

HYBRID BIO-BASED COMPOSITES FROM NANO-REINFORCED BIO-PETRO POLYMER BLENDS AND NATURAL FIBERS

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Abstract

Natural fiber composites or biocomposites have recently gained much attention due to their low cost, environmental friendliness, and their potential to compete with glass-fiber composites. However, the use of all-natural resins is limited due to performance concern, and hence the blending bio-resins in petroleum resins has gained importance due to their improved toughness and environmental friendliness. Nevertheless, addition of bio-resins generally compromises stiffness, barrier and thermal properties. The enhancement of polymer stiffness and barrier properties with small concentrations of layered silicates is well established. With this context, the paper presents the development and thermo-physical characterization of a hybrid composite material with increased environmental friendliness that can retain stiffness without sacrificing toughness, barrier and thermal properties. Hybrid biocomposites were made from bio-based resins (blends of unsaturated polyester and epoxidized soya bean oil) reinforced with organo-nanoclays and natural fibers (unprocessed industrial hemp). Results show that an optimum material design that maximizes the synergy of the constituents is possible and provide an initial benchmark in identifying such balance.

Background

Increasing environmental concerns such as biodegradability, recycling issues and dependability on non-renewable petroleum reserves have propelled the development of alternatives such as natural fiber composites or biocomposites [2][10]. Biocomposites, composed of natural fibers in synthetic or natural based polymer matrices have recently gained attention due to their low cost, environmental friendliness, and their potential to compete with glass-fiber composites [3][10]. The use of all bio-resins has been limited due to performance concerns such as low mechanical and thermophysical properties [6][7]. A promising compromise between environmental friendliness and performance are blends of functionalized vegetable oils (or bio-resins) with synthetic (or petroleum-based) resins, commonly termed as bio-based resins. Combination of petroleum based resins (in this case, unsaturated polyester) as primary constituent and functionalized vegetable oils as secondary constituent has shown to improve the toughness of the resulting resin system [6][7][8]. Soybean oil is abundantly available across the United States, and varieties of epoxidized soybean oils are commercially available. Yet, in spite of the increased interest and environmental appeal, biocomposites have been primarily used for non-structural, or non-load bearing, applications due to their lower strength and

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stiffness relative to synthetic fiber-reinforced polymer composites [2].

Bio-based resins or bio-blends obtained by combining unsaturated polyester (UPE) with epoxidized soybean oil (EMS) have been developed by our group and have found to increase the toughness of resulting resin [6][7]. This increase in toughness is generally achieved by sacrificing stiffness [9], barrier and thermal properties. Stiffness and toughness are opposing performance parameters and a proper balance is required to develop an efficient polymer system. One of the methods of attaining this balance is by the addition of layered silicates, or nanoclays.

Polymers reinforced with layered silicates have shown to exhibit significant enhancements in modulus, thermal and barrier properties at low clay concentrations. The enhancement of mechanical and barrier properties in polymers with addition of small concentrations of nanoclays is well established in the literature. Le Baron et. al [5] provide a good review on polymer clay hybrid nanocomposites. Apart from the increase in stiffness, the inclusion of nanoclay particles introduces multifunctionality to the resulting nanocomposite resin system by enhancing barrier properties, flammability and ablation resistance. The true value of layered silicate nanocomposites is not solely the enhancement of the neat resin but rather the value-added properties it provides to a fiber-reinforced composite. Thus, for a bio-based composite, natural fibers must remain as the predominant reinforcement for providing stiffness and strength. Natural fibers such as flax, hemp, jute and kenaf have been found to have specific strengths comparable to E-glass. Similarly, the elastic modulus and specific modulus of natural fiber composites has been found to be comparable or even superior to E-glass composites [2]. Nevertheless, the use of biocomposites has been limited due to their lower strength and stiffness relative to synthetic fiber composites and conventional materials [2]. Moreover, natural fibers tend to absorb moisture, thereby affecting their performance. The enhancement of barrier properties by nanoclay inclusions in the polymer resin system would also prevent the moisture from reaching the fibers, thereby providing an efficient biocomposite.

This paper provides an overview of a study aimed at developing novel hybrid biocomposite materials by using unsaturated polyester as the primary petroleum based resin and epoxidized methyl soyate (EMS) as the bio-resin. The resulting polymer matrix was reinforced with nanoclay and chopped industrial (unprocessed) hemp fibers. The study was performed by varying the bio-resin (EMS) content in UPE and the concentration of nanoclay while maintaining a constant weight fraction of natural fibers in the composite. This paper provides details on processing along with an overview of hygro-thermal evaluation consisting of tensile modulus, ultimate tensile stress, moisture absorption and microscopic characterization. Full results from the study are provided in reference [4].

Experimental Methods

Materials and Nomenclature

Industrial unprocessed raw hemp (HempLine, Ontario, Canada) was used as natural fiber reinforcement. The fibers were hand chopped for an average length of approximately 25 mm. The primary component of the resin blend was ortho unsaturated polyester resin (*UPE*, Polylite® 32570-00, Reichhold Inc., NC), which contains 33.5 wt.% styrene. The secondary component that replaced parts of UPE was a biobased modifier, epoxidized methyl soyate (*EMS*, Vikoflex® 7010, Arkema Inc, PA). The clay used in this

work to reinforce the resin system was Cloisite 30B® (Southern Clay Products, Inc. TX). The resin blend was processed with cobalt naphthenate (Sigma Aldrich, MO) as a promoter and 2-butanone peroxide (Sigma Aldrich) as an initiator. A constant ratio by weight of the resin system to the promoter and initiator was utilized to cure all of the biocomposites. The mixing ratio was 100 parts by weight of the resin system to 0.03 part promoter and 1.50 parts initiator.

All biocomposite material systems were composed from the natural fibers noted above and a set of UPE-EMS bio-based resin blends. Table 1 provides the nomenclature, composition, concentration of constituents and densities of the 5 biocomposite material systems studied. In the following sections, the properties of all the biocomposite materials will be compared with those using a neat resin system (plate A, no nanoclay and EMS).

Table 1. Biocomposite material properties, Composition and Identification

Specimen Identification and Material Composition							
Specimen Identification	Composition (%)			Fiber Fractions (%)		Density (g/cc.)	
	UPE	EMS	Clay	Weight Fraction	Volume Fraction	Resin	Composite
				W_f	V_f	ρ_m	ρ_c
A	100	0	0	21	18	1.257	1.177
B	90	10	0	21	17	1.234	1.161
C	80	20	0	21	17	1.157	1.157
D	100	0	1.5	22	18	1.245	1.196
E	90	10	1.5	21	17	1.201	1.178

Density of Fiber (ρ_f) = 1.48 g/cc [2].

The nomenclature is also referred as: [UPE / EMS / Clay / W_f / V_f], For example, specimen ID “D” can be referred as [100 / 0 / 1.5 / 22 / 18].

Processing

Plates for the five biocomposite material systems in Table 1 were manufactured by compression molding. The natural fibers were dried in a vacuum oven at 80°C and 100 kPa of pressure for at least 12 hours. The nanocomposite resin was processed by sonicating the clay in acetone for two hours using a solution concentration of 50 liters of acetone to 1 kilogram of clay while it was constantly stirred by a magnetic stirrer. The energy spent on sonication was approximately 30 kJ. The UPE and EMS were then blended and mixed with a magnetic stirrer at approximately 55°C until the majority of acetone was removed. Residual acetone was removed by vacuum extraction at approximately 55°C for 24 hours. The resin system was processed with cobalt

naphthenate (Sigma Aldrich, MO) as a promoter (0.03 wt.% of resin blend) and 2-butanone peroxide (Sigma Aldrich) as an initiator (1.5 wt.% of resin blend). The fibers were then impregnated with the nano-reinforced bio-based resin system (UPE + EMS + nanoclay + initiator + promoter) by hand mixing until the material was consistent (by visual evaluation). The impregnated fibers were then placed in a frame mold. Care was taken to evenly distribute the fiber material in the mold to ensure a uniform sample since natural fibers have a tendency to clump together when mixed. The frame mold was placed between two steel plates covered with Teflon paper. The sample was then cured in a press under 550 kPa of pressure for a total of 4 hours using a time-temperature profile of 100°C for 2 hours, followed by 150°C for 2 hours.

Testing & Characterization

Characterization of the biocomposite material systems was done through coupon samples taken from the compression molded plates. Tensile modulus and strength were measured per ASTM D638. Moisture absorption testing was performed by storing the samples in an environmental chamber at 30°C and 90% humidity and measuring the increase in weight of the samples until steady state was reached. The moisture absorption ratio was evaluated as the percent weight absorbed at steady state. The dispersion and morphology of clay inclusions in the resin systems was observed with transmission electron microscopy (TEM). A JEOL 100CX TEM with LaB₆ filament with 120kV acceleration was used to obtain bright field images. The tensile failure surfaces of biocomposite material systems were observed with a JEOL 6400 field emission scanning electron microscope (SEM) at 10kV acceleration voltage. Specimens were coated with a thin gold film prior to FESEM observations.

Results & Discussion

The biocomposite material system (A), with 100% UPE and no bio-resin content or nanoclay inclusions, is considered as a benchmark material for this study. The addition of EMS or nanoclay may increase or decrease the properties depending on the effect that each of the constituent has on the parameter under consideration. All results in the following sections will thus be compared with the baseline biocomposite (A).

Results for the modulus of elasticity and ultimate tensile strength are given in Figure 1. On an average, the modulus of the biocomposite materials decreased with increasing bio-resin content. The tensile modulus of biocomposites with 10% (B) and 20% (C) EMS was lower by approximately 7% and 40%, respectively, relative to the baseline biocomposite (A). Tensile modulus of the biocomposite is dominated by the natural fibers and hence an increase in tensile modulus due to 1.5wt.% of nanoclay was not expected. Nevertheless, the tensile modulus of biocomposite system (D) with neat resin (no EMS) and 1.5 wt.% nanoclay was approximately 6% higher than the baseline biocomposite. A similar increase was expected for biocomposite (E), with a 10% EMS blend, with respect to biocomposite (B). However, on average, the enhancement in modulus due to the nanoclay reinforcement was not achieved. This could imply that the compliance from the addition of bio-resin was greater than the stiffness enhancement provided by the nanoclay. Nonetheless, it should be pointed out that this reduction could be due to multiple other reasons, including processing issues and slight variations in the amount and distribution of the materials.

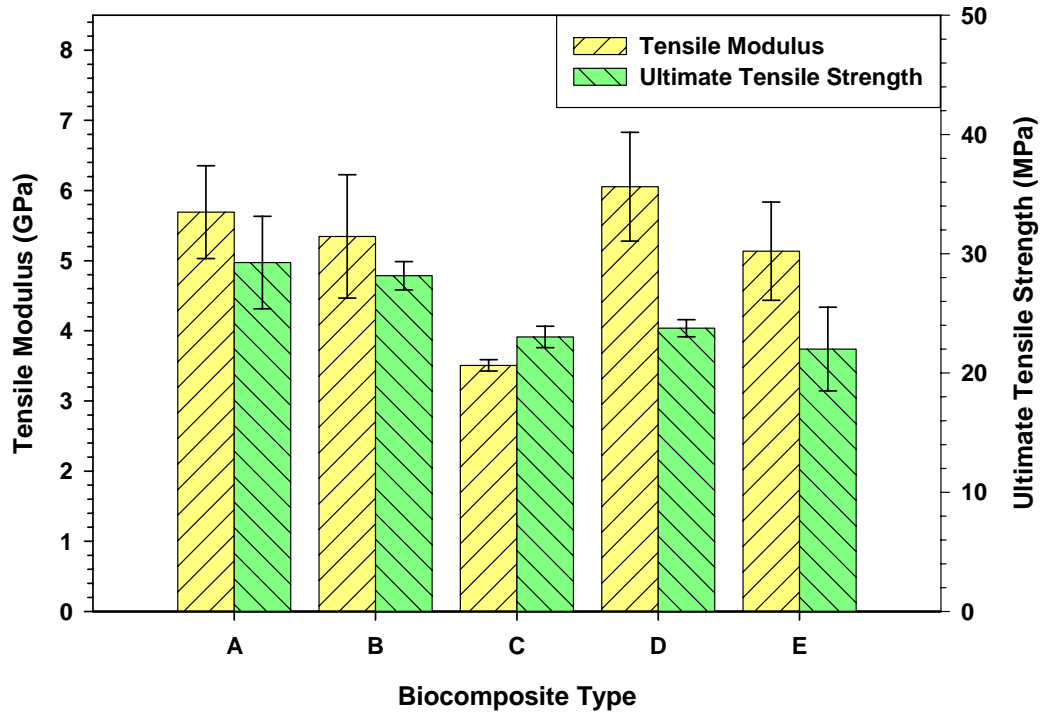


Figure 1. Experimental Tensile Modulus and Ultimate Tensile Strengths of Biocomposites

The addition of bio-resin in UPE seems to lead to a reduction of the ultimate tensile strength, which is attributed to the inherent weak nature of the bio-resin. Ultimate tensile strengths decreased by approximately 4% and 20% for 10% (B) and 20% (C) addition of EMS relative to the baseline UPE biocomposite (A). Similarly, the addition of nanoclay in the resin blends showed decrease in tensile strengths of approximately 20% (D) and 25% (E) relative to benchmark biocomposite (A), respectively. This decrease is attributed to the embrittlement of the resin system. Moreover, the results show high variations which may be due the presence of voids, improper distribution of natural fibers, variation in fiber lengths, distribution of nanoclay etc. Overall, the results show a reduction of tensile modulus due to addition of EMS and an increase in tensile modulus due to addition of nanoclay. Incorporation of higher concentrations of clay and better processing are expected to yield greater enhancement in tensile modulus.

The moisture absorbed by the material systems was measured over a period of 50 days and is shown as a plot of percent weight absorbed versus time in Figure 2. The moisture absorption (MA) of all material systems stabilized after approximately 35 days (800 hours) in an environmental chamber. Results reveal an increase in MA due to addition of bio-resin and a decrease in MA due to addition of nanoclay. An increase of approximately 20% in MA was observed with addition of 20% EMS (C) relative to baseline biocomposite (A). Similarly, the addition of 1.5 wt.% nanoclay in UPE resin biocomposite (D) showed a decrease of about 8% in MA relative to the baseline biocomposite (A). Biocomposite (E) with 10% EMS and 1.5 wt.% nanoclay showed approximately similar MA to the baseline biocomposite (A) with 100% UPE and no clay.

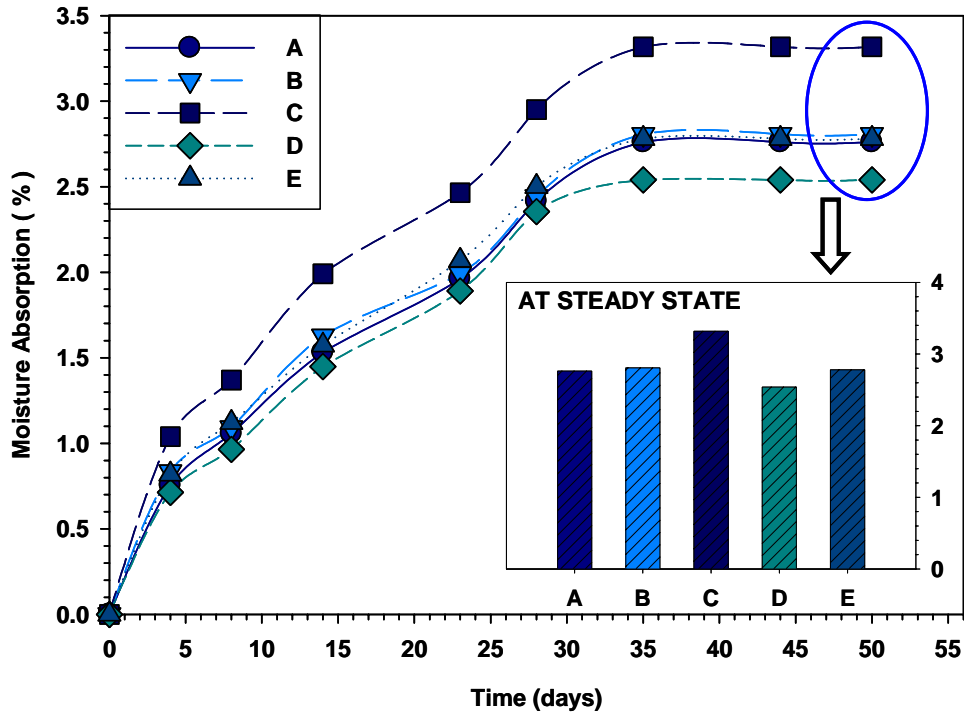


Figure 2. Variation of Moisture Absorption in Biocomposites with time. (Inset: Relative Moisture absorption of biocomposites after steady state has been achieved).

The moisture absorption test results also show that the biocomposite material systems absorbed less moisture than the natural fibers alone. The baseline biocomposite material system (A) absorbed approximately 3% moisture, while the hemp fibers alone are reported to absorb 8% moisture [1]. This data indicates that the matrix material acts as a barrier to help reduce the moisture absorbed by the natural fibers. The addition of bio-resin enables moisture to easily pass through it relative to the primary resin (UPE) and thus reduce the barrier properties of the overall matrix / resin system. The incorporation of nanoclay enhances the barrier properties of the existing matrix / resin system thereby enabling to recover the barrier properties lost due to addition of bio resin.

Transmission electron microscopy was used to observe the dispersion and morphology of nanoclay in the resin system (no fibers). It was observed that the clay platelets were partially exfoliated and partially intercalated, and were well distributed. Scanning electron microscopy (SEM) was used to observe the tensile fracture surfaces and interfacial performance, or pull-out characteristics of the fibers [11]. The failure mechanisms of fiber reinforced polymers are generally: failure of the matrix, fiber or at the fiber and matrix/resin interface [11]. Similar failure morphologies were observed in tensile fracture surfaces of the biocomposites in this study.

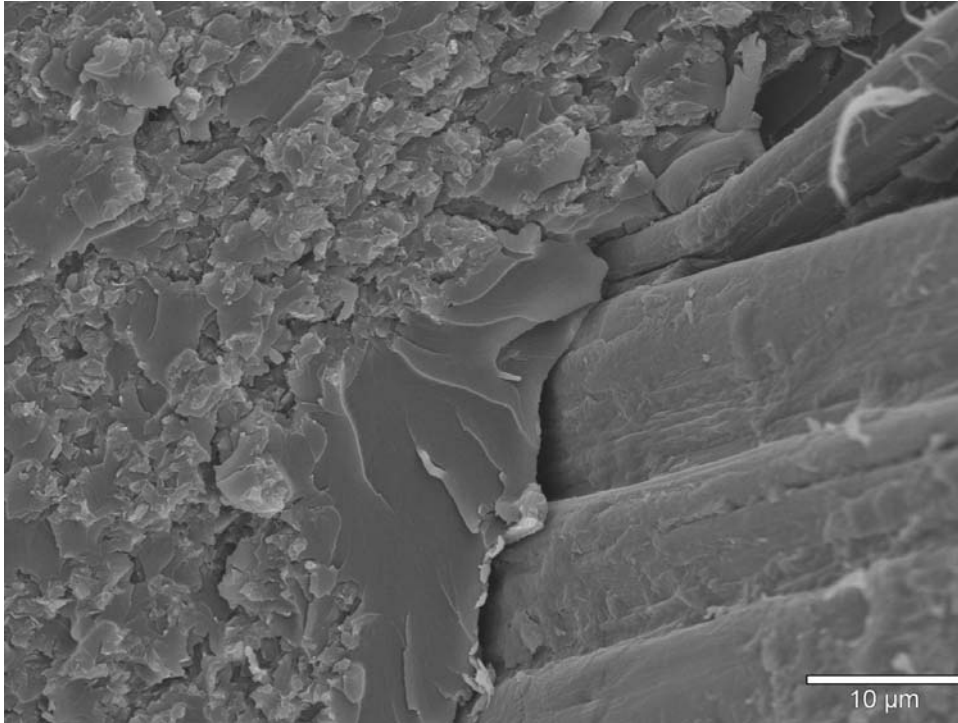


Figure 3. SEM image of tensile failure surface of biocomposite E showing interfacial gap between fiber and matrix

A weak interface, weaker matrix, improper compatibility between natural fiber and the matrix and improper adhesion characteristics may lead to fiber pull-out instead of fracture and may reduce the resulting mechanical properties. A characteristic of fiber pull-out is the interface gap, i.e., the gap between the fiber and the matrix in pulled-out fibers. It was observed that the interfacial gap increased with increasing bio-resin content indicating weaker interface and weaker matrix properties. Figure 3 shows a representative SEM micrograph showing the interfacial gap for biocomposite (E), corresponding to 10% EMS and 1.5 wt.% clay in UPE. The experimental tensile test results support this weaker interface and pull-out phenomena as a reduction in tensile modulus and strength. Nonetheless, the pull-out phenomena enables dissipation of more energy along the interface and hence higher impact strengths and higher ductility was observed for increasing bio-resin content.

The thermo-physical characterization of hybrid biocomposites composed of natural fibers, petroleum based resin, bio based and nanoclay inclusions show a wide variety of multifunctional properties. It was observed that the combination of layered silicates and bio-based resin systems provide biocomposites with similar or better properties than the baseline biocomposite manufactured from natural fibers and UPE without bio-resin and nanoclay. The addition of EMS blends increases toughness but reduces stiffness of the biocomposites. Similarly, the addition of nano-clay platelets increases stiffness along with brittleness of the resin system but reduces the toughness and ductility of the resulting composites. The advantages of combining EMS and layered silicates is not limited to only achieving stiffness-toughness balance of the resulting composites, but similar enhancements were observed in barrier and thermal properties

Conclusions

Results from this study indicate that biocomposites obtained from the combination of industrial raw hemp and blends of unsaturated polyester with epoxidized methyl soyate and nanoclay inclusions can lead to the development of novel hybrid biocomposites. The properties of the resulting biocomposite are tailorable and can be controlled by the amount and distribution of the constituents. Tensile tests showed that the addition of bio-resin lowers the stiffness and ultimate tensile stress, but increases ductility. The addition of nanoclay enhances stiffness but seems to decrease the toughness. Thus, the study shows that a proper stiffness–toughness balance can be obtained by controlling the amount of bio-resin and nanoclay content. Moreover, the resulting biocomposites show value added multifunctional properties, like improvements in barrier properties. Incorporation of higher concentrations of bio-resins and nanoclay along with improvements in processing will enable maximizing the multifunctional properties that the hybrid biocomposites offer. The study shows that biocomposites for structural applications with proper stiffness-toughness balance can be obtained while meeting the objectives of environmental friendliness and cost effectiveness.

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References

- [1] Brouwer W.D. Natural Fibre Composites: Where Can Flax Compete with Glass? *SAMPE Journal* 2000; 36:18-23.
- [2] Burgueño, R., Quagliata, M.J., Mehta, G.M., Mohanty, A.K., Misra, M., Drzal, L.T. "Sustainable cellular biocomposites from natural fibers and unsaturated polyester resin for housing panel applications." *Journal of Polymers and Environment* 2005; 13:139-149.
- [3] Donnell, A.O., Dweib, M.A., and Wool, R.P., "Natural fiber composites with plant oil based resin." *Composites Science and Technology* 2004, 64:1135-1145.
- [4] Haq, M., Burgueño, R., Mohanty, A.K., and Misra, M., "Hybrid Biobased composites from blends of Unsaturated Polyester and Soy Bean Oil Reinforced with Nanoclay and Natural Fibers." *Composites Science and Technology*. Communicated August 2007.
- [5] Le Baron, P.C., Wang, Z., Pinnavaia, T.J., "Polymer – layered silicate nanocomposites: an overview." *Applied Clay Science*. 1999; 15:11-29
- [6] Miyagawa, H., Mohanty, A.K., Burgueño, R., Drzal, L.T., Misra, M., "Novel biobased resins from blends of functionalized soyabean oil and unsaturated polyester resin." *Journal of Polymer Science : Part B: Polymer Physics* 2007; 45: 698-704
- [7] Miyagawa, H., Mohanty, A.K., Burgueño, R., Drzal, L.T., and Misra, M., "Development of biobased unsaturated polyester containing functionalized vegetable oils." *Industrial and Engineering Chemistry Research*. 2006; 45:1014-1018.
- [8] Mohanty, A.K, Misra M, Hinrichsen, G. *Biofibers, Biodegradable Polymers and Biocomposites: An Overview*. *Macromolecular Materials and Engineering* 2000; 276/277:1-24.

- [9] Nair, S.V., Goettler, L.A., and Lysek, B.A., "Toughness of nanoscale and multiscale polyamide -6,6 composites." *Polymer Engineering and Science*. 2002; 42:1872-1882.
- [10] Nickel, J., Riedel, U., "Activities in biocomposites." *Materials Today* 2003; 6:44-48
- [11] Shibata, M., Ozawa, K., Teramoto, N., Yosomiya, R., Takeishi, H., "Biocomposites made from short abaca fiber and biodegradable polyesters." *Macromolecular materials and engineering* 2003; 288:35-43.