GRAFTNING OF POLY(ε-CAPROLACTONE) FROM MICROFIBRILLATED CELLULOSE FILMS – FOR BIOCOMPOSTES APPLICATIONS

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ABSTRACT

Environmental friendly composites can be made using nanosized cellulose fibers. However, in order to fully utilize the nanofibers potential, the compatibility between the hydrophobic matrix and the hydrophilic fibers must be improved. This can be obtained by grafting of nonpolar polymer from the cellulose surface. Films of microfibrillated cellulose (MFC) have been grafted with different molecular weights of poly(e-caprolactone) (PCL). MFC-films have also been modified with xyloglucan (XG), and xyloglucan end-functionalized with 2,2-bis(methylol)propionic acid (XG-bisMPA), before grafting. PCL grafted films were analysed with Fourier Transform Infrared Spectroscopy, and via contact angle measurement. Grafted, and ungrafted, MFC-films were coated with a PCL-film, producing a laminate. Interfacial adhesion was tested using dynamic mechanical analysis (DMA). In case of laminates that consisted of unmodified grafted MFC-films, the adhesion between the layers was significantly improved after grafting. However, laminates produced from XG and XG-bisMPA modified MFC-film showed no improvement of the interfacial adhesion.

KEYWORDS: microfibrillated cellulose, grafting of poly(e-caprolactone), laminate, biocomposite

1. INTRODUCTION

The search for new environmental friendly material has lead to a rapid growing interest in the development of biocomposites.[1] However, the usefulness of these new materials depends on its mechanical properties, requiring that the mechanical properties of conventional composites are preserved or improved in the biocomposites. This may be achieved using cellulose nanofibers as reinforcement in composites as they provide enhanced mechanical properties, even with a low content of nanofibers. Additional benefits using nanofibers are biodegradability, low density and low cost. [2, 3] Microfibrillated cellulose (MFC) consists of moderately degraded cellulose with nano-order scale microfibrils, which have been used as reinforcement in nanocomposites [4, 5] A major disadvantage using cellulose nanofibers, or MFC, as reinforcement is the poor compatibility with hydrophobic polymer matrix, or non-polar organic solvent. Thereby, the full potential of the nanofibers can not be utilized, which limits the possible end-use applications. Nonpolar polymers can be grafted directly off the cellulose surface [6], changing its hydrophobicity - Consequently, the compatibility with a hydrophobic polymer matrix will be improved, and stronger interfacial adhesion can be obtained.

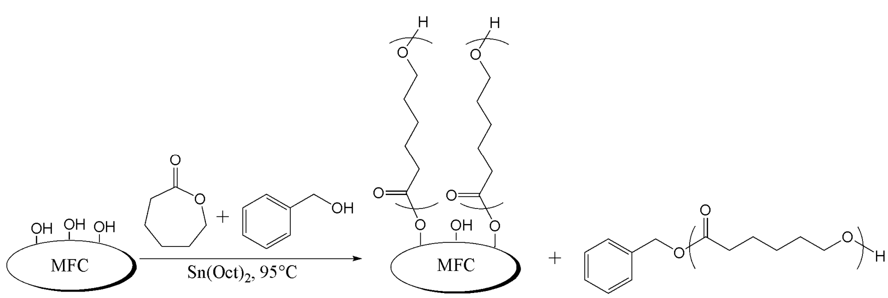
In this study MFC-films have been grafted with poly(ε-caprolactone) (PCL) with aimed DP:s of 300, 600, and 1200; ring-opening polymerization (ROP) was used as polymerization technique, resulting in well-defined polymers from cyclic monomers.[7] MFC-films have also been modified with xyloglucan (XG), and xyloglucan end-functionalized with 2,2-bis(methylol)propionic acid (XG-bisMPA), before grafting with PCL - the aimed DP was then 1200. The PCL grafted MFC-films were finally coated with a PCL film, producing a laminate. The interfacial adhesion of the laminates was evaluated in a peeltest, using dynamic mechanical analysis (DMA).

2. EXPERIMENTS

A typical procedure for the grafting of MFC-film with PCL is as follows: MFC-film was put into a flask with a magnetic stirrer. The initiator, benzyl alcohol, was added to the reaction flask. The flask was sealed with a rubber septum and followed by 3 vacuum/Ar-gas cycles. Thereafter the monomer, ε-CL, and toluene were added to the reaction flask with a syringe under Ar-gas flow. A catalytic amount of $SnOct_2$ was added to the reaction mixture under Ar-gas flow. The polymerization was allowed to proceed at 95°C.

3. RESULTS

MFC-films, both unmodified and XG- and XG-bisMPA-modified, have been grafted with PCL, Scheme 1.



Scheme 1. Ring-opening polymerization of ε-CL from MFC-films, with benzylalcohol as free initiatior.

The polymerizations were monitored with NMR, and high conversion was obtained in all reactions. The free PCL was characterized with NMR and SEC, see Table 1.

Table 1. Characterization of free PCL formed during ROP from unmodified, XG- and XG-bisMPA modified, MFC-films.

MFC-film	Aimed DP	SEC				NMR	
		conventional calibration		*universal calibration*			
		M_n	**PDI**	**M_n**	**PDI**	**MW**	**conversion**
Unmodified	300	14600	1.8	6800	1.7	15200	>99%
Unmodified	600	14100	2.0	6400	2.0	16200	>99%
Unmodified	1200	14600	1.7	6500	1.7	15200	>99%
XG	1200	12700	1.7	5800	1.7		>99%
XG-bisMPA	1200	11700	1.6	1900	1.6		>99%

PCL grafted MFC-films were thoroughly washed before characterization with Fourier Transform Infrared Spectroscopy (FTIR), and contact angle (CA) measurement, Table 2.

Table 2. Contact angles measurement of pure PCL-film, reference MFC-film, and PCL grafted MFC-films.

Sample	**Contact angle (°)**	**Std. dev.**
Pure PCL	84	0.9
Unmodified MFC film	56	1.9
MFC film-XG	81	1.8
MFC film-XG-bisMPA	80	1.3
MFC film-PCL DP300	107	4.3
MFC film-PCL DP600	103	2.2
MFC film-PCL DP1200	115	0.8
MFC film-XG-PCL DP1200	100	0.7
MFC film-XG-bisMPA-PCL DP1200	107	0.6

FTIR-spectra of the PCL grafted unmodified MFC-films, Figure 1, clearly show carbonyl peaks at 1736 cm-1, which confirms the presence of PCL. Results from the SEC and NMR analyses on the free PCL from these films showed that all three samples had approximately the same molecular weight. However, according to FTIR and estimated contact angles, different amounts of PCL were grafted from the films. Figure 2 shows the contact angle images of ungrafted and PCL grafted MFC films.

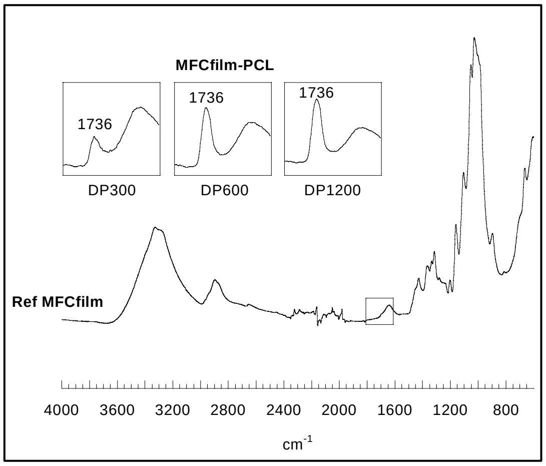
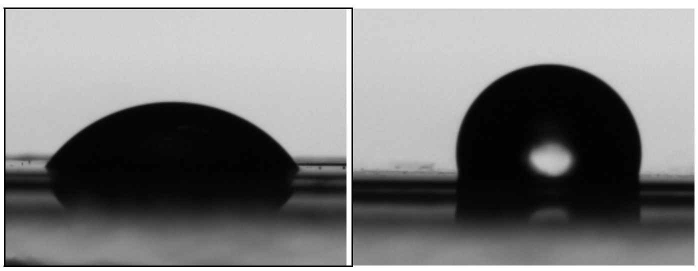


Figure 1. FTIR-spectra of reference MFC film, and MFC-films grafted with different lengths of PCL: DP300, DP600, and DP1200



(a) (b)

Figure 2. Contact angle images of reference MFC-film (a) and MFC-film grafted with DP1200 (b).

Different result was seen in the FTIR spectra of the PCL-grafted MFC-films modified with XG and XG-bisMPA, Figure 3 (A) and (B), respectively; in which a very small carbonyl adsorption was detected, indicating that a very small amount of PCL had been grafted from the films. However, the contact angle measurements showed a pronounced difference in contact angle between the ungrafted and the grafted films, clearly demonstrating the presence of PCL. The probable reason for this inconsistency between the contact angles and the FTIR analysis is that the grafted PCL layer on the MFC films is to thin to be detectable by the FTIR. This might, in turn, be due to the much smoother surfaces of the XG- and XG-bisMPA modified MFC films compared to the unmodified MFC films, demonstrated by the much larger contact angles of the modified MFC films

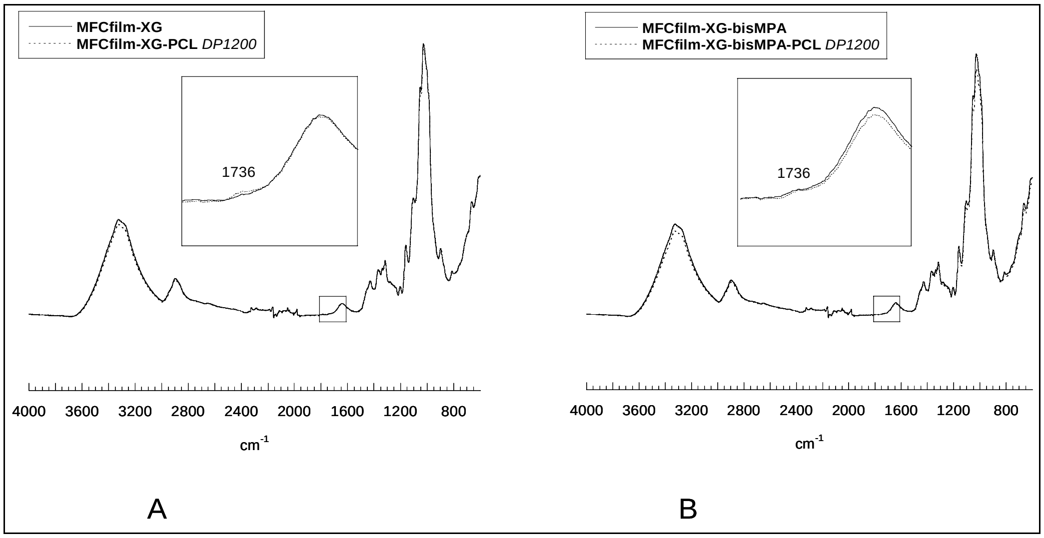


Figure 3. FTIR-spectra: **(A)** MFC-film-XG, and MFC-film-XG-PCL and **(B)** MFC-film-XG-bisMPA, and MFC-film-XG-bisMPA-PCL. In both cases the aimed was DP1200.

Preliminary results from dynamic mechanical analysis (DMA) are shown in Figure 4. The static force, illustrating the strength of the interfacial adhesion between the different layers in the MFC-film and PCL laminate, was significantly increased after grafting with PCL from unmodified MFC-films. However, laminates produced from XG and XG-bisMPA modified MFC-film showed no improvement of the interfacial adhesion.

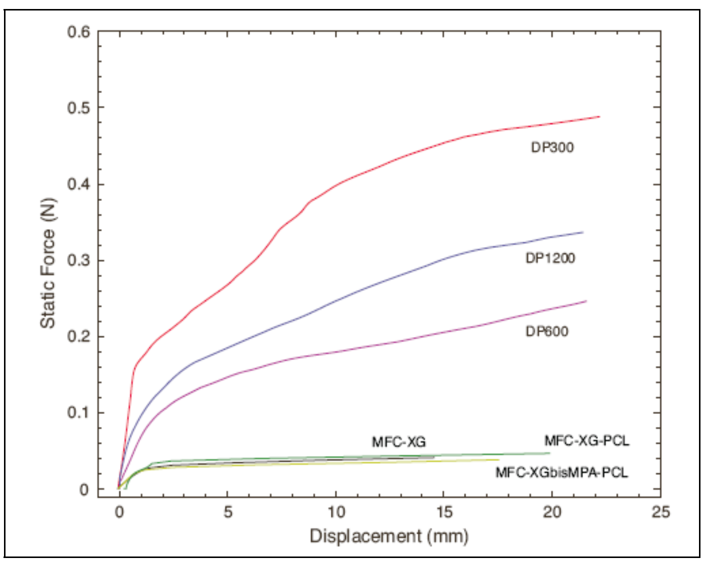


Figure 4. Results from DMA: unmodified MFC-film grafted with PCL aimed DP 300, 600 and 1200, and MFC-film-XG, MFC-film-XG-PCL DP 1200, and MFC-film-XG-bisMPA-PCL DP 1200.

4. CONCLUSIONS

Unmodified, XG, and XG-bisMPA, MFC-films have successfully been grafted with PCL; this was confirmed with FTIR and contact angle measurements. Larger contact angle was estimated after grafting with PCL, hence the hydrophobicity was increased. Initial studies on laminates showed that the interfacial adhesion was significantly improved after grafting with PCL from unmodified MFC-films, but no difference was obtained after grafting from XG and XG-bisMPA modified MFC-films.

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