Mechanical Characterization Study of Additive as Nanofiller in Poly (ε-Caprolactone) Nanocomposite

Prarthana Dhanvijay*

R & D Advisor, Logical Process Engineering Solutions, Mumbai, India

Abstract: In order to keep with ever evolving technology in biomedical field, the demand for Poly (ε-caprolactone) (PCL) is gaining importance due to its biodegradability and biocompatibility. However, the low mechanical, barrier and thermal strength of PCL restricts its widespread use. These drawbacks of virgin PCL can be rectified by incorporating nanofiller into the PCL matrix. Till date, research has been carried out incorporating nano-fiber into PCL but to the best of our knowledge there is hardly any literature regarding organoclay modified nanofiller-PCL composites. The present study represents PCL nanocomposites preparation and characterization. The FTIR and XRD spectra observe uniform distribution of nanofiller in the PCL matrix. The characterization of mechanical properties shows enhancement in strength till 3.5 wt% loading and declining trend afterwards indicating agglomeration of nanofiller at higher wt% ratio. The increase in tensile strength without sacrificing elongation at break provides these composites with very attractive mechanical properties.

Keywords: Biocompatibility, Nanofiller, Poly (ε-caprolactone).

INTRODUCTION

Polymer nanocomposites are already established as materials with remarkably enhanced and improved properties compared to the pure polymers and conventional microcomposites. If a very low amount of nanometer filler is successfully dispersed in a polymer matrix, the interface between the filler and the matrix dramatically increases, allowing a full contribution of the filler to the improvement of the properties. Among polymer/inorganic filler composites, polymer/layered silicate nanocomposites have induced a great interest in industry, as well as in academia. Layered silicates found such a prominent place among other nanofillers due to their natural abundance, high mechanical strength, chemical resistance and well-investigated intercalation chemistry. Different polymers, such as polyamides, polypropylene, polyurethane, aliphatic polyesters, aimed at diverse applications, were investigated as matrices in polymer/layer silicate nanocomposites. The resulting nanocomposites often exhibit higher stiffness, lower permeability, reduced coefficient of thermal expansion and reduced flammability than the corresponding neat polymer [1-4].

Biodegradable polymers like poly(lactic acid) (PLA), poly (glycolic acid) (PGA), poly(trimethylene carbonate) (PTMC) and poly(ε-caprolactone) (PCL) have a very wide spectrum of biomedical applications in tissue engineering and regenerative medicine [5]. Over the years, PCL has gained immense importance in biomedical field due to its various properties such as adjustable biodegradability, compatibility with wide range of drugs, rubbery nature and ease of forming blends, composites and copolymers [6]. The application of PCL ranges from drug-delivery systems [7-10], medical devices using PCL for wound dressing [11-12], fixation devices [13] or in dentistry [14, 15], as well as PCL included in tissue, bone, or blood vessel engineering [16-21]. However, there could be a limitation for many more applications because of its low mechanical, barrier and thermal strength.

It is, therefore, of considerable interest to investigate and develop improvements of PCL-based materials in terms of mechanical, barrier and thermal properties. Judging from the literature citations, a nanocomposite approach has been especially investigated [22-25]. Nanoclays which provide a range of aforementionved improvements of materials seems to be a particularly promising filler for materials based on a PCL-matrix [26].

EXPERIMENTAL

Materials

The PCL used in this study was supplied by Solvay Caprolactones Ltd, Warrington, United Kingdom and of blown film grade with weight-average molecular weight (Mw) of 1,49,775, a number-average molecular weight (Mn) of 97,278, and a polydispersity of 1.54 as determined by high performance liquid chromatography with polystyrene as a calibration standard. The

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*Address correspondence to this author at the R&D Advisor, Logical Process Engineering Solutions, Mumbai, India;
E-mail: dprarthana@gmail.com

E-ISSN: 2311-8792/23

untreated bentonite clay having a cation exchange capacity (CEC) of 104 mequiv/100gms was given by Crystal Nanoclay Pvt. Ltd., Pune, India.

Preperation of PCL-Clay Nanocomposite

The organoclay and PCL were melt-blended using co-rotating twin screw extruder (Model MP 19 PC, APV BAKER, U.K.) having L/D ratio of 25:1. The screw speed was maintained at 60 rpm and the temperature profile for compounding was 60, 70, 80 and 90°C for four zones and 90°C for the die zone. The extrudate from the screw compounder was quenched in water and pelletized. The extruded pellets were dried and blown into films using a fabricated small scale blown film extruder at Ducol Organics Pvt. Ltd., Taloja, India. The temperature profile was same as that for extrusion whereas the nip roll speed was 6m/min. The organoclay content was varied as 0, 0.5, 1.5, 2.5, 3.5 and 5 wt% in PCL matrix and the corresponding pcl-clay nanocomposites were named as VPCL, 0.5 PCL, 2.5PCL, 3.5PCL and 5PCL.

Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of the sample in KBr pellets was recorded using SHIMADZU ATR PRO 450 S spectrometer.

X-ray Diffraction (XRD)

The XRD patterns of samples were obtained with a D8 Advanced Bruker X ray diffractogram from 2 ° to 30 ° at a scan speed of 0.2 sec/step.

Mechanical Testing

This test covers the determination of the mechanical properties of unreinforced and reinforced plastics in the form of standard dumbbell test specimens when tested under defined test conditions. Universal Testing Machine (LR 50K, LLOYD instruments, U.K) was used to carry out the tensile properties. The crosshead jaw speed was 50 mm/min and a load cell of 500 N capacity was used. Standard specimens were exposed to tension and force to elongate and break the specimen and extent of elongation were observed.

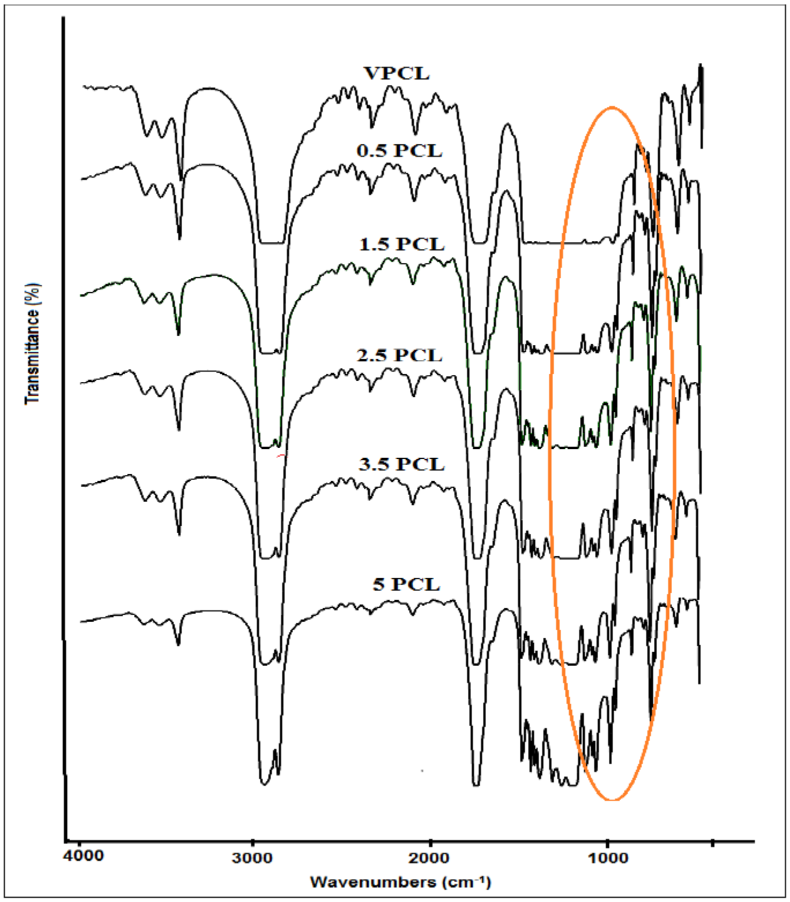

Figure 1: FTIR spectra of PCL clay nanocomposite.

Tensile strength of the samples was evaluated according to ASTM D882-01. Tensile strength, tensile modulus and %elongation data can be obtained with the help of the software.

RESULT AND DISCUSSION

FTIR Characterization of PCL Clay Nanocomposites

As shown in Figure **1** above, the variation the IR spectra is noticed in the range of 952-1100 cm^{-1}. As the concentration of clay in PCL matrix goes on increasing, new peaks emerges with increasing intensity and depth. These peaks are related to Si-O bonding and stretching vibration and they appear to be at 1022 and 1056 cm^{-1} in the FTIR spectrum.

XRD Characterization

Figure **2** shows the XRD patterns for the PCL and PCLNC containing 0.5, 1.5, 2.5, 3.5 and 5% clay. The pattern of the PCL matrix is also presented as a baseline to compare the difference between the matrix and the nanocomposites. The data obtained from the diffractogram is tabulated in the Table **1** below.

PCL did not intercalate into natural montmorillonite because most of the polymers are hydrophobic. Furthermore, MMT layer is made up of the stacking of alumina and silicate, which generate negative charge layers. So, it is not easy to incorporate PCL into the interlayer space of MMT without surface modification or clay treatment. This is evident from the XRD patterns as no significant change in d- spacing is observed (Figure **2**).

However organo-treated montmorillonites produced PCL clay nanocomposites according to the increase in d-spacing, which agrees with the findings of (Lepoittevin *et al*. 2002). PCL is a hydrophobic polymer and is only compatible with “organophilic” clays. Figure above shows that the (001) peak of PCL clay nanocomposites shifted towards lower 2 theta angle with clay loadings upto 2.5 wt%, corresponding to an increase in d-spacing of 31.58 ◦A. This might be due to

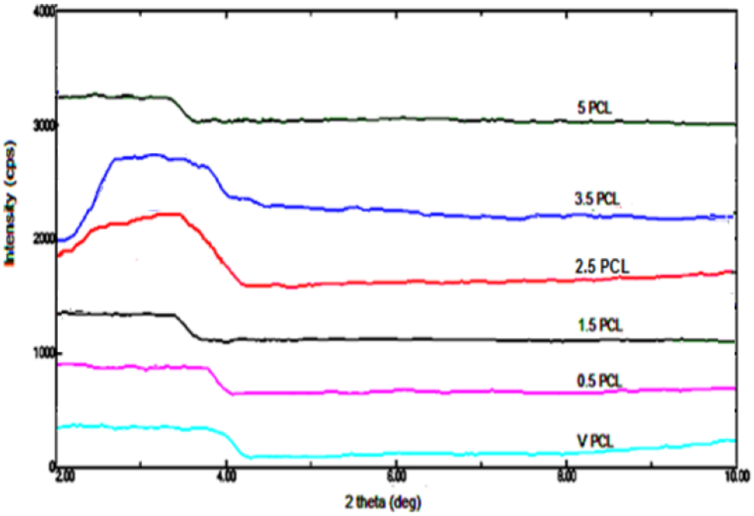

Figure 2: XRD diffractograms of PCL clay nanocomposite.

Table 1: XRD Data for PCL Clay Nanocomposite

Sample	2 theta (°)	d spacing (ºA)
Untreated clay	5.98	14.57
0.5 PCL	3.81	28.56
1.5 PCL	3.68	30.83
2.5 PCL	3.61	31.58
3.5 PCL	3.62	31.44
5 PCL	3.64	29.41

Table 2: Mechanical Testing Data for PCL Clay Nanocomposite

Sample	Tensile Strength (MPa)		Young's Modulus (MPa)		% Elongation	
	MD	TD	MD	TD	MD	TD
0 PCL	24.1	22.6	235.3	210.1	484.1	555.3
0.5 PCL	27.9	26.1	260.4	250.6	498.7	591.9
1.5 PCL	34.5	32.3	391.2	365.3	571.4	635.5
2.5 PCL	36.7	35.1	413.7	387.1	574.5	675.3
3.5 PCL	38.9	37.2	420.3	391.8	564.8	646.4
5 PCL	37.4	36.8	371.5	311.7	488.7	535.3

ordered layer structure as the result of exfoliation. The rise in d spacing was persistent upto 3.5 wt% clay, however as the filler a level increase to 5 wt %, the d spacing slightly decreases.

The XRD spectra data shows that the percentage volume fraction crystallinity of the PCL-clay nanocomposites first increase with increase in clay concentration and then decreases once reached the 5wt % loading. This slight decrease in crystallinity at 5 % clay loading is believed to be due to the irregularity of the agglomerated clay tactoid.

Mechanical Properties

The characteristic properties of the as-prepared nanocomposite films were determined from tensile tests. The results of these experiments, *i.e.,* Young's modulus, stress at break and strain at break are summarized in Table **2**.

It has been observed that the ammonium-treated clays provided a significantly greater increase than the natural clay because they formed nanocomposites with PCL with higher interfacial surface areas and greater effective volume fractions (Chen & Evans 2006). PCL is ductile polymer with moderate values of elastic modulus and high values of strain at break. The usually observed effect of the addition of filler to a polymer matrix is increased stiffness accompanied with embrittlement. The embrittlement is usually ascribed to the formation of agglomerates, particularly at higher clay loadings, which induce weak places in the nanocomposite structure (Nikolić *et al*. 2015).

a) Tensile Strength

The tensile strength shows (Figure **3**) increasing trend with addition of filler, due to good dispersion of nanoparticles into the matrix, yielding a higher reinforcement effect. Acting similarly to a compatibilizing agent, nanoparticles enhance the

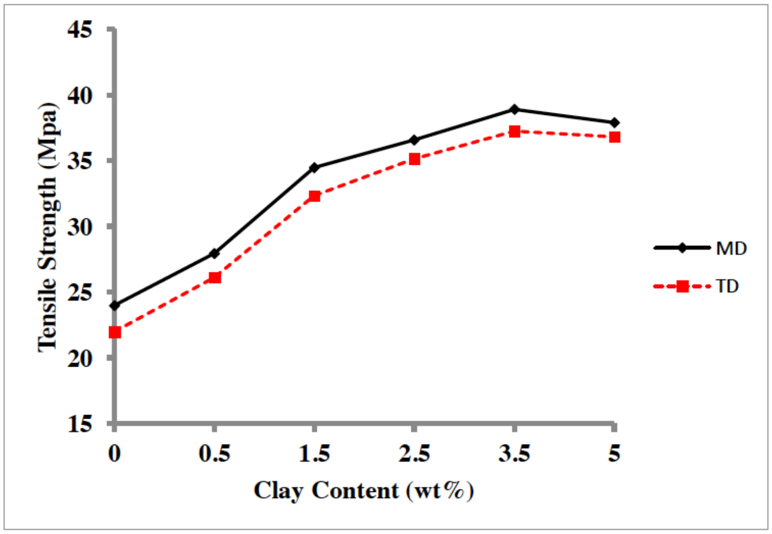

Figure 3: Tensile strength of PCL clay nanocomposite.

dispersion of materials and the interfacial adhesion within the matrix. However the curve leveled off at higher loadings which suggest that the external load could not be transferred effectively to the clay platelets when the clay was at high concentration, possibly due to the presence of clay agglomerates. Particle agglomeration flaws the material's surface, which restrains stress movement, and eventually results in decreased tensile strength. It is further observed that Tensile strength in MD is higher than that for TD. This is due to higher molecular orientation in MD and the presence of more tie molecules between the crystalline lamellae in that direction also help to shrink the film.

The polymer strands are aligned in the machine direction and the film requires the breaking of the bonds within the polymer strands. In TD the polymer strands are held together only by relatively weak intermolecular interactions which require much less energy to overcome.

b) Youngs Modulus

As illustrated in Table **3**, by increasing the amount of nanoparticles, tensile modulus increases. For instance, the Young's modulus is significantly increased from 220 MPa for pure PCL to more than 401 MPa for the composite that contains 3.5 wt% of organically modified clay. The increase in tensile modulus must be caused by rigidity of the filler and strong interaction between the polymer and filler due to the large interfacial area between particles. Figure **4** shows Young's modulus in both machine and transverse direction for PCL-clay composites. As with machine direction, the curve is above that of transverse direction indicating more effective reinforcement.

c) Tensile Elongation

PCL is a ductile polymer able to sustain large deformations (700% at break). Adding nanoclays only slightly decreases the elongation at break, as shown in Table above. PCL remains ductile with an elongation at break higher than 550%. However, higher clay content (above 3.5 wt%) has a detrimental effect, as at higher filler loading, a large amount of agglomeration was more apparent, due to the high surface energy of nanoparticles, thus contributing to the lower elongation at break.

Figure **5** shows the tensile elongation at break as a function of clay loadings. At low clay loadings, test piece underwent yielding during tension, similar to pristine PCL but with dramatic increases in ductility which is quite the opposite of the usual effect of adding particulate filler to a polymer. The improved elasticity due in part to the plasticizing effect of gallery onium ions, which contributes to the dangling chain formation in the matrix. When the clay loading was high, the composites became brittle, there being no yielding stage in the stress-strain curve. The increase in tensile strength without sacrificing elongation at break provides these composites with very attractive mechanical properties, which have also been found by other workers in the nanocomposite field

These different observations show that PCL nanocomposites combine high stiffness and good

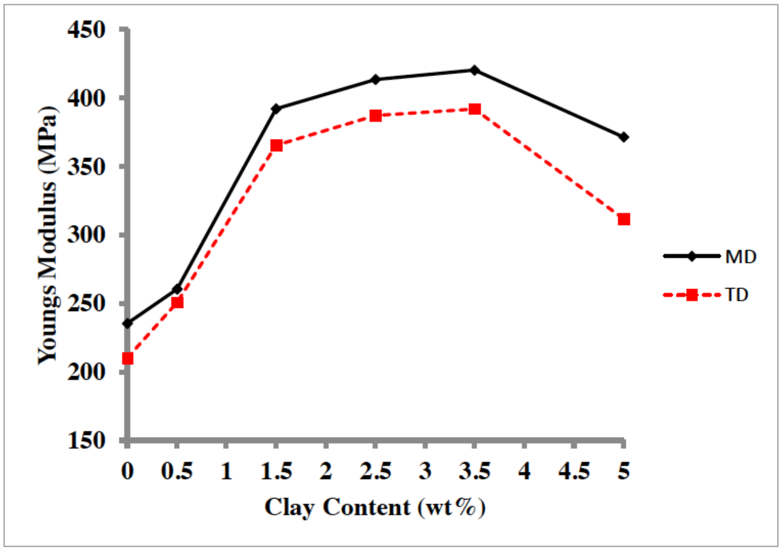

Figure 4: Youngs modulus for PCL clay nanocomposite.

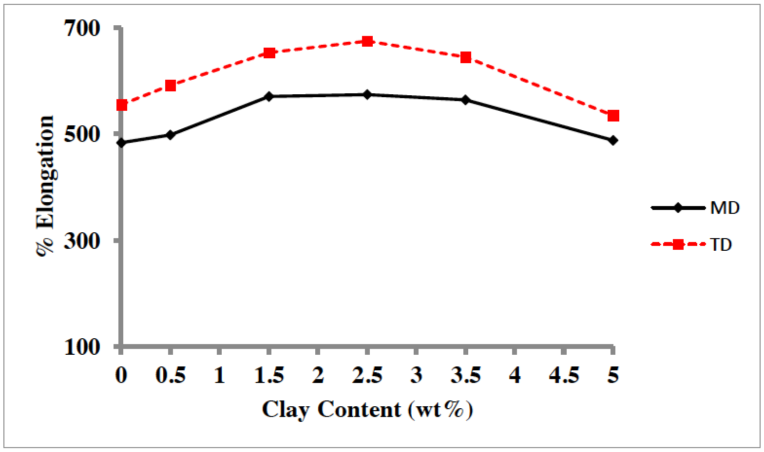

Figure 5: % Elongation for PCL clay nanocomposite.

ductility at least up to a clay loading of 5 wt%. Above this threshold, a drastic loss in ultimate tensile properties is observed.

CONCLUSION

The current research involves in depth study of mechanical properties of PCL nanocomposites which are prepared by using various ratios (0, 0.5, 1.5, 3.5 and 5 wt%) of additive infused nanofiller into PCL matrix. As per FTIR spectra, as the concentration of clay in PCL matrix goes on increasing, new peaks emerges with increasing intensity and depth which are related to Si-O bonding and stretching vibration. XRD diffractograms show that it is easy to incorporate PCL into the interlayer space of MMT with surface modification or clay treatment. Tensile strength in MD is higher than that for TD. This is due to higher molecular orientation in MD. All the other mechanical properties like tensile modulus, young’s modulus show increasing trend till 3.5 wt% wheras elongation at break sustains till 5 wt%. The increase in tensile strength without sacrificing elongation at break provides these composites with very attractive mechanical properties.

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Received on 01-01-2023 Accepted on 29-01-2023 Published on 23-02-2023

DOI: http://dx.doi.org/10.12974/2311-8792.2023.09.1