefins.

Applications

PCL was recognized as a biodegradable and non-toxic material. Its high permeability to low

molecular species at body temperature and biocompatibility makes PCL a promising candidate for biomedical applications, such as controlled drug delivery. PCL is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopaedic splints, and fully biodegradable bags, sutures, and fibres. PCL is often mixed with starch to obtain a good, biodegradable, low cost material.

Due to the presence of chromium in leather fibers, relatively low processing temperatures must be used, which makes PCL a very interesting polymer matrix for the development of PCL/leather composites.

2.2 LEATHER BUFFING WASTE

The leather buffing powder from leather industry is one of the natural resource not utilized for any useful purpose. The finished animal skin, called leather is composed of two layers with distinctly different structure. The upper layer, which includes the entire length of hair follicles, is called grain layer. The second inner layer, composed of mostly thick bundles of collagen fibers, is called corium. These bundles are interwoven in a random, three-dimensional fashion. During the leather products manufacturing process, the inner-collagen layer of the finished leather is buffed to get a smooth and fine finish. This process gives a fine powder of collagen fibrils in large quantities in leather industries, which is a polymer of significant importance. Compared to studies on natural fibers such as jute, sisal, coir, pineapple, and bamboo, less effort has been focused on this type of leather waste. As these waste fibers are found in large quantity, there is a great interest in finding new applications by mixing it with synthetic thermoplastics.

The driving forces behind the use of the leather waste are cost, annually renewable resource utilization, and environmental benefits.

2.3 COMPOSITION OF CROME TANNED LEATHER WASTES

Hongjun H. et al (2001) have investigated the properties and composition of solid wastes generated from different types of leather-producing tanneries i.e. garment, shoe upper sole etc.

Leather fibers show particular characteristics because collagen, the main component of these fibers, is composed of long amino acid chains, as well as chromium oxide complexes, which are added artificially to impart stability and degradation resistance to fungi and other micro-organisms during use.

Leather is made from animal hides, which have been chemically treated to preserve quality and natural beauty. The chemical procedure used to ready raw animal hides for use is called tanning, which is a treatment of the hides so that micro-organisms cannot break them down for food, and thus damage them. Tanning produces a permanent change in the hides that converts them into a useful product. [18]

Before tanning, a process includes curing, soaking, fleshing, liming, de-liming, bating and pickling is used to rid the hides of non-collagenous proteins, epidermis, hair, globular proteins, melamine, components of cell walls, and other foreign substances while keeping collagen fiber skeleton untouched. This process also increases the water in the hide to the amount close to that of "living" hide and loosens the structure. [19] After tanning, hides go through dyeing, rolling and finishing to obtain the final product.

Generally, there are two types of tanning, vegetable tanning and chrome or mineral tanning. Which type of tanning procedure is to use depends largely on the hide itself and the resulting product intended. Hides tanned with chrome are pickled first in an acid and salt mixture to reduce the pH of the pelt to a level suitable for chrome tanning. From there, hides are soaked into a chromium-sulfate solution, in which the free carboxyl groups and other reactive sites in collagen form coordinate complexes with chromium salts. Figure 3 shows the three stages in the cross linkage of a chrome tannage.[20]

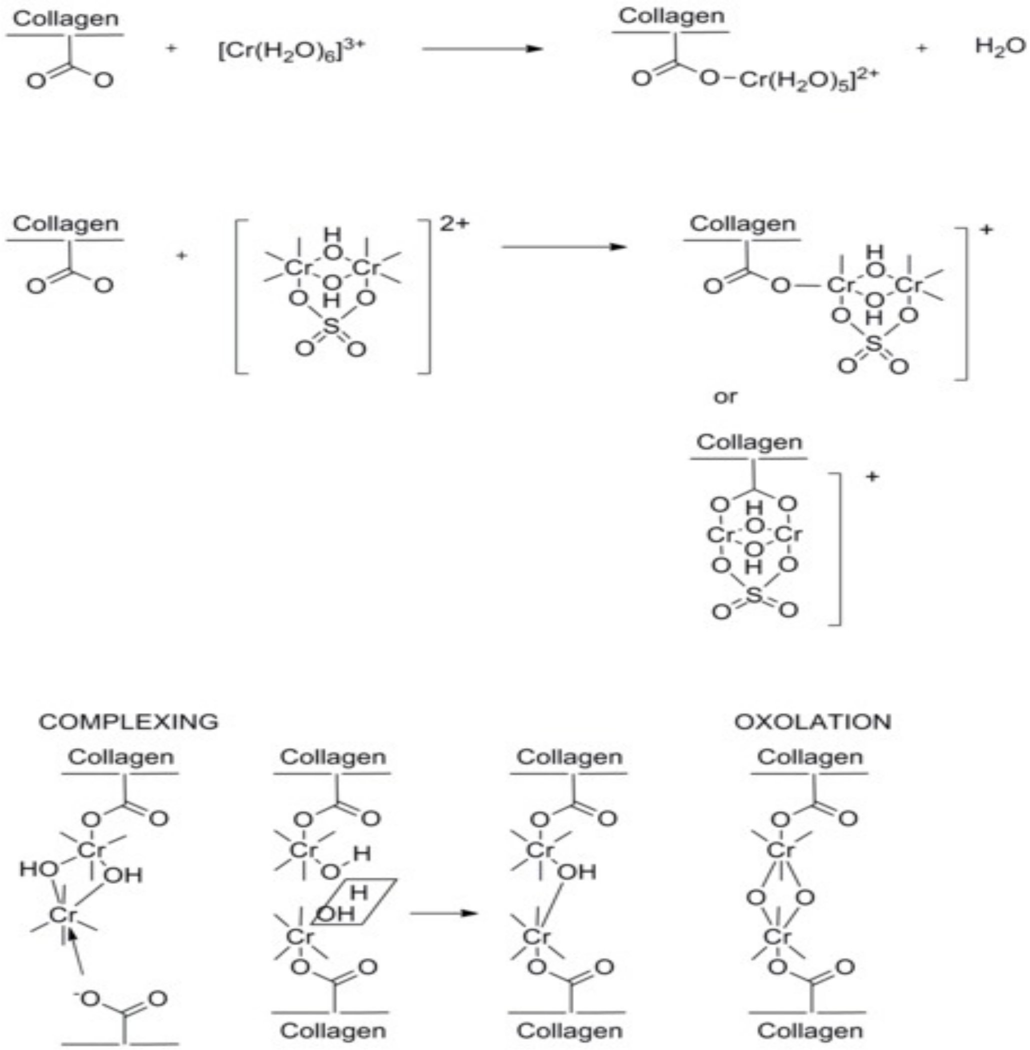


Fig.3: Three stages in the cross linkage of a chrome tannage

(a) **Crosslinking**: the chrome complexes have reacted with the protein carboxyl groups

(b) **Basification-oxolation**: as the pH of the tannage is increased, the sulfate associated with the chromium is displaced by the hydroxyl. The hydroxyl groups become shared by chromium atoms through oxolation.

(c) **Oxolation**: upon drying, the tannage becomes more stable as the complex gives up hydrogen ions and oxolation results.

Every year, there are thousands of tons of leather powder (wet blue shavings)produced in the process of thickness reduction of wet blue in preparation for finished leather manufacture. This waste leather material would have to find its way to our world's land fills and probably cause environmental problem if it is not properly disposed of.

Fortunately, people have been trying to change it into value-added product for thepast two decades.

2.4 POLY (VINYL BUTRYAL)-LEATHER COMPOSITES:

Ambrósio et al., 2011 [17] have prepared & characterized 'All Green Composite' by incorporation of leather fiber waste into a recycled Poly (vinyl butryal) matrix from the laminated safety glass from automotive

Poly (vinyl butyral) is a vinyl butyral and vinyl alcohol amorphous random copolymer produced by the condensation of polyvinyl alcohol with butyraldehyde in the presence of an acid catalyst. Its elastic properties, toughness, and greater adhesion to inorganic materials such as glass can be determined according to the percentage of each monomer present in the chain.

The main application of PVB lies in laminated safety glass, particularly in the automotive, aerospace, and architectural glass sectors. These products generate a large volume of PVB that has not yet been widely destined for recycling.

Prior to the extrusion process, the leather fibers and PVB flakes were dried in a drying oven at 70°C for 4 h to remove moisture and prevent the degradation of PVB under further heating. This drying step is important due to the hygroscopic nature of the materials. Then, the two materials were mechanically mixed in the solid state in three mass proportions (70/30, 50/50, and 30/70) and processed in an extruder equipped with a Maillefer screw with a 45 mm diameter, L/D= 25, from Miotto, Brazil, using a flat die measuring 150.0 mm in width and 2.0 mm in thickness. The temperature profile was 155°C/170°C/175°C in the extrusion barrel and 180°C in the extrusion head, and the screw speed was 20 rpm. After extrusion, the composite plates were compression molded at a temperature of 180°C under 20 ton of pressure to improve surface finishing. A final thickness of 3.50 mm was obtained for the samples to be used in mechanical tests.

Thermal analyses (DSC and TGA) and dynamic mechanical analysis (DMA) of PVB and leather fibers showed important characteristics to consider in the mixing process. TGA analysis showed that the leather fibers are very hygroscopic and showed no significant weight loss up to 250°C; the PVB was thermally stable up to 200°C. The DSC analysis confirmed the loss of water from the leather fibers through an endothermic transformation in the vicinity of 100°C, thermal stability up to 250°C and the initiation of collagen degradation at 325°C. DMA analysis showed that the recycled PVB is plasticized with a Tg around 30°C and that the plasticizer remains in the PBT after extrusion. According to these results, a thermal profile of 180°C for the extruder was adopted, and there was a need to dry the components of the composites before the mixing process.

FTIR analysis of PVB in flakes and after processing by extrusion showed no significant differences between the two samples. The spectra showed stretching of the R1-C(=O)-C-R2 group, which is an ester group and possibly an ester plasticizer. The information provided by the FTIR analysis is in agreement with the DMA results obtained for PVB.

Morphological characterization by SEM of the PVB/ leather composites showed that the leather fibers are present as agglomerates and are well distributed in the PVB matrix. The micrograph analysis showed that there are many interfaces with good interfacial adhesion between the PVB matrix and the leather fibers. Because the paths of the cryogenic fractures occurred within some leather fiber agglomerates, the interface may have transferred the stress of the matrix to the leather fibers. We observed agglomerates that had leather fibers extracted from their central region, while the fibers in the outer region, in contact with the matrix, remained unchanged. The good interfacial adhesion was attributed to the interaction between the molecular structures of the PVB, fibers, and collagen.

The mechanical properties of the PVB/leather composites were strongly influenced by the leather fiber concentration. The tensile strength of the composites was lower than that found for neat PVB. However, the tensile strength tends to increase slightly when increasing the amount of leather in the composites. This behavior was attributed to good interfacial adhesion and the fact that, with increasing wt% of leather, the fiber agglomerates are closer to each other. Therefore, the PVB may have acted as an adhesive between the agglomerates and transmitted the stress of one agglomerate to another. The elastic modulus increased considerably with increasing amounts of leather fiber in the composite. This behavior was attributed to the fact that the leather fiber agglomerates are very close to each other, with possible entanglement between them. With the flexibility of the leather fibers and the matrix of plasticized PVB, the leather fiber agglomerates could be closer and experience entanglement with increasing wt% of leather. The entangled agglomerates covered by the PVB matrix could strongly increase the stiffness of the composite and hence the elastic modulus.

The properties of hardness, wear resistance and tear resistance of the PVB/leather composites were considered satisfactory and showed behaviors expected for this type of composite.

2.5 POLYVINYL CHLORIDE-LEATHER COMPOSITES

Babanas et al. (2001) [7] have studied plasticized PVC filled with waste leather particles.

PVC plasticized with 80 parts of diisooctyl-phthalate (DOP) per 100 parts of resin (w/w) was used as matrix. Chormiumtanned, finished leather granules were mixed in laboratory scale banbury mixer at 160°C at 30 rpm. Different compositions prepared with leather content 0, 20, 30, 40, 50 & 60 phr. These compositions are moulded into sheet using hydraulic press with heated plates, on which further mechanical tests are carried.

Further improvement of mechanical properties of the produced specimens is attempted by surface coating treatment of the leather granules with thin film of ethylene-vinyl acetate copolymer. This treatment aims at the improvement of interfacial characteristics between matrix and filler which is necessary in order to obtain good final properties.

Based on the results of mechanical testing, It is concluded that this work showed that chromium treated, finished waste leather granules could be useful as filling material for PVC, in order to design final products suitable for the shoe industry or even for other uses, due to their leather-like appearance. However, the use of those products is restricted to applications where dark colors are acceptable. It is found that the density, wear resistance and Shore D hardness of the leather containing specimens improve, whereas their mechanical properties are considerably deteriorated with the incorporation of leather. The upper level of leather content, is set at the concentration of 40 phr. Treatment of the leather granules with EVA solution seems to produce a coating that promotes adhesion and proper wetting of the granules, thus improving the tensile strength of filled specimens up to 30%.

T. J. Madera-Santana et al (2002) [12] have examined the mechanical performance of composites formulated with PVC and short leather fibers (SLF) chemically modified with PMMA.

Chrome tanned short leather fibers were chemically modified by emulsion polymerization of PMMA onto them, producing a significant polymer coating, which is partially deposited & partially grafted on the surface of collagen chains. The chemical modification was carried out by aqueous emulsion polymerization initiated by a redox system (potassium persulfate and sodium metabisulfite). Three different formulations of reactive systems were used with Monomer/Leather ratio as 0.5, 1 & 2.5. PVC plasticized with Di-isodecyl phthalate was used as matrix

The pPVC-leather fiber composites were prepared in a Haake Rheocorder (Model Rhecocord 90) coupled to a mixer head (Model Rheomix 600). The mixing temperature is fixed at 170°C and the mixing sequence was designed so as to allow the dispersion of the fibers. The pPVC was poured into the chamber and stirred for 14 min at 10 pm in order to ensure a homogeneous melt. Subsequently, the loading of the SLF was varied from l0%, 20%. 30%, and 40% by weight of the whole mixture. The mixing was carried out for 10 min at a rotor speed of 50 rpm. Finally, the mixture was removed from the chamber and compression molded using a laboratory press. The compression was performed at a pressure of 10.4 MPa. The sample was heated at 180°C for 5 min, and subsequently cooled using re-circulating water for 10 min. DuPont Mylar foil was used between the mold surfaces in order to reduce marks on the sheets. The composites based on treated and untreated leather fibers were produced using the same procedure.

Each composite sample was kept at room temperature for 3 days before testing. Tensile and tear tests were carried out following ASTM Standards D638 and D624, respectively. Both tests involved the use of a universal tensile machine (J. J. Lloyds Instruments, Model 2001, with a 2.5 KN load cell and a crosshead speed of 5 mm/min. A scanning electron microscope (Cambridge SEM-Stereoscan) was used to analyze the fracture surfaces resulting from the tensile and tear tests.

From these results, a number of conclusions about the mechanical performance of these composites were made.

- As the amount of grafted/deposited PMMA onto SLF increases, the tensile strength of the resulting composite also increases. This result is assigned to a better stress transfer between matrix and fiber, resulting from the known compatibility between pWC and PMMA [21, 22]. Similarly, the elastic modulus of the composites begins to increase as the fiber content in the composite increases. The treated fibers enhance composite stilbess when the fiber content is above 20 wt%. This is attributed to higher fiber-matrix interaction.
- SEM observations of fractured surfaces in mechanically tested composites show the existence of bonding between the treated SLF and the pWC matrix, and There is an improvement in interfacial adhesion. Fiber adhesion improvement also plays a role in the decreasing tendency of the composites to elongate. The failure of the material is caused by fracture of the interface rather than by fiber pullout from the matrix.
- Finally, this work demonstrates that SLF wastes treated chemically on the surface can be used to produce composites with improved properties, at certain concentration of fibers, that could be suitable for certain applications in the footwear or leather industry. Chemical treatment techniques to improve mechanical properties are similar to other treatments used to enable natural fibers to be incorporated into composites as filler. Furthermore, it provides a feasible solution to reduce the pollution generated by short chromium tanned leather fibers. The composites produced could be used as a replacement for synthetic leather-like materials.

2.6 POLYAMIDE-LEATHER COMPOSITES

O. Mohamed et al (2009) [23]have investigated use chrome leather waste as reinforcement in Nylon 6 matrix, to satisfy the environmental needs, reduce cost of polymer production, and finally to improve the properties of polymer. The influence of this addition as a filler on mechanical, physical and thermal stability properties are investigated.

Nylon 6 based composites were prepared by mixing the components in a Brabender apparatus operating at 230°C and 70 rpm for 5 min. The mixing ratios of Nylon 6/leather wastes were 98 : 2, 96 : 4, 92 : 8, and 88: 12 in addition to blank sample. Nylon 6 and Nylon 6 based leather wastes composites were compressed to sheets form between two stainless plates pressed at 160°C for 5 mins at 100 bar was for 5 min, then the plates were rapidly cooled to room temperature.

Physical, Mechanical & Thermal characterization of composite was carried out. It can be seen from the results that with increasing percentage of leather waste in composite hardness, Water absorption increased. Mechanical properties i.e. Tensile Strength, Percent Elongation values were decreased with increasing leather contents.

Degradation temperature for composites was reduced from 320°C to 290°C as leather content increase from 0 to 12 Percent, as understood from TGA results.

These work demonstrated that leather waste could be used as filler to produce composites of Nylon which are suitable for replacement of nylon for cost reduction in certain applications where reduced mechanical properties are tolerable.

2.7 ABS-LEATHER COMPOSITES

B. Ramaraj (2006), [24] reported the preparation & evaluation of ABS/Leather Waste Powder composites.

Among the synthetic thermoplastics materials, ABS is a popular plastics in industrial as well as commodity applications and being used in many fields like defence, aerospace, automobile, electrical, computer, telecommunications, and appliance applications. ABS is a hard and tough thermoplastic terpolymer with good impact strength and surface gloss. However, it is not an environment friendly material, resistant to environmental degradation after its use, and becomes a critical problem to the plastics industries.

The thermoplastic polymer–ABS was used as the matrix and leather buffing powder material as the filler to prepare a particulate reinforced composite to examine the possibility of using leather waste as reinforcing filler and to test for the physical, mechanical and thermal properties of the composites according to the reinforcing filler content with respect to thermoplastic polymer.

The ABS granules and powder were premixed in a high speed mixer (Henschel, Germany, Model FM 10 LB). The mixed material was extruded in a twin screw extruder (Berstorff, Germany) with L/D ratio of 33 with temperature profile of 175–215°C. The extruded strand was pelletized and stored in sealed packs containing desiccant. Six levels of filler loading (2.5, 5, 7.5, 10, 12.5, and 15 wt %) were designed in sample preparation.

These specimens were tested for mechanical and thermal properties. The test results indicate that the incorporation of leather waste powder does not affect the tensile, flexural strengths, Izod impact strength, abrasion resistance, Rockwell hardness, density, and HDT and VSP values drastically. However, the tensile modulus, tensile elongation, and Charpy impact strength values are reduced significantly. These results are generally observed phenomena in non-compatible polymer blends. However, the main purpose of this work was to study the effect of leather waste on the mechanical and thermal properties of the ABS resin to reduce the cost, resource utilization, and get environmental benefits.

2.8 RUBBER-LEATHER COMPOSITES

Leather waste fibers added to elastomers could function as short fiber reinforcement for the matrix, provided their inherent fibrous nature is retained during processing [25, 26]. However, since processing of elastomers is carried out at relatively high temperatures, retention of the fibrous nature may be difficult. Additionally, use of leather in rubber formulations is prone to affect the vulcanization characteristics and vulcanizate properties due to the presence of reactive functional groups, trivalent chromium content, and its acidic nature. Procedures for neutralizing the acidic nature of the leather may be employed before they are added to rubber. However, these procedures require several preparation steps including wet treatments followed by fiber drying.

Ravichandran et al. [26,27] have studied scrap rubber recycling in natural rubber using untreated and neutralized fibrous particles of leather shavings (material just tanned with no retanning, fatliquoring, dyeing, or finishing applied) as processing aid. The untreated material being acidic in nature, reduces the vulcanization characteristics and mechanical properties of the compound, but improves the incorporation of higher amount of scrap rubber. To overcome the acidic nature, 1% solution of urea, aqueous ammonia, and sodium bicarbonate were used separately as neutralizing agents. Results indicate that neutralized leather wastes can assist the addition of large quantities of scrap rubber into a virgin rubber matrix without affecting the vulcanization characteristics seriously. Mechanical properties of natural rubber-scrap vulcanizates containing neutralized leather particles are better when compared with the vulcanizates containing untreated leather particles. The natural rubber-scrap compositions containing treated leather could be processed safely in the temperature range of 413-423 K without much reversion in the matrix.

Neutralized leather shavings have also been studied as filler for nitrile rubber reinforcement. Shavings neutralized with $Na_2CO_3$and NH_3showed improved vulcanization characteristics and mechanical properties, whereas NaOH neutralized shavings exhibited poor properties. Swelling of the vulcanizates in water and 1% NaOH was found to increase with leather loading, whereas in methyl ethyl ketone a reversed trend was observed. Thermogravimetric analysis indicates that thermal stability of the vulcanizates fall between those of pure leather and nitrile rubber vulcanizate [28].

Aldehyde-tanned leather powder and chrome shavings reduced to powder (< 0.2 mm), either in the tanned or detanned condition, were added to synthetic isoprene rubber (IR). The thermal measurements indicate the three types of powders decomposed to a minor extent at the vulcanization temperature of 423 K. The tensile strength before and after aging the vulcanizates filled with chrome-tanned leather powder is slightly higher than those obtained with detanned or aldehyde-tanned leather powder [29].

Shavings of chromium-tanned wastes have been used to fill (with five parts by weight) IR, carboxylated acrylonitrile butadiene rubber (XNBR), and acrylonitrile butadiene rubber (NBR), and the obtained vulcanizates are reported with good usable properties and as being biodegradable [30]. Chromium-tanned fat-liquored leather buffing dust was recently used as a filler for XNBR and NBR, and the dust added to rubber mix brought about an improvement in mechanical properties, and increased thermal aging as well as electrical conductivity [31]. The best properties are shown by vulcanizates containing five parts by weight of the buffing dust after previous blending with five parts by weight of ZnO (renders dust surface more alkaline favoring dispersion and vulcanizate properties).

The effect of incorporating finished chromium-tanned leather short fibers on the properties of the two polymeric bases more frequently used in shoe rubber soles, respectively, SBR and NBR, has been studied by Maria J. Ferreira And Fernanda Freitas[32]at Portuguese Footwear Technological Centre. The leather fibers employed when added in the range of 10-20 phr originate composites that fulfil the day-to-day soles use criteria defined by CTCP for materials with this application. The composite materials obtained have a noticeable 15% improvement in the tear strength, compared with the base gum vulcanizates, and the remaining properties are within the recommended values for that kind of application. As expected, tensile strength and elongation at break are the more adversely affected properties. So, these properties in the composite materials produced for sole application need to be assessed case by case.

The composites in the range of above 20 and till 100 phr leather fibers incorporation present physical properties acceptable for in-shoe applications.

The possibility of using the leather fibers as additives in shoe rubber components and the large availability of the leather waste material creates the opportunity of improving certain properties while reducing the price of the final product and gives a better option for finished leather wastes generated in the leather industries than the usual landfilling.

CHAPTER 3

EXPERIMENTAL WORK

3.1 OBJECTIVE

Main purpose of the current work is to develop completely degradable composite of Polycaprolactone by incorporating chrome-tanned leather buffing waste. Other objectives of the project are as follows:

1. Find the maximum weight percent of leather waste that can be incorporated in PCL.
2. Study the effect of leather waste on the mechanical & thermal properties of PCL resin to reduce cost, resource utilization & get environmental benefits.
3. Examine the compatibility between leather and PCL.
4. Synthesis of Maleic Anhydride grafted PCL & its use as compatiblizer for PCL-Leather composites.

3.2 MATERIALS

1. Polycaprolactone (CAPA 6800) was supplied in pellet form by Perstorp UK Ltd. (Warrington, UK).

Properties	**Value**	**Unit**
Avg. Molecular weight	80000	
Melting point, Tm	58-60	ºC
MFI (2.16Kg, @190º C)	7.29	g/10 min
Crystallinity	56	%
Crystallization temperature	27.4	ºC
Glass transition temperature, Tg	-60	ºC

Solubility parameter	9.34	$(\text{cal/cm}^3)^{1/2}$
Tensile Modulus	500	MPa
Density	1.1	g/cm3

Table2: Properties of PCL

2. Chromed-Leather buffing waste in the form of fibrous particles was supplied by Central Leather Research Institute (CLRI), Chennai.

Test	**Value**
Humidity, (wt%)	7.92
Greases and oils, (wt%)	1.97
Ash, (wt%)	12.86
Chrome oxide, (wt%)	3.41
pH in water extract	4.15
Nitrogen, (wt%)	9.71
Protein, (wt%)	54.58
Decomposition temp, (°C)	323
Diameter average, (µm)	4.52
Length average, (µm)	258.5

Table3 : Composition of chrome tanned Leather buffing waste

3. Maleic Anhydride laboratory grade

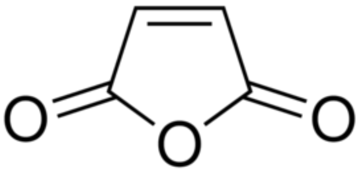


Fig.4: Maleic Anhydride structure

4. Benzoyl Peroxide laboratory grade

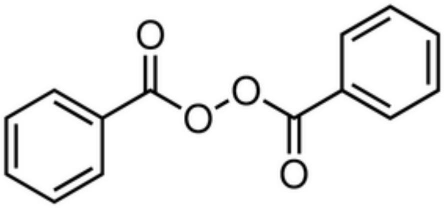


Fig.5: Benzoyl Peroxide structure

3.3 PREPARATION OF PCL/LEATHER COMPOSITES.

Leather buffing waste was dried in a recirculating convection oven at 70°C for 4 hours to remove moisture. Melt mixing of the PCL/Leather blend was carried out in a batch-operated lab-scale twin-screw DSM Micro Compounder, with operating parameters as follows:

1. Residence time- 5 min.
2. Screw speed- 100 rpm.
3. Temperature - 120°C.

Extruded strands are cut into pellets, which further used for sample preparation by compression molding.

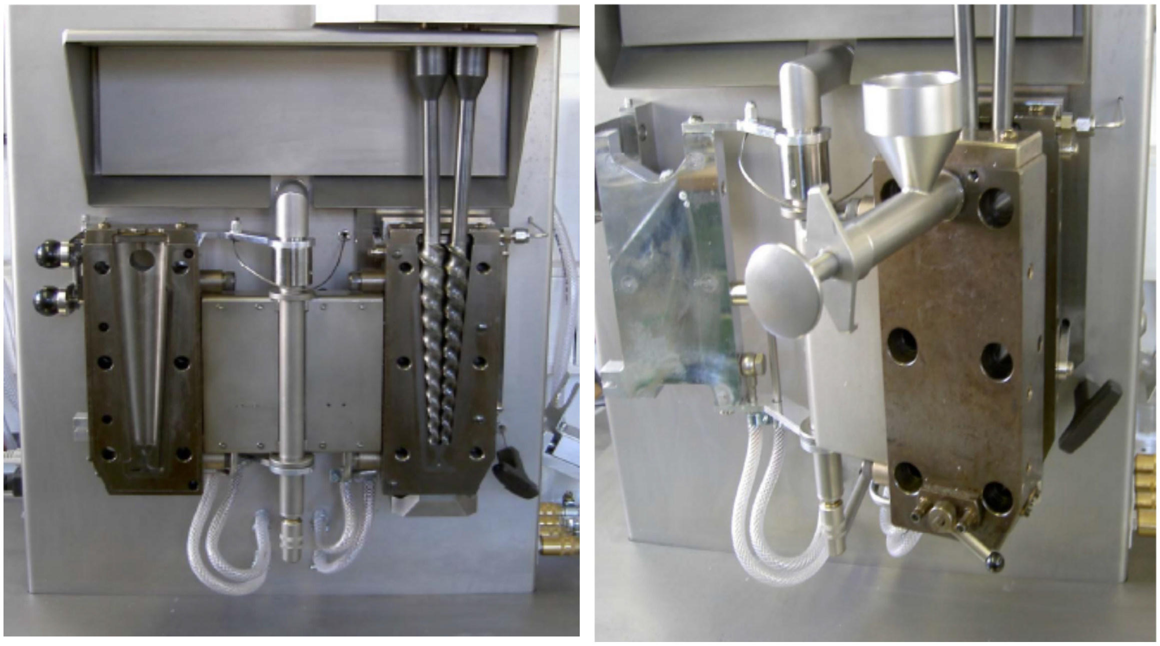


Fig 6: DSM Xplore micro-compounder

Blends of LEATHER and PCL are prepared on DSM Micro-compounder for the following compositions:

Sample Name	PCL %(w/w)	LEATHER %(w/w)
LPCL 0	100	0
LPCL 2	98	2
LPCL 5	95	5
LPCL 10	90	10
LPCL 20	80	20
LPCL 30	70	30
LPCL 40	60	40

Table 4: Composition of PCL-Leather blends

3.4 SYNTHESIS OF MALEIC ANHYDRIDE GRAFTED PCL (MA-PCL)

J.John et al reported the laboratory scale procedure for synthesizing Polycaprolactone-graft-maleic anhydride (PCL-g-MA). [33]. Similar procedure is adopted here following the optimum composition and processing conditions.

Polycaprolactone powder with 4.5% Maleic Anhydride and 0.5% Benzoyl peroxide (initiator) charged to batch extruder operating at 150°C and 100 rpm. 10 minutes of residence time is given for mixing. During all the processes, inert atmosphere is maintained to eliminate the role of oxygen in mixing reaction by maintaining continuous flow of nitrogen in mixing chamber.

Strands from the extruder are allowed to cool and then cut into pellets. The obtained grafted polymer was completely dissolved in chloroform with stirring and the resulting homogeneous solution was slowly precipitated into a large excess of methanol. The precipitated polymer was washed with fresh methanol and dried in a vacuum oven at 50° C for 24 h.which further used as compatiblizer for PCL-Leather composites.

PCL-Leather composite containing 30% of leather waste and compatiblized with 5% PCL-g-MA is melt blended by same procedure described before.

3.5 SAMPLE PREPARATION

- Specimens for Tensile Testing (ISO 527 type 5A):

  Dumb-bell shaped with cross-section of 4×2.5 mm^2 and a gauge length of 20 mm.

Fig.7: Tensile Testing Specimens

- Water Absorption:

  Square of 10 mm and 2.5 mm thickness.

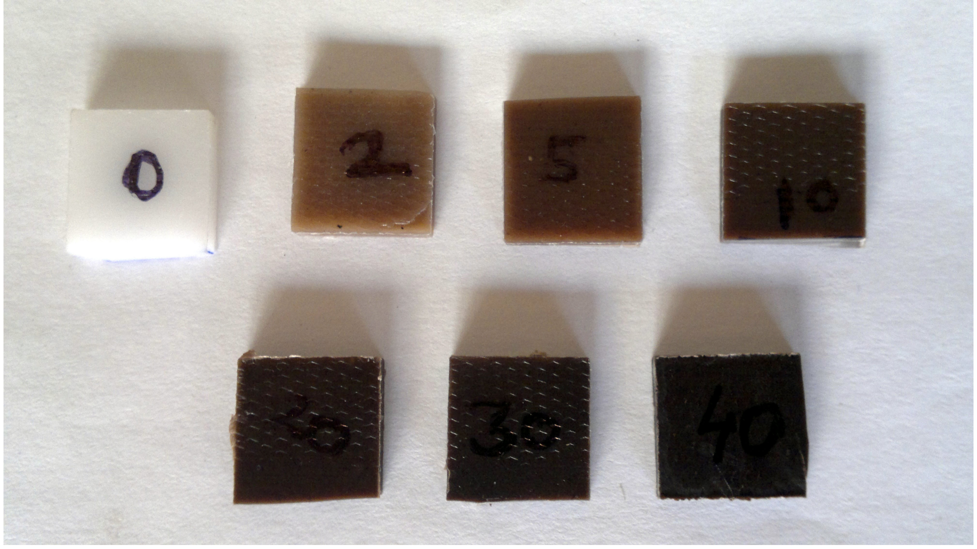


Fig.8: Water absorption test specimens

- Dynamic Mechanical Analysis samples

  Length: 44 mm

  Width: 8 mm

  Thickness: 2.5mm

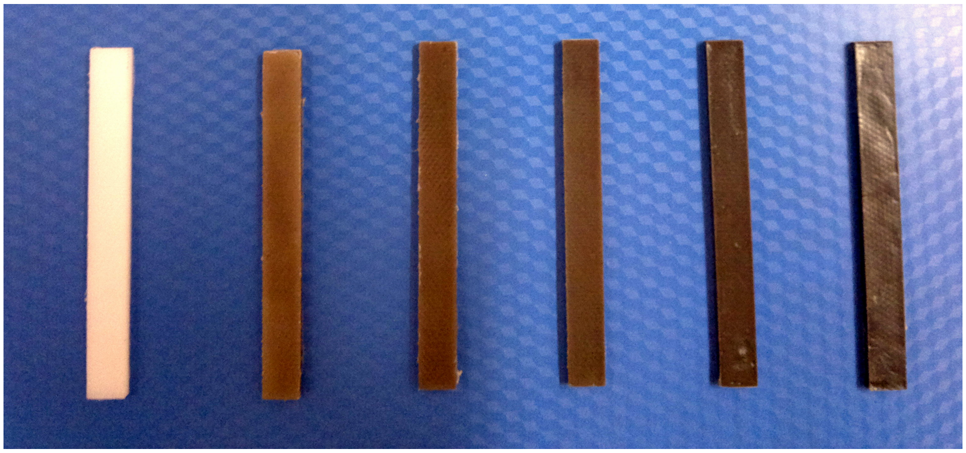


Fig.9: DMA testing samples

- FTIR samples

  Disc of 25mm diameter and 0.5 mm thickness.

Fig. 10: FTIR analysis samples

- SEM samples:

Compression molded specimens for DMA are used for SEM analysis. To study the morphology samples were freeze fractured in liquid nitrogen.

These sample are prepared by compression molding (hydraulic) process with following processing parameters

Pressure – 4000 psi

Temperature – 130^{0}C

Cycle Time – 15 min. (10 min cooling)

a.) b.)

Fig. 11: a) Polymer compression molding machine, b) compression mold

3.6 CHARACTERIZATION METHODS

3.6.1 MECHANICAL PROPERTIES

Tensile

The specimens of the type 5A (according to the ISO 527 standard) with cross-section of 4×2.5 mm^2 and a gauge length of 20 mm were tested with a crosshead speed of 5 mm/min in accordance with ISO 527.

Three replicate specimens were tested for the tensile properties of each composite formulation.

3.6.2 WATER ABSORPTION

The conditioned specimens were entirely immersed for 1 day, 3 days in a container of water at 23-28°C. At the end of each immersion time, the specimens were taken out from the water and all surface water was removed with a clean dry cloth. The specimens were weighed to the nearest 0.001g (using precision balance) immediately.

Water absorption (WA) was calculated according to the following formula:

$$WA\ (\%) = (M_e - M_o)/\ M_o \times 100$$

Where, M_e is the mass of sample after immersion (g)

M_o is the mass of sample before immersion (g)

3.6.3 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analysis (DMA) is a non-destructive technique widely used in the characterisation of polymer-based systems, including thermoplastics, thermosets, rubbers and composites, which is getting increasing importance in biomaterials research. Basically, it allows to characterize the viscoelastic properties of materials in a wide temperature and frequency ranges, by monitoring the sample's response upon an imposed controlled cyclic loads (with the corresponding development of stresses) or strain.

DMA of Polymers Provides Information on the Glass Transition Temperature, Sub T_g Transitions and Variation of Modulus With Temperature.

Samples were tested in 3-point bending fixture for Dynamic Temperature Ramp Test using RSA III model by TA instruments.

Dynamic Ramp Test: Temperature Ramp testing takes place at selected temperature ramp rates while holding a constant frequency and strain. Temperature is automatically incremented or decremented from selectable lower and upper temperature limits at selected rates.

DMA Test parameters are set as follows and change in modulus with temperature is recorded:

Initial Temperature: 25°C

Final temperature: 70°C

Temperature ramp: 10°C/min

Strain: 0.1%

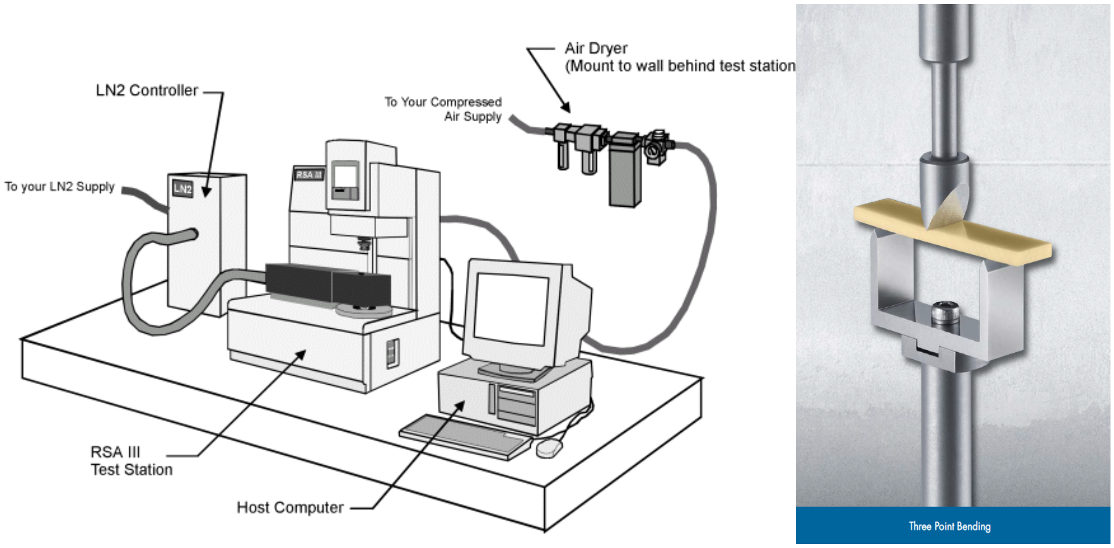


Fig 12: DMA analyzer with 3 point bending fixture

3.6.4 THERMAL ANALYSIS

Differential Scanning Calorimeter (DSC):

Differential Scanning Calorimetry is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature program.

DSC gives information about thermal transitions taking place in polymers such as melting, glass transition, oxidation etc. Also miscibility of Polymeric blend system can be examined by analysing shifts or change in crystallization peaks.

The crystallization and melting of PCL was measured using a Perkin–Elmer differential scanning calorimeter (DSC 2B) interfaced to a personal computer.

Samples were contained in aluminium pans, and an empty pan was used as a reference. Melting& cooling traces were obtained by heating from -90 to 100°C & then cooling back to -90°C at 10°C /min. The results were further analyzed by using TA Universal V4.0C software to obtain the melting temperature (T_m) and the corresponding enthalpy (H_m). The degree of crystallinity was calculated as follows, a linear baseline was drawn from the first onset of melting to the last trace of crystallinity and the enthalpy of fusion was then calculated from the area under the endotherm. The results were further analyzed by using TA Universal V4.0C software to obtain the melting temperature (T_m) and the corresponding enthalpy (H_m).

Degree of crystallinity (Xc) was defined as

$$Xc = \frac{\Delta H_f (T_m)}{\Delta H_f^0 (T_m^0)}$$

Where $\Delta H_f(T_m)$ is the enthalpy of fusion measured at the melting point and $\Delta H°_f(T°_m)$ is the enthalpy of fusion of the completely crystalline polymer (139.5 J/g for 100% crystalline PCL)

Thermo-Gravimetric Analysis (TGA)

Thermo-Gravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C.

The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.

The dynamic weight loss tests were conducted on a TA instrument 2050 thermogravimetric analyzer (TGA). All tests were conducted in a N2 purge (25mL/min) using sample weights of 5–10 mg over a temperature range 30–600°C at a scan rate of 10°C/min.

3.6.5 FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

FTIR spectroscopy of blend films was carried out in order to detect any peak shift that could be attributed to weak interactions between the two polymers, such as hydrogen bonding or complexation. Disc shaped samples of thickness 0.5mm prepared by Hot Press are used to perform infrared spectroscopy with attenuated total reflectance (ATR-FTIR). FTIR spectra were obtained using Perkin Elmer FTIR spectrometer with a DTGS detector at a resolution of $2cm^{-1}$ in the range 4,000 - 400 cm^{-1} with 32 scans for a signal averaging. This technique measures the surface composition, bonding, and structure and provides a limited compositional profile.

3.6.6 INTERFACIAL MORPHOLOGICAL ANALYSIS

Samples prepared of DMA analysis are freeze fractured in liquid nitrogen. The fracture surface was observed with a scanning electronic microscope (ESEM, FEI QUANTA 200) under an acceleration voltage of 30 kV. The morphology such as filler dispersion and interfacial adhesion of the components was investigated.

3.6.7 XRD ANALYSIS

The XRD intensity curves, recorded using a Rigaku Micromax-007HF X-ray diffractometer with a Cu target and Kα radiation at scanning rate of 2°C/min

CHAPTER 4

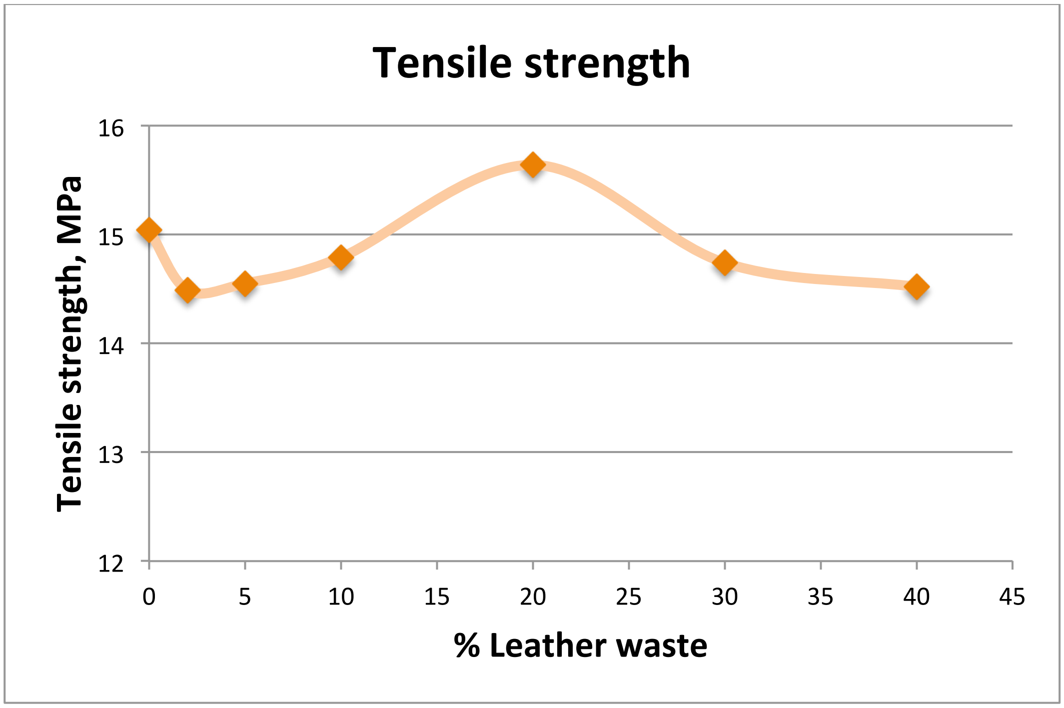
RESULTS AND DISCUSSION

4.1 MECHANICAL PROPERTIES

4.1.1 TENSILE STRENGTH

Sample Name	Tensile Strength (MPa)	Modulus (MPa)
LPCL0	15.04	359.5
LPCL2	14.49	380.0
LPCL5	14.55	397.6
LPCL10	14.79	468.6
LPCL20	15.64	601.7
LPCL30	14.74	663.6
LPCL40	14.52	953.4

Table 5: Mechanical properties of PCL-Leather composites

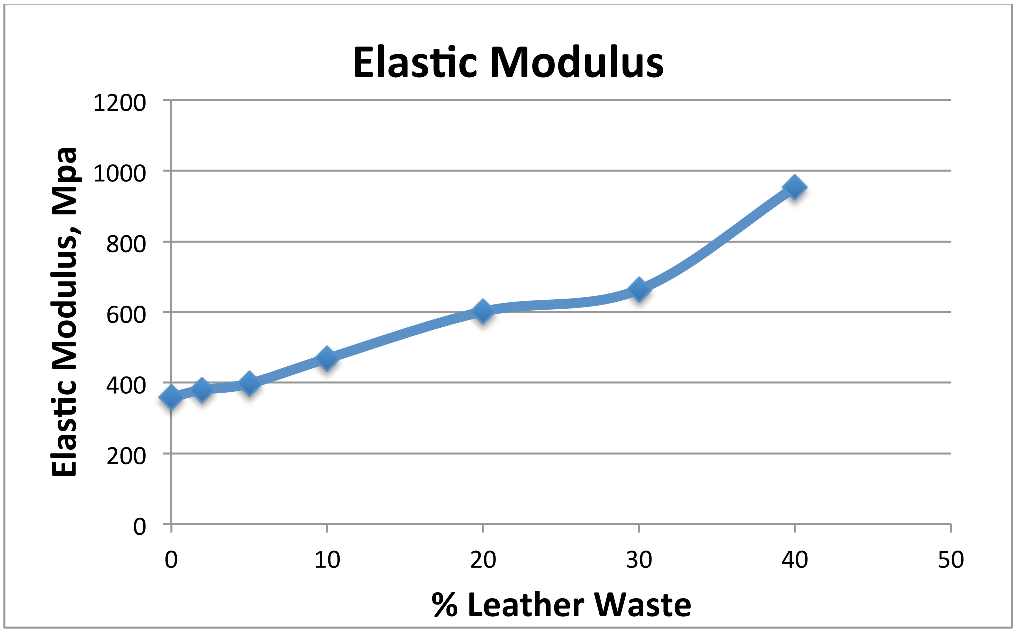


Graph 1: Tensile properties of PCL-Leather composite

The tensile test results of the composites made of leather waste and PCL matrix at different filler loadings are shown in Table 5. From the table, it is seen that for neat PCL, the tensile strength is 15.04 MPa. Though there is an insignificant drop in the tensile strength with a small amount (2%) of leather fibre inclusion, it is also observed that there is a slight increase in tensile strength from 14.49 to 15.64 MPa with increase in leather fibre loading from 2 to 20%. With further increase in filler content up to 40%, the tensile strength drops from a peak strength of 15.64 MPa to 14.52 MPa.

At lower percentages of leather fibers, fibers are well distributed as isolated fibers in the PCL matrix and are poorly bonded to the matrix. This lack of adhesion is mainly due to chemical and physical differences between leather fibers (made up of collagen macromolecules) and thermoplastic [34]. This lead to reduced tensile strength for compositions upto 10% loading compared to neat PCL. As leather percentages increases recovery in tensile strength is observed, which is attributed to formation bundles and agglomerates of leather fibers. The addition of further leather fiber contributes to an increase in the number and size of agglomerates, but not the number of isolated fibers. This means that the number of micro fractures originated in such fibers remains constant, leading to a net improvement of tensile properties as the non fissure-producing reinforcement volume fraction is increased. This is a kind of compound that "benefits" from having an increase in the number of fibers not leading to fissure. This result produces a positive balance and a consequential increase in tensile strength [5].

4.1.2 ELASTIC MODULUS



Graph 2: Elastic modulus of PCL-Leather composite

Graph 2 shows the variation of elastic modulus of PCL-Leather composite with percentage of leather waste incorporated. The elastic modulus shows an increase for filler concentration up to 30 percent, accompanied by a sharp increase beyond this point. The elastic modulus increased from 359.5 MPa for neat PCL to 953.4 MPa for composite with 40% leather fiber. Such a rapid and nonlinear increase of the elastic modulus with the concentration of fibers is not usually observed in thermoplastic composites with natural fibers.

Thus, the strong influence of the concentration of leather fibers on the elastic modulus of PCL/leather composites were attributed to the fact that leather fiber agglomerates are very close to each other, with possible entanglements between them. For composites with leather, this hypothesis is plausible because, when compared to wood fibers, which are rigid, the leather fibers are more flexible due to the presence of collagen. So the leather fiber agglomerates could be closer and experience entanglement with increasing wt% of leather. The entangled agglomerates covered by the PCL matrix could strongly increase the stiffness of the composite and hence the elastic modulus.

Studies related to PCL wood fiber composite have reported that improvements in the interfacial adhesion between the thermoplastics matrices and natural fibers do not have any significant influence on the elastic modulus [35].

Composite with 20 % percent of leather content shows optimum mechanical properties. Above which slight reduction in tensile strength with brittle fracture is observed. Considering processability of the composite in extruder 30% leather content represents a maximum tolerance of the polymer matrix under investigation, in order to produce workable materials with acceptable mechanical properties. High torque values, improper mixing, non-uniformity & high brittleness of the composites limit the further addition leather.

4.2 WATER ABSORPTION

Table 6 shows the effect of leather percent on water absorption of composite in 1 day & 3 days duration.

As the percentage of leather loading increases water absorption of composite increases, which is obvious behavior because the leather fibers are hydrophilic in nature. This property is of commercial significance in footwear and clothing industry.

Sample Name	Water Absorption (%)	
	1 day	3 days
LPCL0	0.274977085	0.412465628
LPCL2	0.812064965	1.044083527
LPCL5	1.294642857	1.830357143
LPCL10	2.386014647	3.543586109
LPCL20	4.113636364	5.909090909
LPCL30	6.85483871	9.520609319
LPCL40	11.90525232	14.02677652

Table 6: Water absorption of Leather-PCL composite

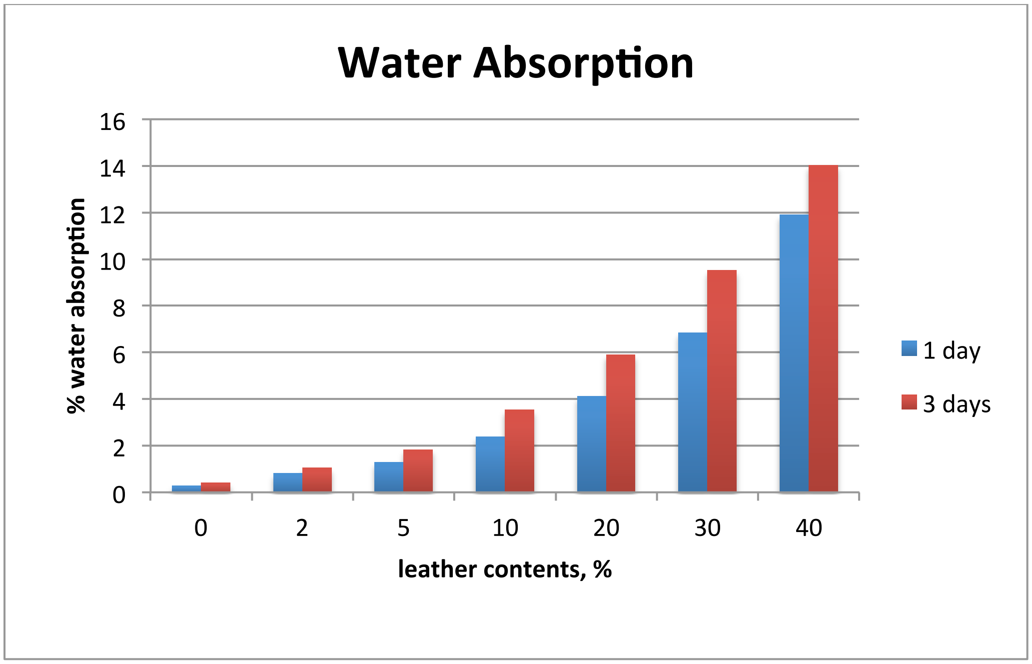
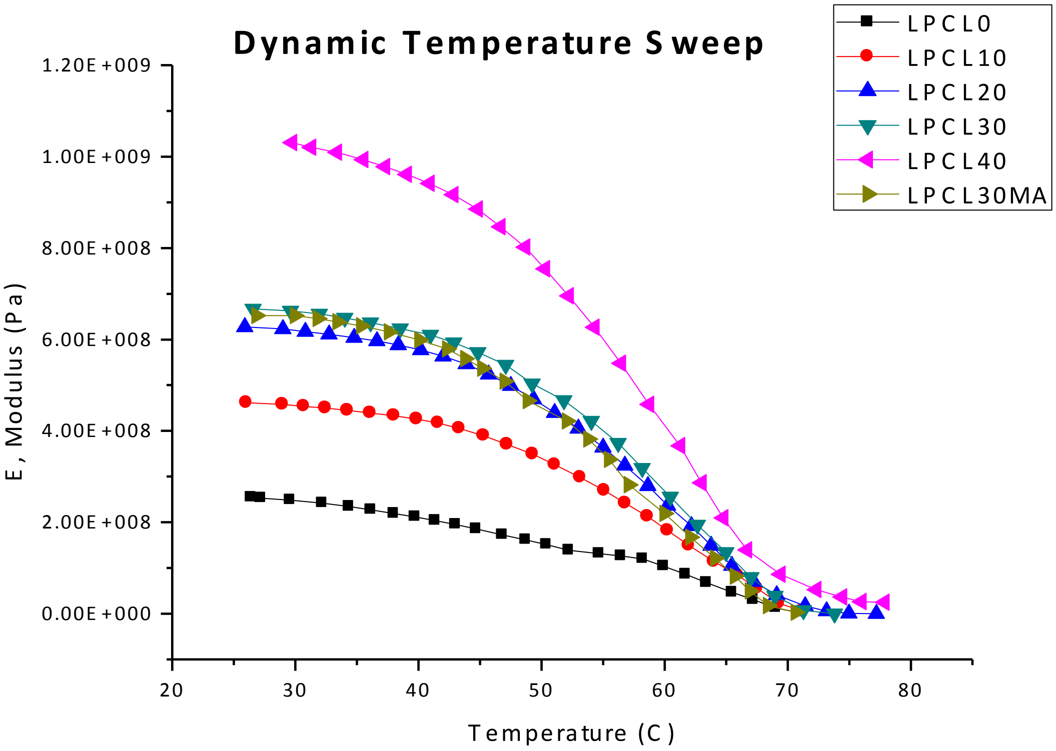


Fig.13: effect of leather contents on water absorption of PCL-leather composite.

4.3 DYNAMIC MECHANICAL ANALYSIS

Graph 3 shows the storage modulus E versus temperature curves obtained by DMA for leather-PCL composites. Sufficient formability or shapability of material at processing temperature is of crucial for many applications which can be determined by analysis of reduction in storage modulus at temperature of use.



Graph 3: DMA analysis curves.

As we can see from the dynamic temperature sweep curves addition of leather waste to PCL matrix improves stiffness at high temperature. DMA analysis is useful to evaluate use of leather polymer composite for splinting application, which is one of the major applications for PCL. As per the different modulus and temperature requirements of application blend composition can be determined from DMA analysis so as to get optimum performance at reduced cost.

Sample Name	Modulus, MPa		
	E @27°C	E @60°C	E27/E60
LPCL0	253	103	2.456311
LPCL10	462	187	2.470588
LPCL20	626	244	2.565574
LPCL30	666	268	2.485075
LPCL30MA	653	219	2.981735
LPCL40	1030	412	2.5

Table 7: DMA analysis results.

4.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Following method is used to get DSC thermogram for each sample

TA Instruments Thermal Analysis DSC

Method Log:

1: External event: On

2: Equilibrate at -90.00°C

3: Isothermal for 1.00 min

4: Data storage: On

5: Ramp 10.00°C/min to 100.00°C

6: Mark end of cycle 1

7: Data storage: Off

8: Isothermal for 1.00 min

9: Data storage: On

10: Ramp 10.00°C/min to -90.00°C

11: Mark end of cycle 2

12: Data storage: Off

13: Isothermal for 1.00 min

14: Data storage: On

15: Ramp 10.00°C/min to 100.00°C

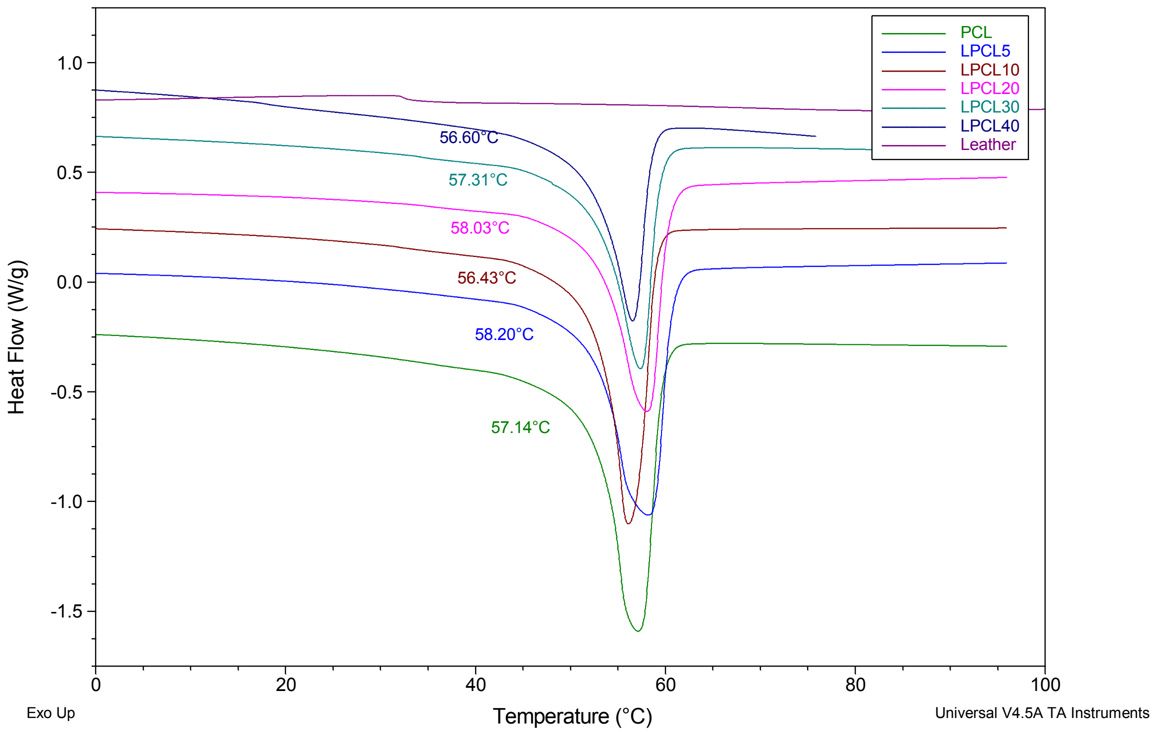
16: Mark end of cycle 3

17: Data storage: Off

18: End of method

As we can see from the DSC melting thermograms shown in Graph 4, there is no melting peak for pure leather sample which concludes that the leather waste is completely amorphous in nature. For pure PCL sample, a significiant melting peak is observed at 57.14°C. For other compositions containing leather and PCL, only one peak is observed which corresponds to melting of PCL also there is no shift in position of peak. This result confirms that there is no interaction between PCL & leather. The intensity of peak decreases proportionately to the increase in leather content. There is negligible effect of leather on melting temperature of composites. The melting temperature ranges from 56.6°C to 58.2°C.

Calculation of crystallinity & quantitative analysis of composite is reported in table 8.



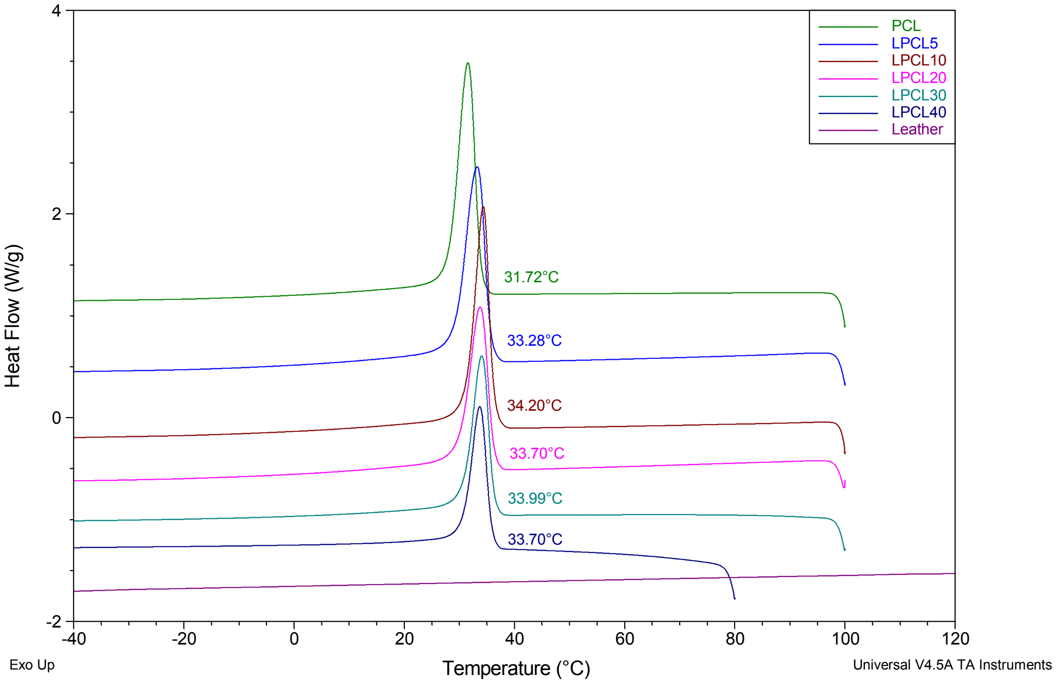
Graph 4: DSC melting thermograms for Leather-PCL composites.

$\Delta H^{\circ}_{f}(T^{\circ}_{m})$ for 100% crystalline samples of (From literature)

Polycaprolactone :$\Delta H_{f\ 100\%} = 135.4$ (J/g)

Sample Name	ΔH (J/g)	% Crystallinity	Leather %
LPCL0	62.95	46.5	-
LPCL5	59.31	43.8	5.78
LPCL10	55.05	40.6	12.5
LPCL20	48.38	35.7	23.14
LPCL30	41.15	30.3	34.6
LPCL40	composites.34.01	25.1	45.97

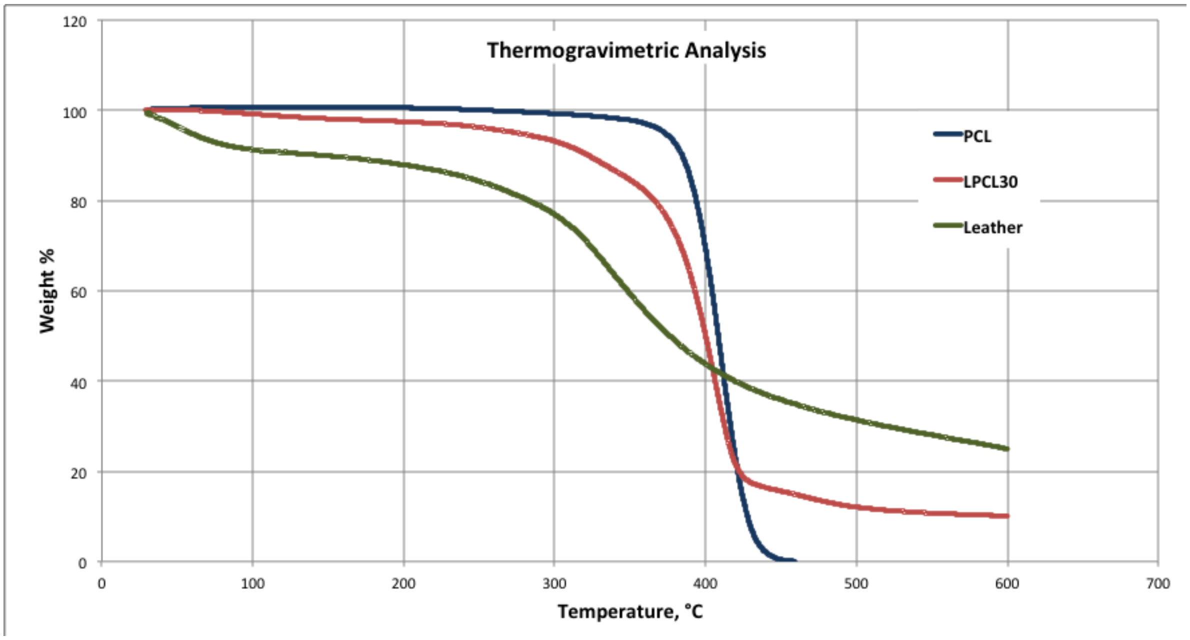
Table 8: crystallinity & compositional analysis of Leather PCL



Graph 5: DSC crystallization thermograms for Leather-PCL composites.

Crystallization thermograms in Graph 5 show the effect of leather content on crystallization temperature of composite. By incorporation of leather in PCL, crystallization temperature increased by 2°C to 34°C. This property can be beneficial for processing this composition by extrusion or injection molding in final products, as it will reduce the cooling time & so overall cycle time.

4.5 THERMOGRAVIMETRIC ANALYSIS (TGA)



Graph 6: TGA thermograms of leather waste, PCL & PCL with 30% leather waste

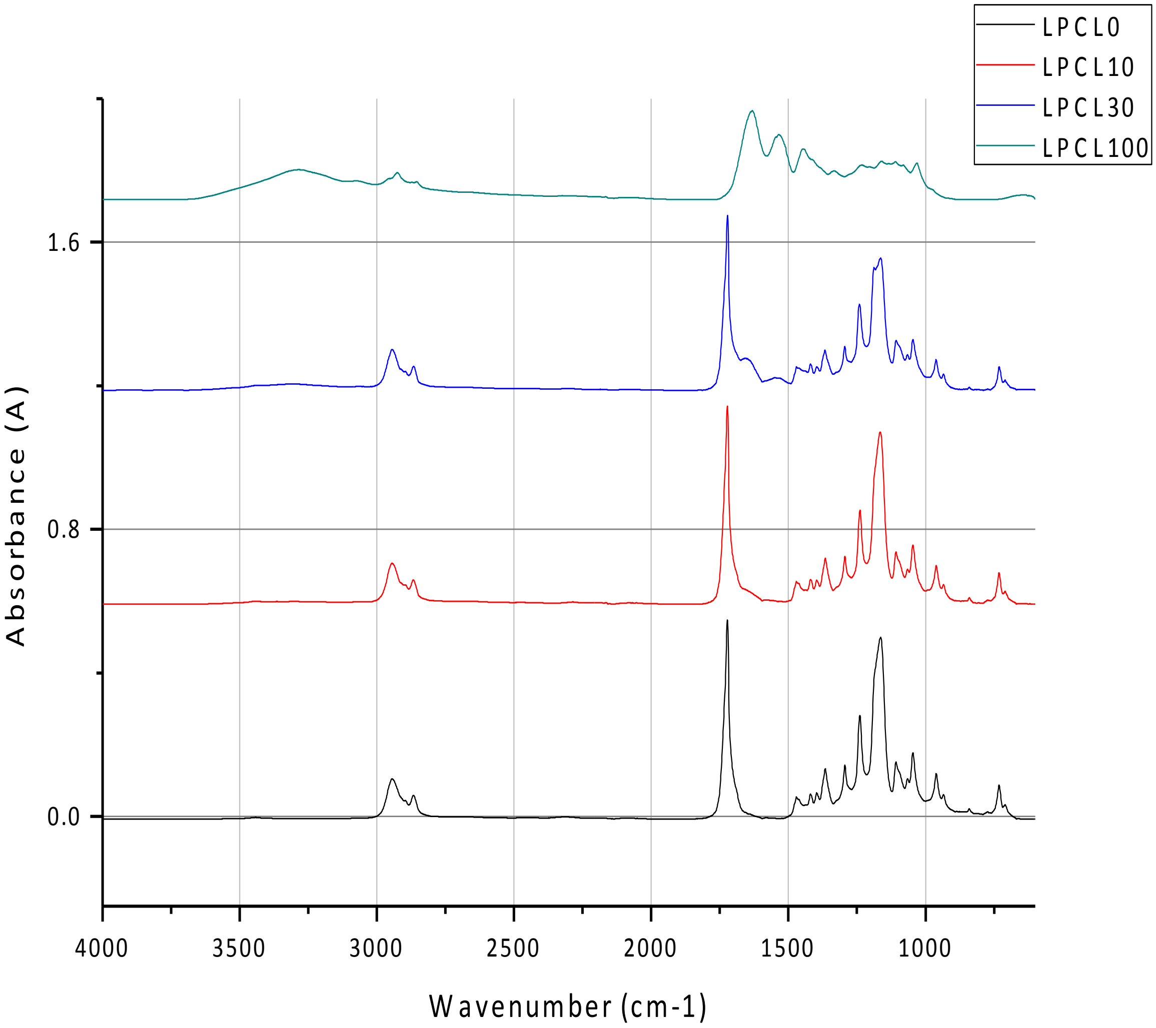
Leather fibers are mainly composed of collagen, which consists of long amino acid chains, chromium oxide, and other chemical components that are artificially added to leather to provide chemical stability, adequate finish, and resistance to degradation by fungi and microorganisms during use.

Graph 6 shows the TGA thermograms of leather waste, PCL resin, and 30wt % filler PCL resin. From graph, it is clear that the leather sample exhibits two mass loss steps. The initial mass loss below 100°C is due to gradual evaporation of absorbed moisture. The mass loss continued to occur between 100 and 150°C and was attributed to volatile components such as oils and low-molecular-weight greases present in the leather fibers from the leather preparation process [5, 36, 37]. The second mass loss step is from 300 to 600°C because of the decomposition of collagen. In PCL resin, the mass loss occurs in a single step process, which started at 325°C and completed at 450°C. However the major sources of degradation in leather powder is collagen. Figure 1 further shows that effect of mixing leather powder with PCL resin was to improve the thermal stability of composites in comparison with that of leather powder. Leather powder and its blends show more ash content than the PCL matrix.

Maximum temperature of 130°C for processing of blend is fixed which ensured the integrity of the stable valence of Cr+3 present in the leather fibers because thermal oxidation can occur above this temperature, and the chromium valence may change to Cr+6, which is highly toxic.

4.6 FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

Graph 7 shows the FTIR spectra of Leather, PCL & PCL composite with 10 & 30% leather.



Graph.7: FTIR spectrums of Leather PCL composites

Characteristic peaks of PCL at 2944.5 (asymmetric CH2 stretching), 2866.1 (symmetric CH2 stretching), 1721.1 (carbonyl stretching), 1294.2 (C–O and C–C stretching in the crystalline phase), 1240 (asymmetric COC stretching), 1190 (OC–O stretching), 1163 cm^{-1} (symmetric COC stretching) appear in all composites containing PCL.

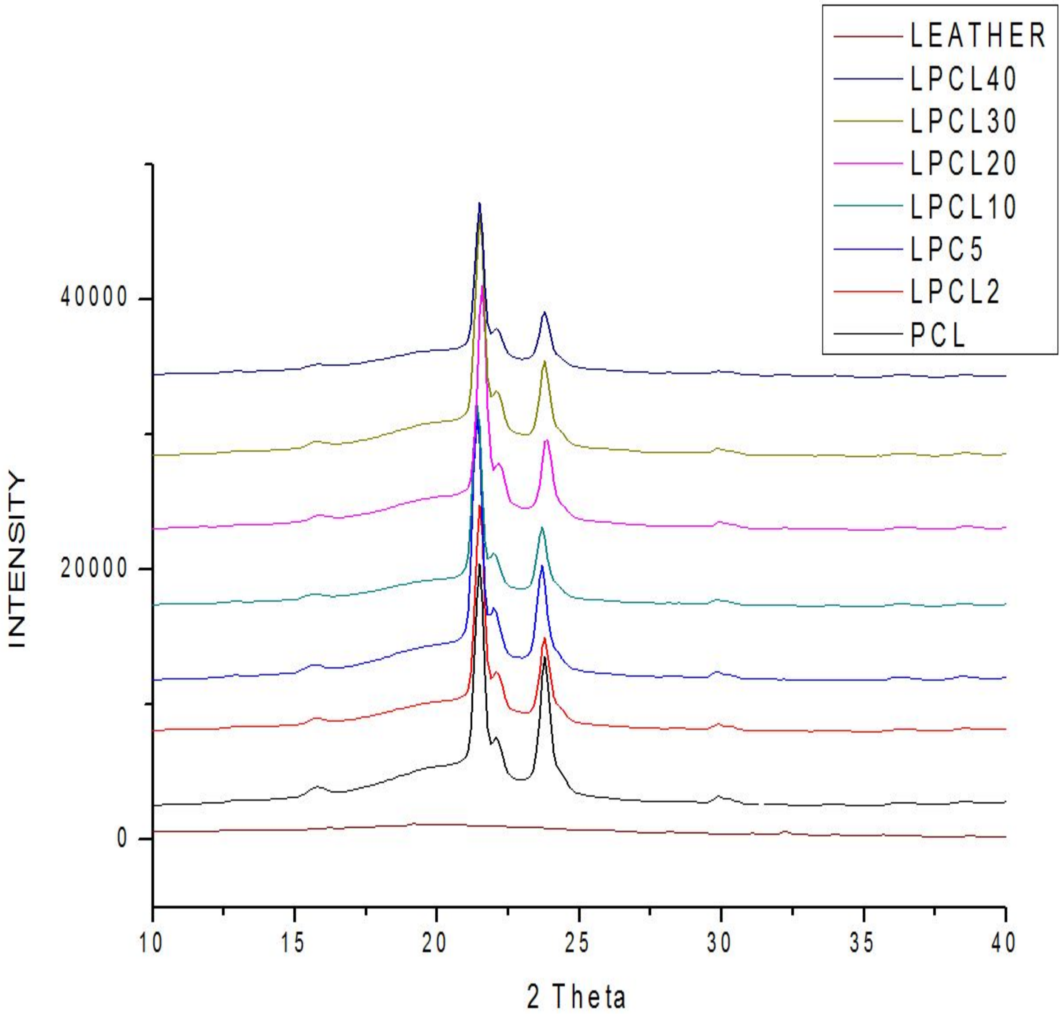
In FTIR spectrum of leather waste a broad band can be seen between 3300–3500 cm^{-1} corresponding to the presence of −OH and −NH stretching of amino acid in leather wastes, band at 1650 corresponding to C=O of amide group, band at 1540 correspondingto NH bending of amino acids, and weak bandsin region 1000–1250 resulting from −CN and −COgroups of leather amino acids.

In leather-PCL composites, intensity of these peaks increases as the leather content increases. There are no other peaks than that of characteristics peaks for leather & of PCL in leather-PCL composite, which confirms that there is no chemical interaction between Leather and PCL as previously found by DSC results.

4.7 X-RAY DIFFRACTION ANALYSIS (XRD)

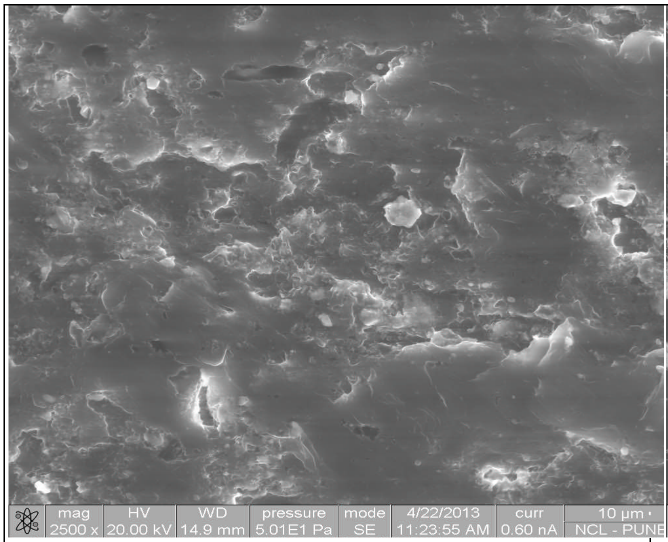
The crystalline phases present in the samples were identified by XRD. XRD patterns of the resulting PCL scaffolds are shown in Graph 8.

There are no diffraction peaks of other substances and all diffraction peaks are corresponding to PCL. PCL is a semi-crystalline polymer with two diffraction peaks, around 21 and 23. Moreover, the peaks were sharp and distinct, which indicated that the samples were highly crystalline materials

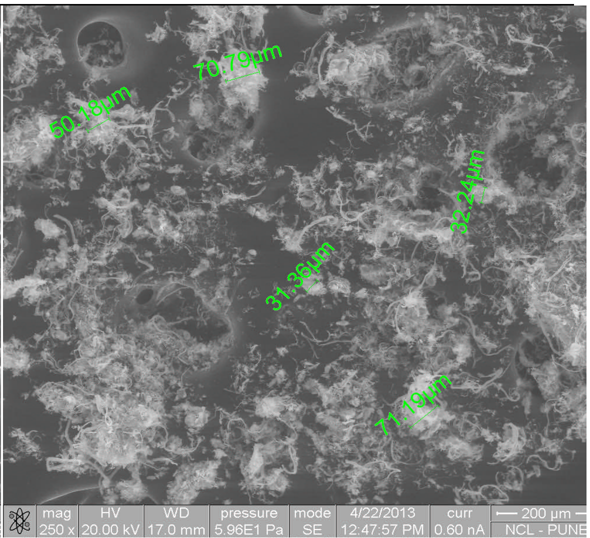


Graph 8: X-ray Diffraction spectrum for Leather-PCL composites

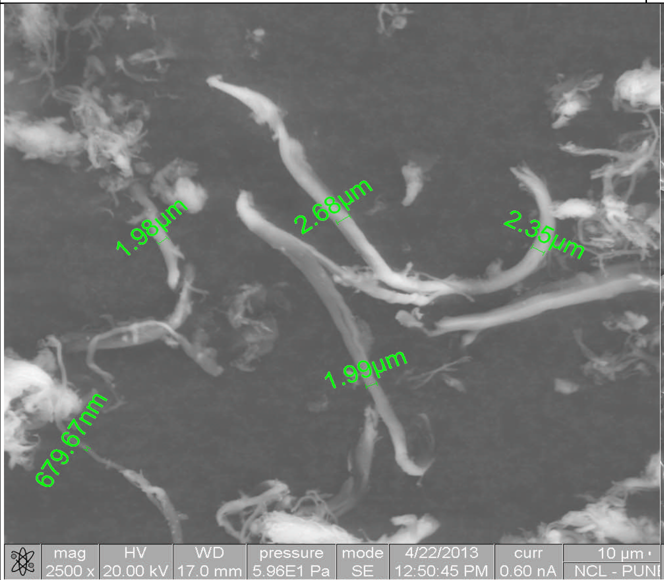
4.8 INTERFACIAL MORPHOLOGICAL ANALYSIS



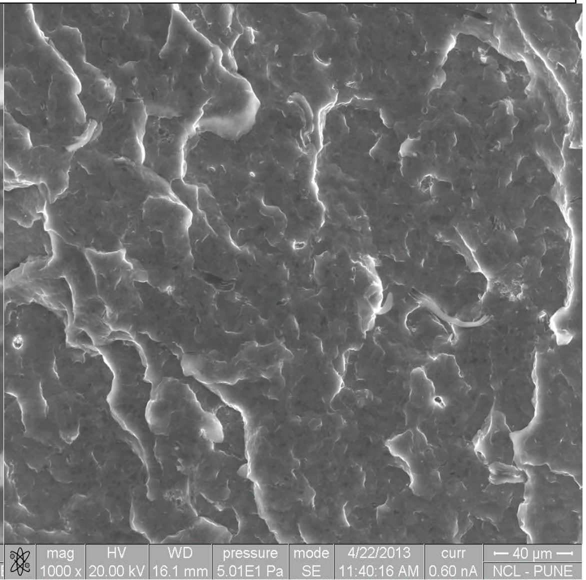
PCL



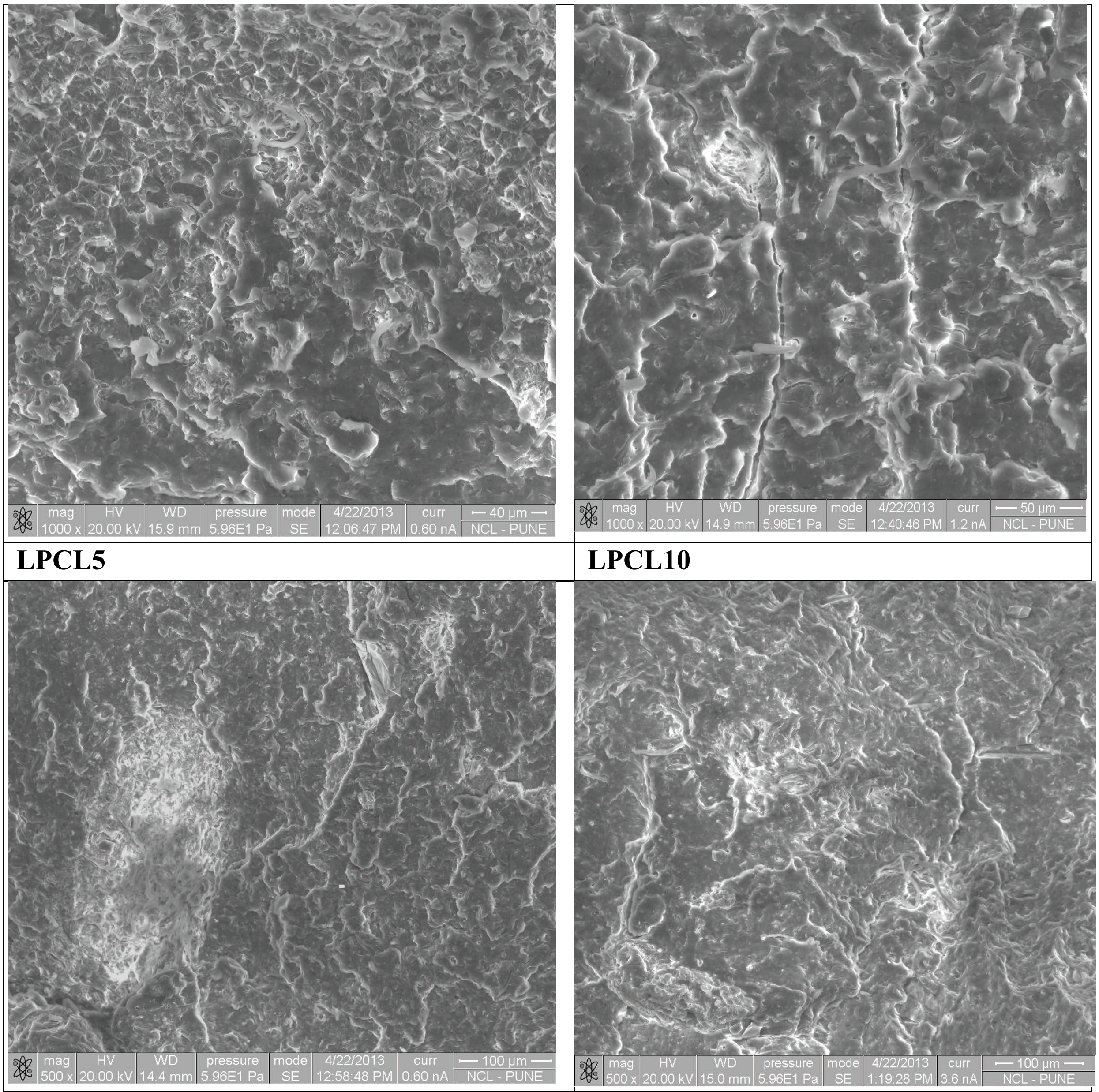
Leather fibrus particles



Seperated fibers



LPCL2



LPCL5 **LPCL10**

LPCL20 **LPCL30**

Fig.14: SEM micrograph of Leather PCL composites.

SEM micrographs shown in figurereveal that the leather fibers are well distributed over the surface as well as a poor adhesion of leather fibers to the PCL matrix. At lower concentration isolated fibers are seen, this may be due to shearing forces applied during the extrusion process of composition. As the concentration of fibres increases more aggregation and entanglement of fibres is seen. Penetration of PCL through entanglement is observed which is responsible for physical adhesion between matrix and fibres, thus improved tensile strength around 20% of leather content is obtained.

4.9 INVESTIGATION OF PCL-g-MA & ITS EFFECT ON COMPOSITE PROPERTIES.

Maleic Anhydride grafted PCL is synthesized by procedure described in earlier section. Investigation of grafting is done by performing FTIR spectroscopy of the sample & comparing its result with that of unmodified PCL.

Probable mechanism for grafting maleic anhydride onto Poly-ε-caprolactone is shown in Figure 15. As a first step, homolytic scission of each molecule of peroxide produces two radicals and is followed by the hydrogen abstraction from the α- carbon atom relative to the carbonyl group. In the second step, the radical onto a PCL chain can lead to a **b** -scission, which is a fast intra molecular reaction and seems predominant in the melt state in the presence of organic peroxide. The third step involves the addition of a double bond to the radical from β -scission, leading to the end chain grafting of maleic anhydride. The recombination reaction will lead MA grafted PCL as shown in figure.

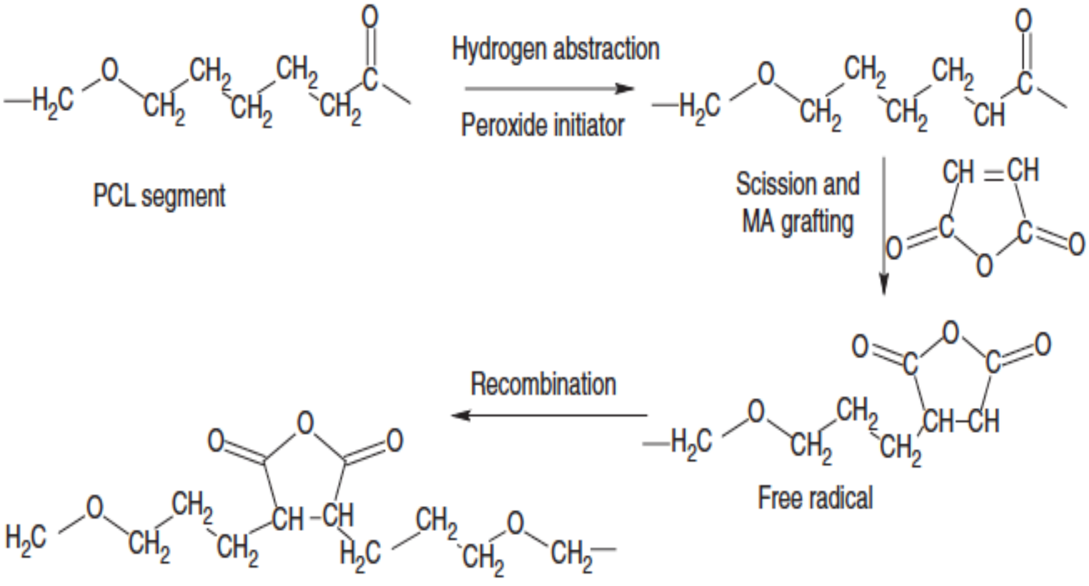
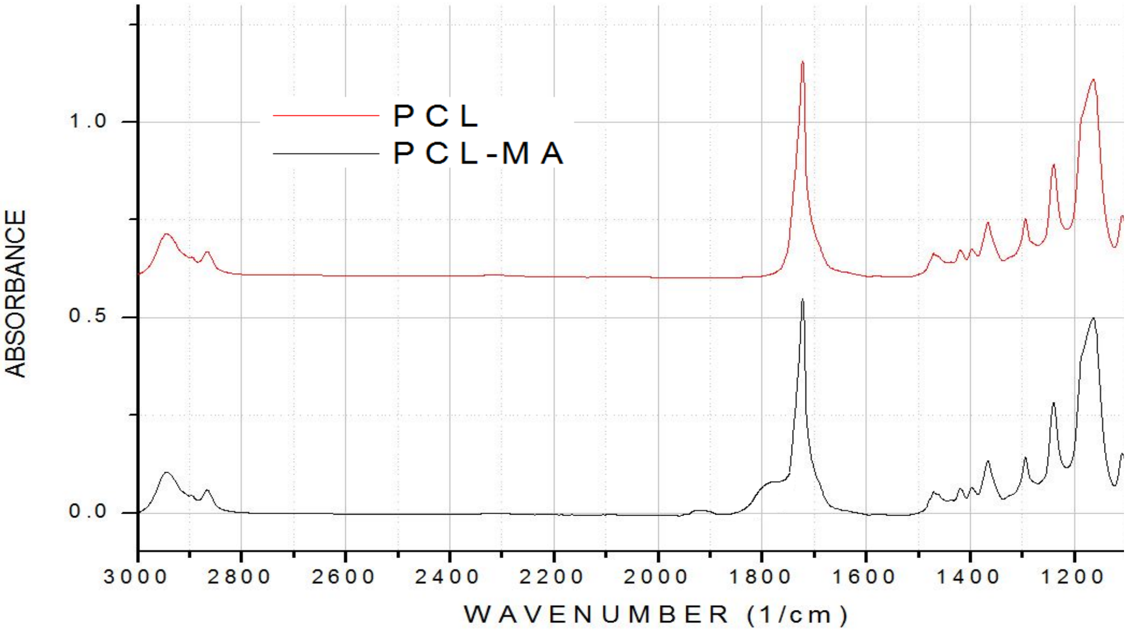


Fig.15: mechanism of grafting MA onto PCL [33]

FTIR spectrum of PCL-g-MA is showing in Graph 9. The FTIR spectra of pure polymer and grafted polymer were scanned separately from 1000to 3000 cm $^{-1}$ Spectra of pure PCL 787 did not show any peaks in this region other than the carbonyl peak at 1725 cm $^{-1}$. Two clear bands one around 1785 and the other around 1858 cm $^{-1}$shown in the spectra of PCL-g-MA, must be due to the grafted anhydride, since cyclic anhydrides exhibit an intensive absorption band near 1780 cm $^{-1}$and a weak band near 1850 cm^{-1}due to the symmetric and asymmetric stretching of C=O. This confirms the grafting of MA on PCL.



Graph 9: FTIR spectra of PCL & PCL-g-MA

We examined the effect of MA grafted PCL as compatiblizer on Leather-PCL composites. This was done by incorporating 5% PCL-g-MA in Leather PCL composite containing 30% leather(LPCL30MA). Then the composite is characterized for mechanical, thermal& morphological properties as done earlier with PCL-Leather composites & results are compared with PCL containing 30% leather (LPCL30).

A. Mechanical Properties:

LPCL30MA shows higher tensile strength of 19.7MPa compared to that of LPCL30, which is 14.74 MPa. Thus 33.5 % increase in tensile strength is achieved by incorporation of compatiblizer.

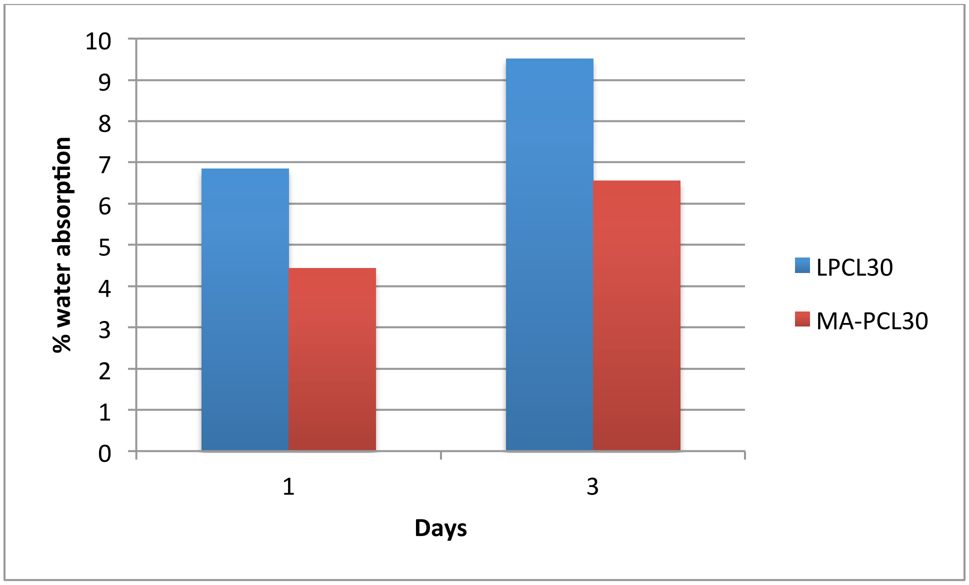
The result is attributed to improvement of interfacial adhesion between leather fibers & PCL matrix so giving better load transfer from matrix to leather fibre thus improving tensile strength.

Elastic modulus also increased from 663 MPa to 693 MPa, the increment being relatively lesser than the increase in tensile strength. This is in agreement with previously reported literature.

B. Water Absorption:

As we can see from graph shown in Graph 10, water absorption percentage decreased with addition of PCL-g-MA to leather PCL composite.This is because incorporation of compatiblizer results in reduced voids and defects between the filler and polymer matrix.

Also efficient dispersion of the leather fiber within the polymer matrix due to the addition of the PCL-g-MA forms more tortuous path for penetrating water, slowing down the whole process.



Graph 10: Water absorption of LPCL30 & LPCL30MA

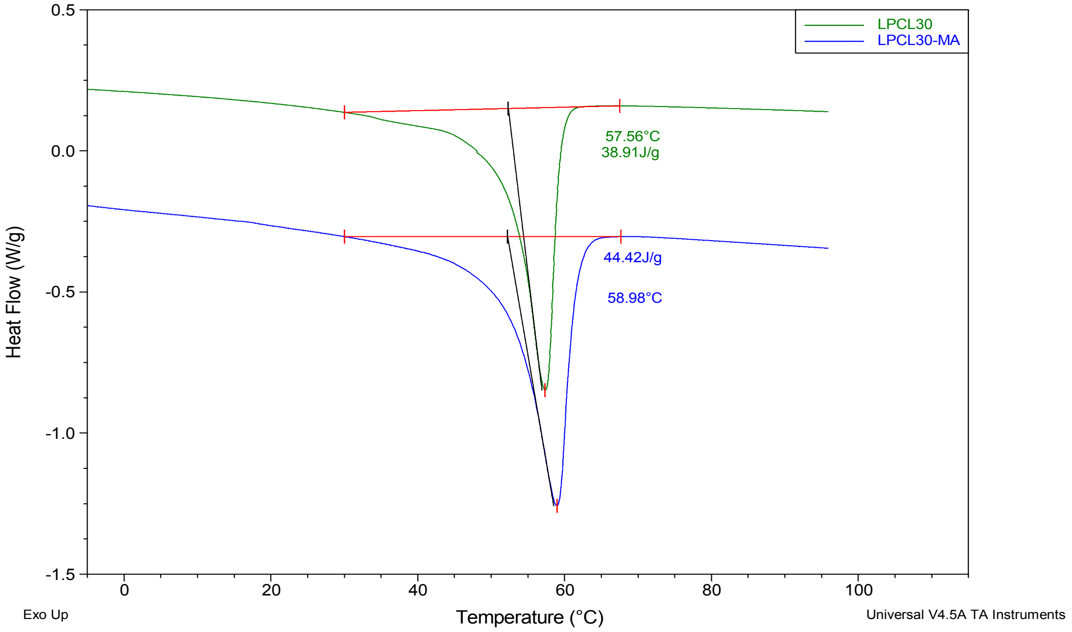
C. Dynamic Mechanical Analysis (DMA):

Composite prepared with PCL-g-MA as compatiblizer shows nearly same values of modulus for all temperature as that of composition without compatiblizer. This confirms that compatiblizers do not have significant effect on modulus for PCL composites.

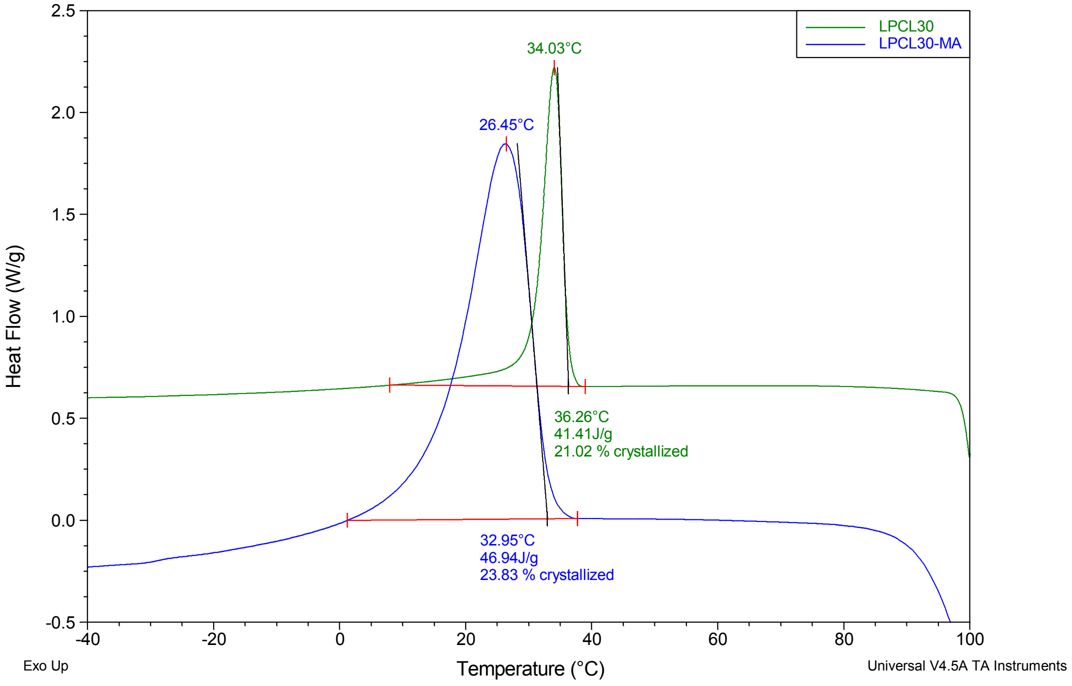
D. Differential Scanning Calorimetry (DSC):

As shown in Graph 11, there is slight increase in melting temperature from 57.5 to 59°C of LPCL30 with addition of 5% PCL-g-MA with almost same degree of crystallinity. Whereas crystallization thermograms (Graph 12) show that there is reduction in crystallization temperature from 34 to 26.45°C. This could be associated to formation of crystals of lager size with addition of MA-PCL.

Depression in crystallization temperature could be positively used for splinting application where higher work time window can be achieved with use of this composition.

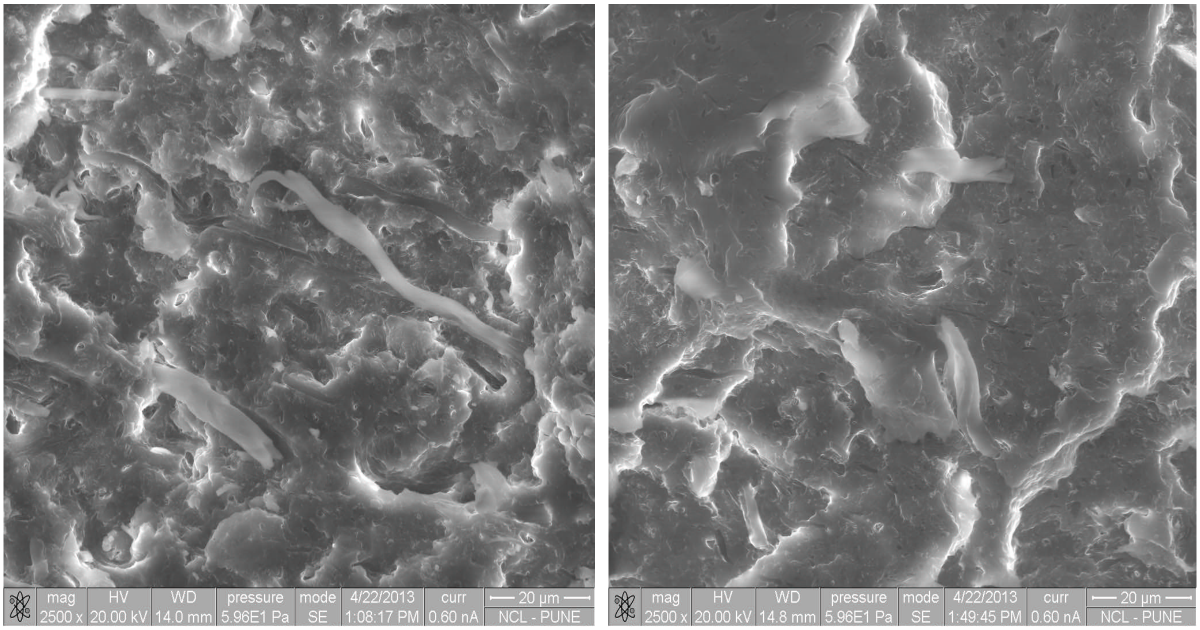


Graph 11: DSC melting thermograms for LPCL30 & LPCL30MA

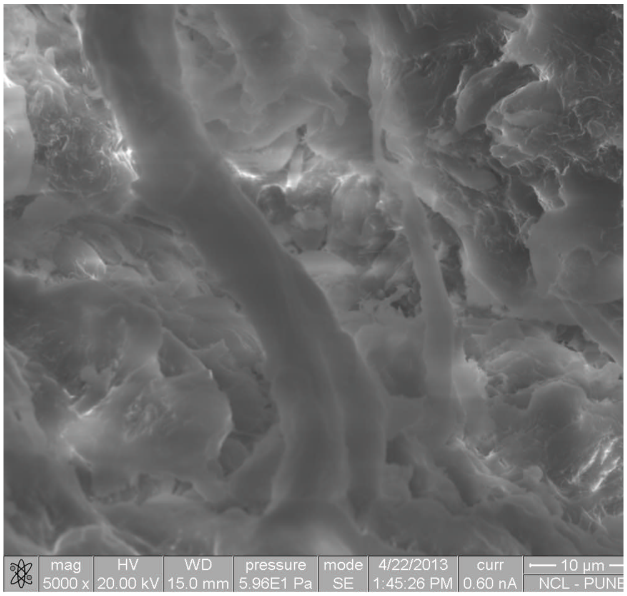


Graph 12: DSC crystallization thermograms for LPCL30 & LPCL30MA.

E. Interfacial Morphological Analysis



a. LPCL30 b. LPCL30MA



c. Residue of PCL on fiber surface

Fig.16: SEM micrograps of LPCL30 & LPCL30MA

SEM micrographs of Leather PCL LPCL30 & LPCL30MA are shown in figure 16. In composite without compatiblizer poor interfacial adhesion and vacant fiber places can be clearly seen. This confirms the improvement in tensile strength is only due to formation of entanglement at higher percentage of fibers for composite without compatiblizer.

In case of composite prepared with 5% MA-PCL as compatiblizer, improved adhesion at interface is seen, also the residue of PCL is observed on the fiber surfaces. This confirms that improvement in mechanical properties of composite is due to addition of compatiblizer. The probable reaction between leather fibre and MA grafted PCL is shown in the figure 17.

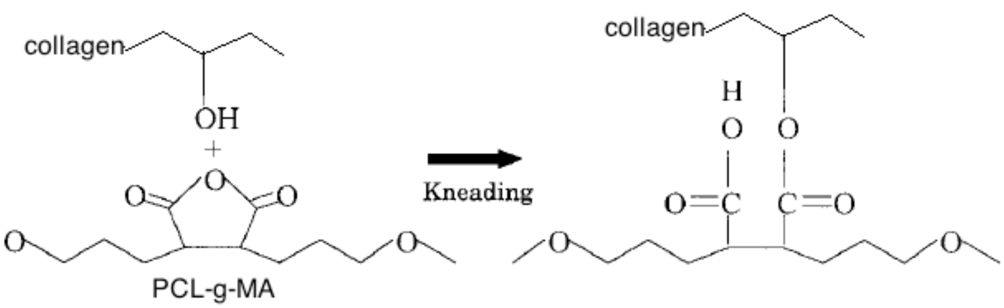


Fig 17: Possible reaction between Leather fibre waste & PCL-g-MA

CONCLUSION & SUMMARY

Based on the above discussion, we can conclude that this work showed that chromium treated, finished waste leather granules could be useful as filling material for PCL, in order to design completely biodegradable composite. This work demonstrates the feasibility of producing low cost "leather-like" composites (with a leather fiber content as high as 40 wt%) at high production rates. The production methods described could help eliminate the major pollution environmental problems associate with leather wastes.

An increase in elastic modulus with fiber content was found for all the composites formulations investigated. Composite showed sustained tensile strength values with slight drop at low concentration and then increase in strength surpassing the strength for pure PCL. Optimum value of tensile strength of 15.64MPais observed at 20 wt% of reinforcement. Moisture absorption increases proportionally to the increase in leather content. With leather contents stiffness of composite at elevated temperature is increased, as shown by DMA results.

Grafting of MA on PCL is executed successfully by melt extrusion and using benzoyl peroxide as initiator. Grafting is confirmed by FTIR analysis. PCL-g-MA was found to be useful as compatiblizer for Leather-PCL composite, as the tensile strength increased by 33% for composite containing 30% Leather waste reinforcement compared one without compatiblizer.

APPLICATIONS AND FUTURE SCOPE

The composite presented adequate standard properties for its use in upper shoe sole and other leather-like personal goods. However, the use of products is restricted to applications where dark colors are acceptable. The composite can be used for automotive decorative interiors due to their leather like appearance and ease of processing using injection molding, extrusion sheet molding or thermoforming.

The composite requires biocompatibility evaluation for extending its application as thermoplastic splinting material, which is one of the major applications of PCL. Furthermore, applications such as floorings, personal safety goods, clothing etc. could be possible provided that some critical properties, e.g., wear resistance, thermal stability are acceptable.

Leather-polymer composites can be seen as effective material for “Leather-Laminates”, which is emerging material for decorative furniture application. Properties such as sheet formation paintability, texture formation on surface, flexibility etc. are need to be evaluated for this application.

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