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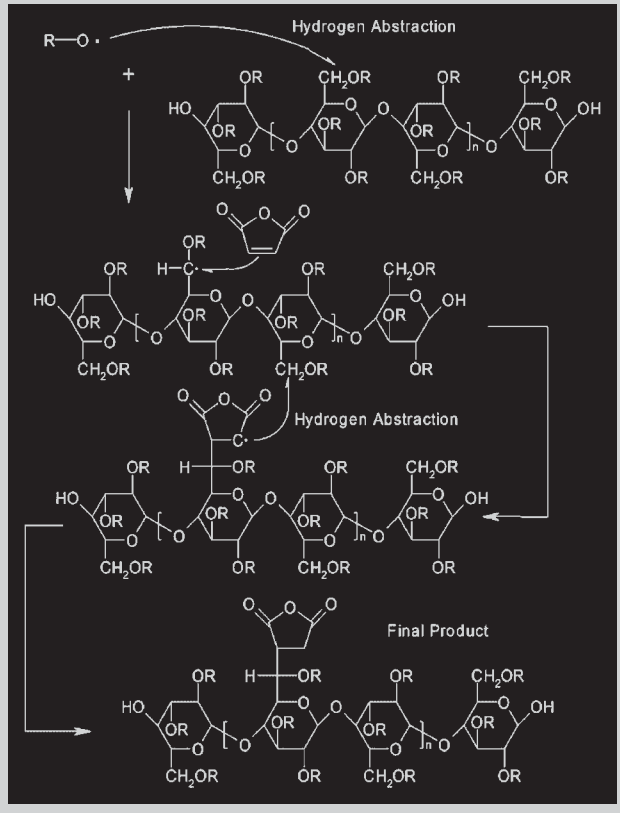
**Summary:** Interfacial adhesion between fibers and matrix is a crucial factor for effective stress transfer from matrix to fiber; especially in short fiber reinforced composite systems. The use of a chemical compatibilizer is an efficient means to achieve such adhesion. Maleic anhydride-grafted-cellulose acetate butyrate (CAB-g-MA) is one such compatibilizer which can be used in biocomposite fabrication, and this has been synthesized in our laboratory by utilizing a twin-screw reactive extrusion process in the presence of a free radical initiator (2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane). The unique feature of this process is its solvent-free approach for grafting of maleic anhydride onto CAB, without hydroxyl group protection. CAB-g-MA was characterized using FTIR as well as by a non-aqueous titration method. The effects of initiator and monomer concentrations and various processing conditions on the graft content were also investigated. The preliminary results show that by adding approximately 10 wt.-% of CAB-g-MA into a plasticized cellulose acetate butyrate (TEB)-industrial hemp fiber biocomposites system, an improvement in tensile strength (20%) and in tensile modulus (45%) were obtained. These results are promising in that they pave the way for future studies involving the use of CAB-g-MA as a suitable compatibilizer for cellulose ester-natural fiber biocomposites.




# A Solvent Free Graft Copolymerization of Maleic Anhydride onto Cellulose Acetate Butyrate Bioplastic by Reactive Extrusion

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## Introduction

Sustainable biocomposites can be fabricated using biopolymers derived from biomass as matrices, and natural plant fibers (PF) as reinforcing materials. A potentially useful biodegradable, biobased polymer that is compatible with polar plant fibers (PF) is cellulose ester (CE). Our initial work has shown that cellulose esters particularly plasticized cellulose acetate (CAP) and cellulose acetate butyrate (CAB) have better mechanical and damping

properties than those of non-polar, petroleum based poly(propylene) matrices in composites prepared from industrial hemp (a bast natural fiber) as reinforcing material.[1,2] The polar-polar interaction between the PF and CE produces good interfacial adhesion and thus better stress transfer from matrix to fibers, resulting in high performance biocomposites.

In order to compete with petroleum based glass-reinforced poly(propylene) for structural applications, the interfacial adhesion between PF and CE has to be improved further. To improve adhesion, the addition of a suitable coupling agent would be an economically feasible option as an alternative to surface treatment of fibers. Significant enhancement of mechanical properties was achieved for poly(propylene) based composites after addition of maleated poly(propylene) (PP-g-MA).[3,4] Currently, a number of maleated poly(propylene)s with varying acid numbers and molecular weights are commercially available.[5] No reports have been made concerning the grafting of MA onto cellulose ester bioplastics. The main motivation of the present investigation is to investigate the mechanism of maleation onto polar bioplastics which is known to be significantly different to maleation onto nonpolar plastics. In this study, maleic anhydride grafted CAB (CAB-g-MA) has been synthesized as a compatibilizer by reactive extrusion and characterized with FTIR and acid base titration. Initiator and monomer concentrations were optimized based on the FTIR and titration results. A preliminary study was conducted in order to investigate the effect of this CAB-g-MA compatibilizer on the adhesion of industrial hemp fiber reinforced plasticized CAB (TEB) biocomposites system.

## Experimental Part

*Materials*

Cellulose acetate butyrate (CAB 381-20) free from any plasticizer and additives, was supplied by Eastman Chemical Co., Kingsport, TN, with a butyryl content of 37%, acetyl content of 13.5%, hydroxyl content of 1.8% and melting and glass transition temperatures of 195 and 141 °C, respectively. Maleic anhydride (MA), acetone, and 0.1011 N methanolic KOH were purchased from Aldrich Chemical Co and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane (Luperox 101) was obtained from Akzo Nobel, USA. Sodium hydride (NaH), sodium hydroxide (NaOH) were purchased from Aldrich Chemical Co and used as received.

*Instrumentation*

The FTIR spectra of neat CAB and CAB-g-MAs were recorded in absorbance mode from compression molded thin films using a Perkin-Elmer Spectrum 2000 FTIR spectrophotometer.

*Preliminary Experiment to Determine Reactivity of Existing OH Group*

Free hydroxyl groups are normally expected to react with anhydrides under suitable reaction conditions leading to anhydride ring opening reactions. Thus, grafting of maleic anhydride onto cellulose esters would require hydroxyl group protection in order to avoid the reaction with anhydride. We allowed these OH groups in cellulose acetate butyrate (CAB) to react with NaH, NaOH, and maleic anhydride to determine their reactivity with the following procedures:

1) Reaction of NaH with CAB

$$\mathrm{NaH} + \mathrm{R-OH} \underset{\text{Dry acetone}}{\longrightarrow} \mathrm{R-ONa} + \mathrm{H_2}$$

NaH was added into dissolved CAB in dry acetone in a 1:1 molar ratio. The mixture was heated while stirring until NaH dissolved. CAB-ONa was obtained after precipitation using methanol and the precipitate was vacuum dried overnight at 80 °C prior to FTIR analysis.

2) Reaction of NaOH with CAB

$$\mathrm{R-OH} + \mathrm{NaOH} \underset{\text{Heat}}{\longrightarrow} \mathrm{R-ONa} + \mathrm{H_2O}$$

CAB was diluted in DI water at a temperature ranging from 60–70 °C. The free OH groups of CAB need effective swelling agent (water) to be reactive.[6] Aqueous NaOH (20 wt.-%) was added into diluted CAB while stirring. The mixture was left for reaction for 6 h. CAB-ONa powder was collected after filtration on a Buchner filtration system and vacuum dried overnight at 80 °C prior to FTIR analysis.

3) Extruded CAB + MA and CAB + MA + Initiator

These experiments were done in order to find out whether MA reacts with the free OH groups and if so to what extent. Premeasured amounts of CAB and 5 wt.-% MA were mixed in small beaker. For the second experiment 1 wt.-% of the liquid initiator was added dropwise into CAB and 5 wt.-% MA mixture using a syringe while stirring. Each resultant mixture (about 12 grams total) was fed separately into a DSM Research 15 cc Micro Extruder, (DSM Research, Netherlands), under the following conditions: temperatures in zone 1, 2, and 3 were kept between 195 to 205 °C, screw speed was 100 rpm, cycle time was 3 min. The resultant thin strands (extrudate) was collected and pelletized into granules. All samples were put in vacuum oven for overnight at 80–90 °C to eliminate unreacted MA. This vacuum dried samples were compression molded (in a Carver Press SP-F 6030) into thin films at 197 °C for FTIR measurements.

*Synthesis of Maleic Anhydride Grafted CAB (CAB-g-MA)*

Two processing techniques were adopted for the synthesis of CAB-g-MA:

 

Table 1. Effect of initiator concentration (CAB-g-MA 1, 2, and 3) and effect of MA concentration (CAB-g-MA 2, 4, and 5) on acid number (*AN*) and % MA grafting.

| Material | Description | *AN* | StDev | % MA | StDev |
|---|---|---|---|---|---|
| CAB, neat | 100% CAB powder 381-20 | – | – | – | – |
| CAB-g-MA 1 | 0.5 wt.-% Initiator + 5 wt.-% MA + 94.5 wt.-% CAB, neat | 12.8 | 0.0 | 0.6 | 0.0 |
| CAB-g-MA 2 | 0.9 wt.-% Initiator + 5 wt.-% MA + 94.1 wt.-% CAB, neat | 19.7 | 1.1 | 0.8 | 0.2 |
| CAB-g-MA 3 | 1.4 wt.-% Initiator + 5 wt.-% MA + 93.1 wt.-% CAB, neat | 18.2 | 0.0 | 0.8 | 0.0 |
| CAB-g-MA 4 | 0.9 wt.-% Initiator + 7.5 wt.-% MA + 91.6 wt.-% CAB, neat | 31.7 | 1.5 | 1.8 | 0.4 |
| CAB-g-MA 5 | 0.9 wt.-% Initiator + 10 wt.-% MA + 89.1 wt.-% CAB, neat | 24.2 | 0.0 | 1.2 | 0.0 |

Process I: Small-Scale Extrusion Using DSM Micro Extruder

Pre-measured amounts of CAB and MA were mixed in a beaker and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane was added dropwise using a syringe and stirring continuously. List of compositions of MA and initiator used was described in Table 1. The resultant mixture (about 12 grams total) was fed into a DSM Research 15 cc Micro Extruder (DSM Research, Netherlands), under the following conditions: temperatures in zone 1, 2, and 3 were kept between 195 to 205 °C, screw speed was 100 rpm, cycle time was 3 min. Thin strand (extrudate) was collected and pelletized into granules.

Process II: Pilot-Scale Extrusion Using ZSK-30 Twin-Screw Extruder

Premeasured CAB and MA were mixed in a kitchen mixer. Liquid initiator was added dropwise while stirring. The resulting mixture (about 1 500 g in total) was hand fed into ZSK-30 twin screw extruder and processed under the following conditions: temperatures in zone 1 to 6 were kept between 190 to 195 °C with die temperature of 200 °C, 150 rpm screw speed and 50% torque reading. Extrudate was collected and pelletized.

*Characterization of CAB-g-MA by FTIR (Qualitative)*

The pellets as obtained by Process I and II were vacuum dried overnight at 80 to 90 °C to remove unreacted maleic anhydride. All unreacted maleic anhydride (MA) was removed after the granulated samples were put inside vacuum oven at 80–90 °C and left overnight. This is evidenced by FTIR analysis (Figure 1) which shows the disappearance of the small peak at 1 850 $cm^{-1}$ which is attributed to the unreacted MA. Some of the vacuum dried CAB-g-MA was compression molded (in a Carver Press SP-F 6030) into thin films at 197 °C for FTIR measurements.

*Characterization of CAB-g-MA by Titration (Quantitative)*

Purified CAB-g-MA was used to determine acid number (*AN*) and percentage MA grafting (% MA) using titration method.

The following procedure was adopted in this quantitative measurement: 0.2 g of CAB-g-MA was dissolved in hot acetone (≈200 ml) on a hot plate whilst stirring. The hot solution was then titrated against 0.1011 N methanolic KOH adding 5 drops of thymol blue in DMF (1%) as indicator. The appearance of a stable yellow color indicated the end point. The acid number (*AN*) and grafting percentage (% MA) were calculated using the following equations:

$$AN = \frac{V_{KOH}N_{KOH}(EW)}{\text{weight of sample}}\left(= \frac{\text{mg KOH}}{\text{g of sample}}\right) \quad (1)$$

$$\%\text{MA} = V_{\text{KOH}}N_{\text{KOH}}(EW)(\text{g of sample})(100\%) \quad (2)$$

$$\text{where } EW = \frac{MW}{\text{number of } H^+ \text{ or } OH^- \text{ donor}}$$

*V*, *N*, *EW*, *MW* are volume, normality, equivalent weight, and molecular weight, respectively. A blank titration on neat CAB was also carried out and this procedure is described elsewhere.[7]

## Results and Discussion

Cellulose is a linear polysaccharide which comprises of cellobiose repeat units linked $\beta$-1 to 4.[8] A cellobiose unit consists of two anhydroglucose repeat units with two hydroxyl groups located on opposite sides of the backbone. In general, cellulose extracted from natural resources is high molecular weight non-branching polysaccharides and has a conformation with great tendency to form

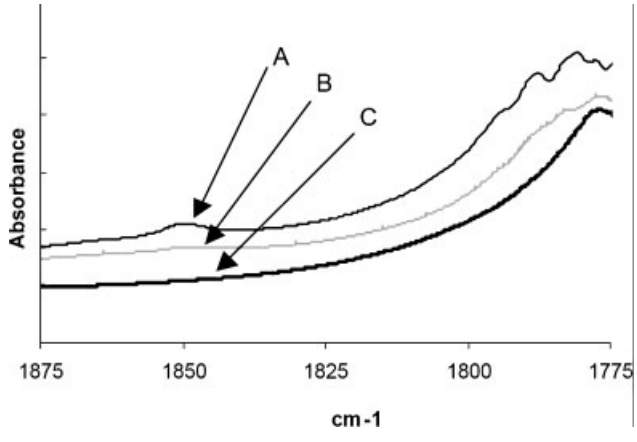


Figure 1. FTIR curve showing unreacted maleic anhydride (MA) peak before putting in vacuum oven (A) and after putting in vacuum oven at 80–90 °C for overnight (B), and (C) is neat CAB.

 

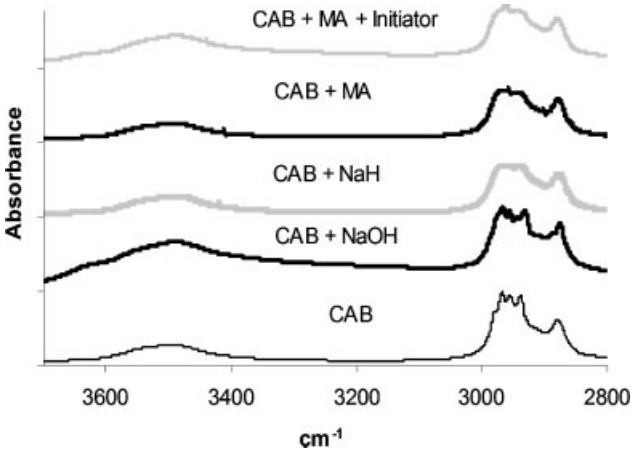


Figure 2. FTIR analysis of OH protection on cellulose acetate butyrate (CAB) using different materials: NaOH, NaH, and MA with and without initiator.

intermolecular hydrogen bonding. Extensive hydrogen bonding produces cellulose fibers which are highly insoluble and relatively impermeable to liquids.[9] The inherent rigidity of cellulose originates from inter- and intra-molecular hydrogen bonding of the free hydroxyl groups in the anhydroglucose repeating unit of the chains. The stability of the structure, thus mainly depends upon the ability to form hydrogen bonds. As a consequence, cellulose is not a thermoplastic but degrades on heating before the theoretical melting point is reached. Breaking the hydrogen bonds by solubilization and reacting the free hydroxyl groups yields a thermoplastic, such as cellulose ethers and cellulose esters.

FTIR spectra (Figure 2) of these reacted CAB (preliminary experiment section) did not show any changes in the intensity of OH peak (around 3 500 $cm^{-1}$), indicating that almost all reactive (primary and secondary) hydroxyl groups are esterified in CAB. The remaining free hydroxyl groups are either hindered or docile and do not react with maleic anhydride. Thus, free radical grafting of MA onto CAB could be carried out without OH group protection.

The proposed mechanism of CAB maleation is schematically represented in Figure 3. The process involves free radical generation on the CAB backbone using a peroxy radical initiator. The free radicals on the polymer chains react with the MA to give CAB-g-MA (Note: hydrogen abstraction is from the CAB backbone). The compositions of process I yielding the best results of MA grafting were chosen for process II (using a chosen temperature and rpm). The repeatability of Process II was measured in terms of having similar acid number and percentage grafting to that of Process I.

Two parameters investigated in this paper were initiator concentration and monomer concentration. The initiator concentration was varied as follows: 0.5, 0.9, and 1.4 wt.-%

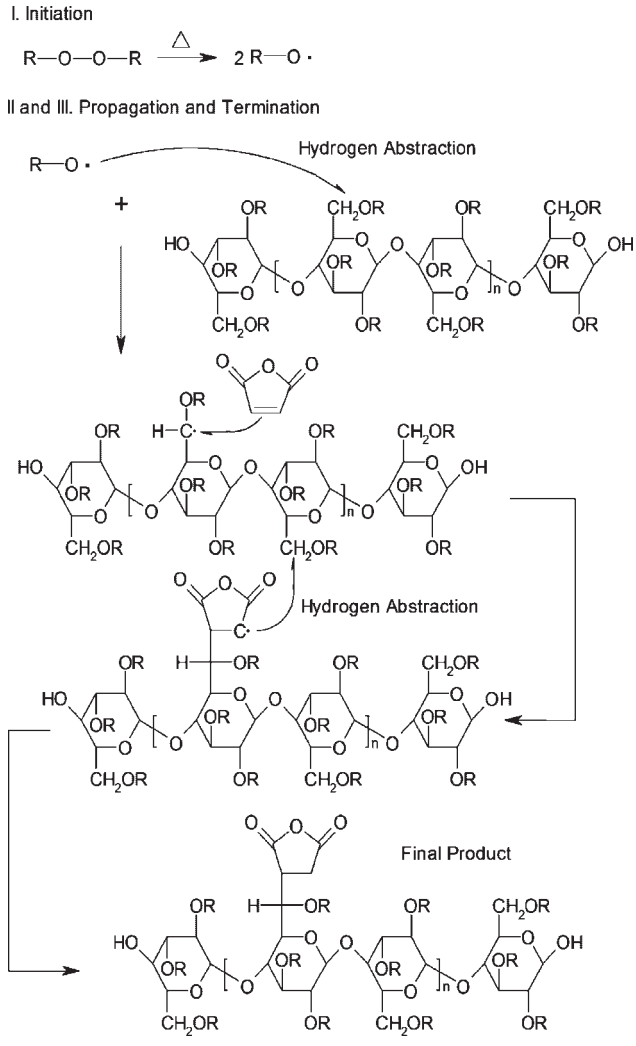


Figure 3. Proposed mechanism of maleic anhydride grafted cellulose acetate butyrate (CAB-g-MA).

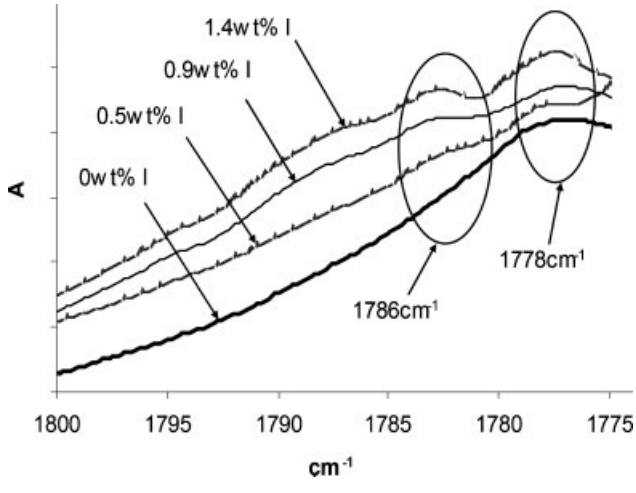


Figure 4. FTIR analysis of varying initiator (I) concentration (0, 0.5, 0.9, and 1.4 wt.-%) with 5 wt.-% maleic anhydride (MA) content kept constant.

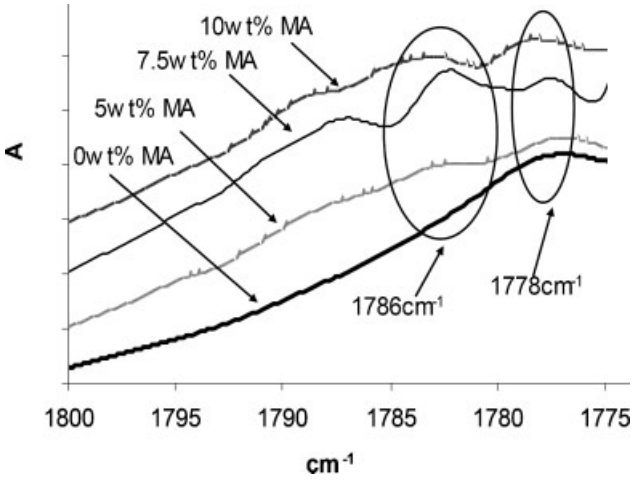


Figure 5. FTIR analysis of varying maleic anhydride (MA) concentration (0, 5, 7.5, and 10 wt.-%) with 0.9 wt.-% initiator content kept constant.

while keeping 5 wt.-% MA constant with the following nomenclature: CAB-g-MA **1**, **2**, and **3**, respectively (Figure 4 and Table 1). Here, anhydride groups belonging to MA were assigned to a peak value of 1 786 $cm^{-1}$ whereas carbonyl groups of neat CAB were designated by 1 778 $cm^{-1}$ peak. Silverstein et al. reported that C=O of MA showed band at 1 788 $cm^{-1}$ corresponding to the symmetric C=O stretch of a saturated cyclic five membered anhydride.[10] The increase in the anhydride peak intensity with initiator concentration is apparent in the FTIR spectra. As initiator amount increased, acid number and % MA increased up to 0.9 wt.-% initiator and then leveled off due to the lack of free radicals on the CAB backbone. From above results, 0.9 wt.-% was set as optimum amount for initiator for this system.

The initiator amount of 0.9 wt.-% was kept constant while varying MA concentration from 5 to 10 wt.-%. Figure 5 and Table 1 shows that acid number and % MA increases with the amount of MA in the reaction mixture. Maximum grafting was observed for 7.5 wt.-% of MA in the reaction mixture. This result is supported by the increase in the intensity of the anhydride peak in CAB-g-MA samples. The grafting reached steady as the formed radicals was fully consumed hence extra MA could no longer be grafted. Based upon FTIR, *AN*, and % MA results, compositions for CAB-g-MA 2 and CAB-g-MA 4 (Table 1) were chosen for higher quantity scale up.

One of the aims of this research was to develop a commercially and industrially feasible process for the production of CAB-g-MA with predetermined acid number and % MA content. With such conditions described in experimental part for Process II, we have successfully developed products as shown in Table 2 in which equivalent values of acid number and % MA (considering the overlapping error bars) were observed for Process II as compared to those of Process I.

Interfacial adhesion between fibers and cellulose ester matrices can be enhanced by the addition of small amount of a suitable compatibilizer. Our preliminary results have shown that by addition of ≈10 wt.-% of this compatibilizer (CAB-g-MA) into plasticized cellulose acetate butyrate (TEB)-industrial hemp fiber biocomposites system; an improvement in tensile strength of about 20% and a 45% enhancement in tensile modulus (Figure 6) were obtained.

## Conclusion

We have successfully synthesized maleated cellulose acetate butyrate (CAB-g-MA) with controlled acid number by a solvent free process for a compatibilizer in cellulose ester based biocomposites. It is shown that OH group protection is not necessary since the reactivity of the OH groups on the CAB backbone was low. The effects of initiator and maleic anhydride (MA) concentration on the synthesis of CAB-g-MA were studied by Process I (DSM micro extruder – small scale). Acid numbers of the maleated CAB increased with the MA and the initiator concentrations. Using chosen reaction conditions and reagent compositions, the grafting reaction was reproduced by Process II in a pilot-scale fabrication using ZSK-30 Twin Screw Extruder – to achieve similar acid numbers and percentage grafting to those of Process I. Our initial study showed an improvement in mechanical properties of industrial hemp fiber reinforced TEB (plasticized CAB)

Table 2. Acid number and maleic anhydride percentage (% MA) comparison between samples obtained from Process I (DSM micro extruder) and Process II (ZSK-30 pilot extruder).

| Material | Description | Process I (DSM Microextruder) | | | | Process II (ZSK-30 Large extruder) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Acid number | StDev | % MA | StDev | Acid number | StDev | % MA | StDev |
| CAB-g-MA 2 | 0.9 wt.-% Initiator + 5 wt.-% MA + 94.1 wt.-% CAB, neat | 19.7 | 1.1 | 0.8 | 0.2 | 18.8 | 1.7 | 0.8 | 0.1 |
| CAB-g-MA 4 | 0.9 wt.-% Initiator + 7.5 wt.-% MA + 91.6 wt.-% CAB, neat | 31.7 | 1.5 | 1.8 | 0.4 | 33.2 | 1.4 | 1.5 | 0.1 |

 

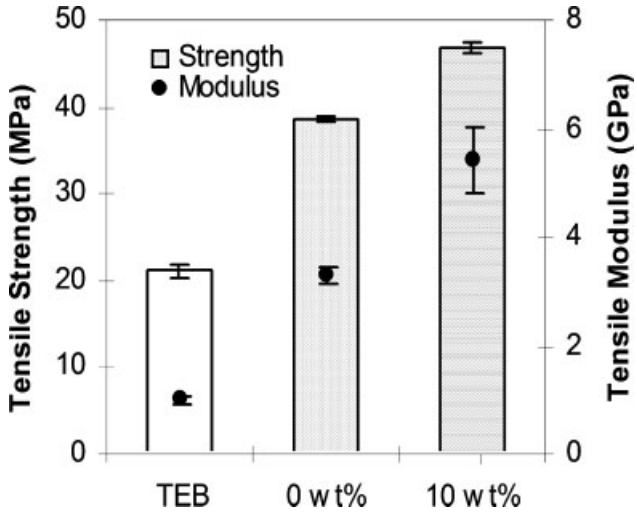


Figure 6. Effect of addition of 10 wt.-% CAB-g-MA compatibilizer on tensile properties of industrial hemp fiber reinforced TEB (plasticized CAB) biocomposites.

biocomposites due to addition of CAB-g-MA compatibilizer. Detailed investigation on the effect of CAB-g-MA compatibilizer on adhesion of various cellulose fiber based biocomposites will be presented in future publications.

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[1] A. K. Mohanty, A. Wibowo, L. T. Drzal, M. Misra, *Compos. Part A: Appl. Sci. Manufact.* **2004**, *35*, 363.
[2] A. Wibowo, A. K. Mohanty, M. Misra, L. T. Drzal. *Ind. Eng. Chem. Res.* **2004**, *43*, 4883.
[3] L. Haijun, M. M. Sain, *Polym. Plast. Technol. Eng.* **2003**, *42*, 853.
[4] A. K. Mohanty, L. T. Drzal, M. Misra, *J. Adhes. Sci. Technol.* **2002**, *16*, 999.
[5] T. J. Keener, R. K. Stuart, T. K. Brown, *Compos. Part A: Appl. Sci. Manufact.* **2004**, *35*, 357.
[6] K. C. Gupta, *Cellulose* **2001**, *8*, 223.
[7] D. Carlson, L. Nie, R. Narayan, P. J. Dubois, *J. Appl. Polym. Sci.* **1999**, *72*, 477.
[8] R. D. Gilbert, J. F. Kadla, in: ''*Biopolymers from Renewable Resources*'', D. L. Kaplan, Ed., Springer-Verlag, New York 1998, chapter 3.
[9] J. F. Robyt, in: ''*Essentials of Carbohydrate Chemistry*'', Springer-Verlag, New York 1998.
[10] R. M. Silverstein, ''*Spectrometric Identification of Organic Compounds*'', John Wiley & Sons, New York 1981.