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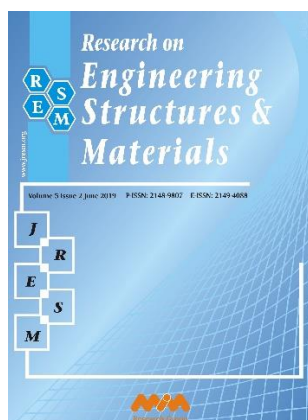
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Mechanical and thermal behavior of natural fiber-polymer composites without compatibilizers

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Abstract

The present study aims at understanding the mechanical and thermal properties of natural fibers in a polymer matrix without strong adhesion between the two constituents. For this purpose, four types of pulps, which are refined and unrefined pine and birch kraft pulps, were used together with polypropylene without any compatibilizer. One constituent pulp based and composite pulp fiber-polypropylene handsheets were prepared by standard laboratory sheet preparation method followed by hot pressing process. In addition to these handsheets, pure polypropylene sheets were also formed as the reference. The produced handsheets were tested to determine their tensile properties following the ISO 1924-2 standard for paper and board. During these tests, infrared thermal imaging was also carried out with FLIR A655SC thermal camera with frame rate of 200 Hz and thermal resolution of 50 mK so as to investigate the thermal behavior. As a result of the experiments, it was deduced that the chosen methods produced composites with unsatisfactory properties. In addition, microstructures of the investigated handsheets were analyzed with scanning electron microscopy (SEM) indicating the heterogeneous mixing of constituents and existence of material defects, which was mainly due to the inherent incompatibility of hydrophilic natural fibers and hydrophobic thermoplastics. The study aims at paving a way for improved natural fiber-polymer composite manufacturing methods, a requirement for better understanding the natural fiber and polymer matrix bonding practices.

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1. Introduction

Since the natural fibers are abundant, ecological, economical, light and have high specific mechanical characteristics, they have been widely used as reinforcement in natural fiber-polymer composites with applications in paper and packaging, construction and automotive industries [1, 2]. Thus, biocomposites based on natural fibers and especially thermoplastic polymer blends are being widely investigated to minimize the plastic waste problem [3-5]. The mechanical properties of these composites primarily depend on the elastic behavior and strength of fibers, fiber network, matrix and interfacial bonding [6-10]. Especially, a strong adhesion between the fiber and the matrix is of great importance for the effective load distribution and reinforcement throughout the composite [11-13]. However, in case of natural fiber-polymer composites, fibers are hydrophilic for most of the cases and incompatible with the common hydrophobic thermoplastics, which can limit the proper bonding [14, 15]. Thus, various compatibilizers, such as phosphate titanite, or wood surface modification treatments, like acetylation, are used to bind the constituents together [16-18].

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In order to create an in-depth understanding of the bonding limits of natural fibers and thermoplastics, different natural fiber types with and without polymer matrix were investigated. For this purpose, four types of wood fiber; refined and unrefined birch kraft pulp and refined and unrefined pine kraft pulp; were investigated in polypropylene PP matrix without any compatibilizer. Mechanical properties of these composites were evaluated and compared to the papers made of either wood or PP that can be co-polymerized to increase its strength and durability [19]. Thermal camera recordings were also used to understand the thermal characteristics of the investigated materials which were subjected to tensile loading. Therefore, the present study aims at providing an advancement in natural fiber-polymer composite design and manufacturing with findings on the effects of compatibilizers on the physical and mechanical characteristics of final products.

2. Methodology

As listed in Table 1, nine types of laboratory handsheets were formed out of four types of pulps by following the ISO 5269-1:2005 laboratory sheet preparation standard so as to conduct subsequent physical tests [20]. Sheets had a rectangular shape and a side-length of 16.5 cm and a grammage of ~ 120 g/m². PP melting temperature was measured as 163 °C using hot plate and infrared thermometer in the Aalto University facilities. The measurements were in well alignment with the ones in the literature [21]. Composite handsheets were thereafter prepared adding PP granules to fiber-water suspension before forming process. Some adjustments, the details of which are elaborated below, were needed for these handsheets compared to the standard formation process due to the hydrophobic and light nature of the PP.

Based on the ISO-187:1990 standard atmosphere for conditioning and testing in line with ISO 5269-1:2005 laboratory handsheet preparation standard, the handsheets were kept in a room of 50% relative humidity and at 23°C temperature for minimum 24 hours for conditioning and drying [20, 22]. Thereafter, the handsheets were hot pressed under steady conditions for 2 minutes at 180 °C temperature with 50 kN force with Vakomet KRO-260 press and Siemens Simatic HMI KTP400 controller system. PP sheets of the same size and grammage as paper sheets were prepared by laying 3.267 g of PP granules in a paperboard frame, letting the specimen to melt on the hot press plate and pressing it to shape using 200 kN force and 200 °C temperature.

Retention was determined at 95 % and 94 % with refined birch and pine, respectively. Unrefined pulps were assumed to have 100 % retention due to non-existence of fines. PP retention was determined at 55 %, although it varied a lot due to challenging nature of PP granules in papermaking. PP had virtually no adhesion to fibers in aqueous phase and stuck easily to the walls of the handsheet trough. Also, PP interfered the process of removing fresh fiber mat from wire for drying. Being lighter than water and the fibers, PP granules settled on top of fiber matrix which resulted in very low adhesion of wet composite handsheets with the suction board. Additionally, PP granules detached easily out of the composite handsheets after drying the samples. Composite handsheets with unrefined pulps of low wet strength were especially challenging, the problem that was tackled adding part of the PP granules to dried handsheets just before the hot press. Due to these factors, the PP amount in these sheets varied profoundly.

Table 1. Handsheet materials, identification, their fiber and polymer fractions, physical characteristics

Material	ID	Fiber (mass %)	PP (mass %)	Thickness (μm)	Grammage (g/m^2)
Birch, refined	BR	100	0		
Mean				169	122
Std. dev.				1%	1%
Birch, refined, with PP	BRPP	50	50		
Mean				302	122
Std. dev.				5%	5%
Birch, unrefined	BU	100	0		
Mean				253	126
Std. dev.				2%	2%
Birch, unrefined, with PP	BUPP	50	50		
Mean				279	121
Std. dev.				3%	11%
Pine, refined	PR	100	0		
Mean				190	124
Std. dev.				1%	1%
Pine, refined, with PP	PRPP	50	50		
Mean				244	127
Std. dev.				4%	15%
Pine, unrefined	PU	100	0		
Mean				268	118
Std. dev.				1%	2%
Pine, unrefined, with PP	PUPP	50	50		
Mean				317	127
Std. dev.				8%	2%
Polypropylene	PP	0	100		
Mean				244	127
Std. dev.				4%	15%

Specimens were cut to dog-bone shape with mid-width of 10 mm and span length of 100 mm to determine their tensile properties by following the ISO 1924-2:2008 testing standard for paper and board [23]. Tensile tests were conducted under 50% relative humidity and at 23°C temperature by using MTS 400/M vertical tensile testing system equipped with 200 N load cell. The cross-head speed was fixed to 12 mm/min and the clamp span of 100 mm was used in these measurements. In this setup, displacement and strain readings were recorded via crosshead position while force and stress measurements were obtained through force transducer and the measure cross-sectional areas per specimen. Temperature difference at breakage point was determined using FLIR A655SC

thermal camera with frame rate of 200 Hz, optical resolution of 640 x 480 pixels and thermal resolution of 50 mK. The thermal images of the selected specimens can be found in the Appendix.

3. Results and Discussions

3.1 Tensile properties and thermal characterization

The tensile test results with mean and standard deviations are tabulated in Table 2 while the stress-strain curves are depicted in Figures 1 and 2 following the fiber content for birch and pine. Literature values for the elastic modulus of birch and pine based handsheets are between 1 and 10 GPa depending on the fiber orientation [24, 25]. In these one constituent handsheets, the fibers were randomly oriented and the handsheet elastic moduli obtained for the refined birch BR (4854 MPa) and the refined pine PR (4436 MPa) were well aligned with the previous investigations [26]. This was an expected outcome since the handsheets with one constituent have well established and standard production method. Nevertheless, in case of unrefined pulps, fiber bondings inside the handsheets were deduced to be weak since there was only mechanical and heat treatment for the formation process. Therefore, without the enhanced fiber bonding, interfiber breakage should prevail intrafiber failure, which results in lower elastic moduli as seen in unrefined birch and pine BU and PU, respectively, in Table 2. The same phenomenon explains the differences in tensile index, break strain and absorbed tensile energy. On the other hand, composite handsheets were deduced to have a lot of variation in their mechanical and thermal characteristics. This shows that importance of compatibilizers in composite handsheet formation, for which the bonding should be well built. Based on the present investigations, the compatibilizers are deduced to play a critical role especially in case of hydrophilic and hydrophobic constituents.

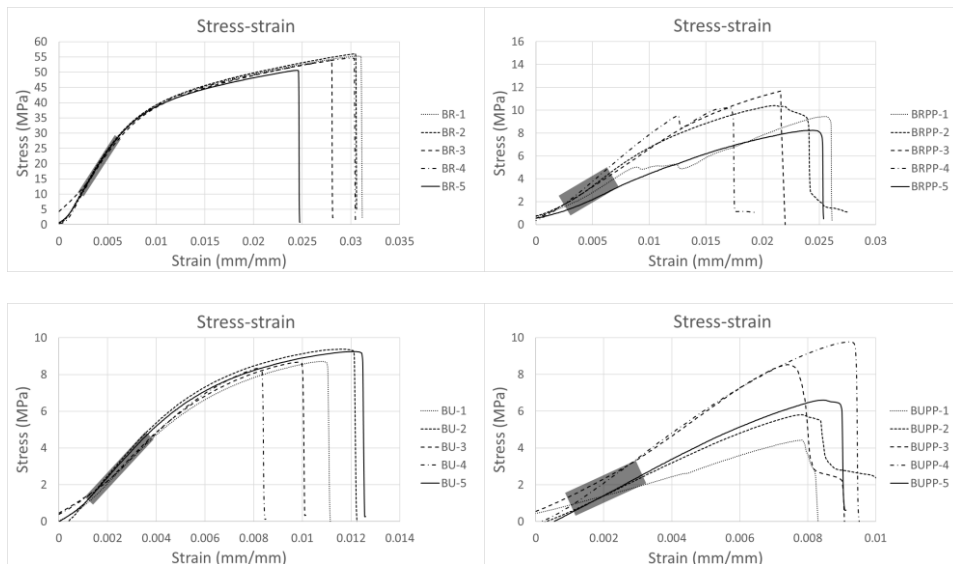


Fig. 1. Stress-strain curves obtained from tensile testing of handsheets from refined BR and unrefined birch BU and their blends with polypropylene PP. Highlighted domains represents the stress-strain ranges for the elastic modulus computations.

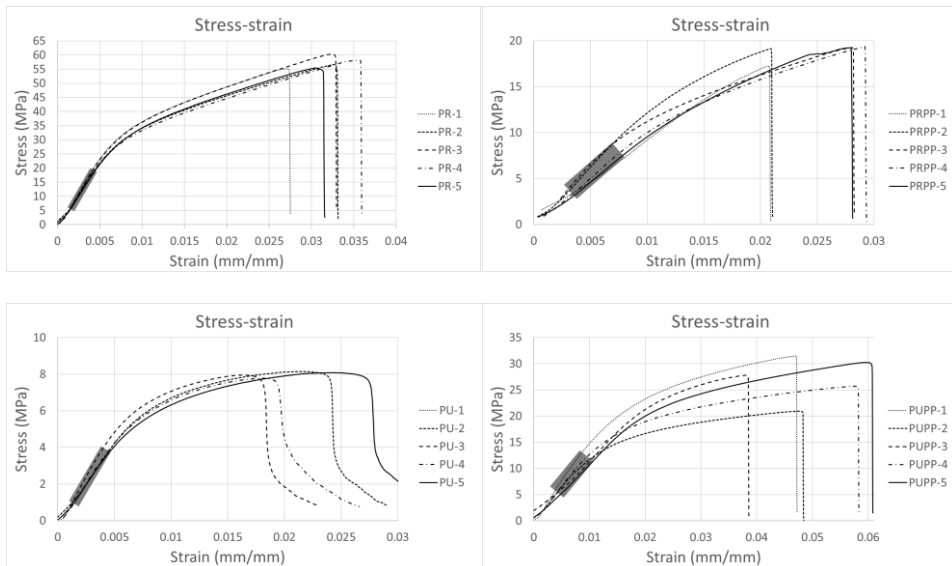


Fig. 2. Stress-strain curves obtained from tensile testing of handsheets from refined PR and unrefined pine PU and their blends with polypropylene PP. Highlighted domains represents the stress-strain ranges for the elastic modulus computations.

It is also observed that the produced composite handsheets did not follow the general rule of mixtures, i.e. neither Voigt model (upper-bound modulus) nor Reuss model (lower-bound modulus). This has been also observed by other researcher working on the natural fiber composites [11] when the fraction of pulp fibers in a PP matrix was over 20 % by mass. For example, refined pulp-polymer composites BRPP and PRPP are significantly weaker than plain fiber or polymer sheets. On the other hand, the unrefined pulps seem to gain strength with the addition of polymer. The strength of these sheets primarily comes from the polymer phase as their grammage and fraction is much higher than those of the other composites due to modifications in the manufacturing method. The scanning electron microscopy (SEM) images in the following section support the postulate.

3.2 Scanning electron microscopy

In order to understand the details of the apparent properties of the handsheets, SEM images were recorded with Hitachi TM1000 tabletop microscope in charge-up reduction mode with acceleration voltage of 15 kV recommended by the manufacturer. In contrast to the conventional sample preparation techniques, samples imaged by the TM-1000 required no special preparation such as metal coatings of non-conductive samples, which was very useful in terms of time and labor efficiency [27]. For the imaging, samples with surface areas of $2 \times 2 \text{ mm}^2$ were cut from the handsheets, the thicknesses of which are same as the ones listed in Table 1. A wide range of magnifications from 100 to 2000 times was utilized to investigate the sample structure and constituents. The images presented in Figures 3-6 indicate the importance of the compatibilizers since the matrix and reinforcement were not mixed well enough to fulfil the reasonable mechanical characteristics. No polymer matrix is visibly present in between the fibers in the side and cross-section images of the refined birch-PP composite as shown in Figure 3. As also stated

previously, this confirms the importance of the compatibilizers to bind matrix and fiber material together in natural fiber polymer composites.

Table 2. Tensile test results of different composite handsheets. Please, refer to Table 1 for the handsheet abbreviations BR, BRPP, BU, BUPP, PR, PRPP, PU, PUPP and PP.

	Elastic modulus (MPa)	Tensile index (kNm/kg)	Break strain (%)	Tensile energy absolute index (J/m ²)	dT (°C)
BR					
Mean	4854	75	2.8	1564	2.9
Std. dev.	5.3 %	3.3 %	7.6 %	11 %	33 %
BRPP					
Mean	726	19	2.3	270	1.6
Std. dev.	27 %	21 %	39 %	55 %	74 %
BU					
Mean	1161	18	1.0	117	2.6
Std. dev.	9.8 %	4.3 %	13 %	21 %	9.4 %
BUPP					
Mean	1243	28	1.6	417	2.3
Std. dev.	44 %	63 %	63 %	18 %	41 %
PR					
Mean	4436	87	3.0	1794	9.3
Std. dev.	7.8 %	3.8 %	11 %	15 %	10 %
PRPP					
Mean	1295	44	2.2	597	4.5
Std. dev.	17 %	5.1 %	21 %	26 %	31 %
PU					
Mean	975	18	1.8	243	1.1
Std. dev.	9.7 %	1.4 %	18 %	21 %	18 %
PUPP					
Mean	1258	51	3.6	1415	3.0
Std. dev.	22 %	25 %	47 %	63 %	49 %
PP					
Mean	1400	40	3.2	844	1.7
Std. dev.	23 %	30 %	45 %	55 %	59 %

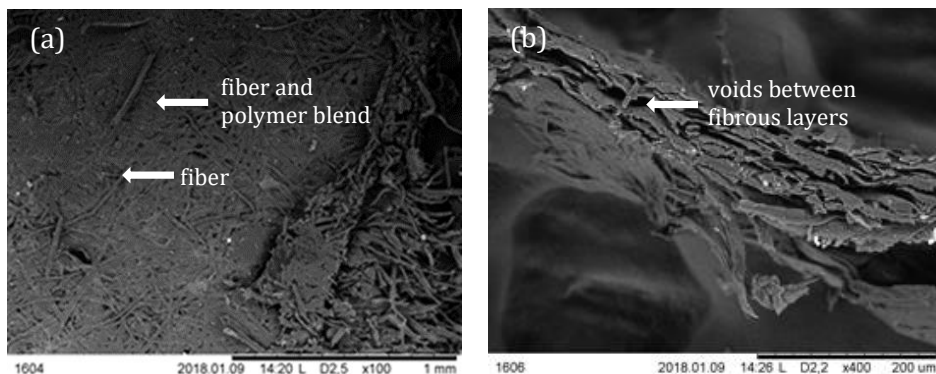


Fig. 3. SEM images of BRPP: (a) bottom side and (b) cross-section.

The layered structure is even more evident with top and bottom images of BUPP depicted in Figure 4. Considering the increasing porous structure of unrefined pulp compared to refined one, it is very unlikely that any melted polymer could have penetrated the fiber network in the heat press for any of the investigated birch samples.

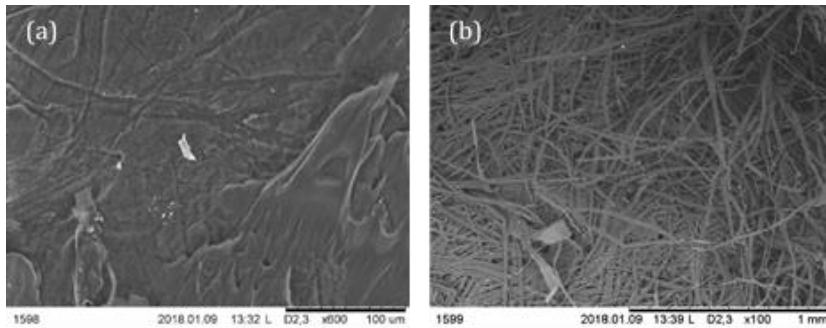


Fig. 4. SEM images of BUPP, (a) top side and (b) bottom side

Figures 5(a) and (b) show the layered structure of PRPP with a partially peeled off polymer coating on top of the fiber network. Through the thin polymer layer, the fiber network underneath is somewhat visible. The polymer layer contains pores in the magnitude of several tens of microns wide. These could be due to escaping water from the hydrophilic fibers during the hot pressing, though the sheets were thoroughly dried before the pressing. In addition to these, the cracks in Figures 5 (c) and (d) also indicate the brittle nature of polymer matrix resulting in poor and unstable mechanical properties.

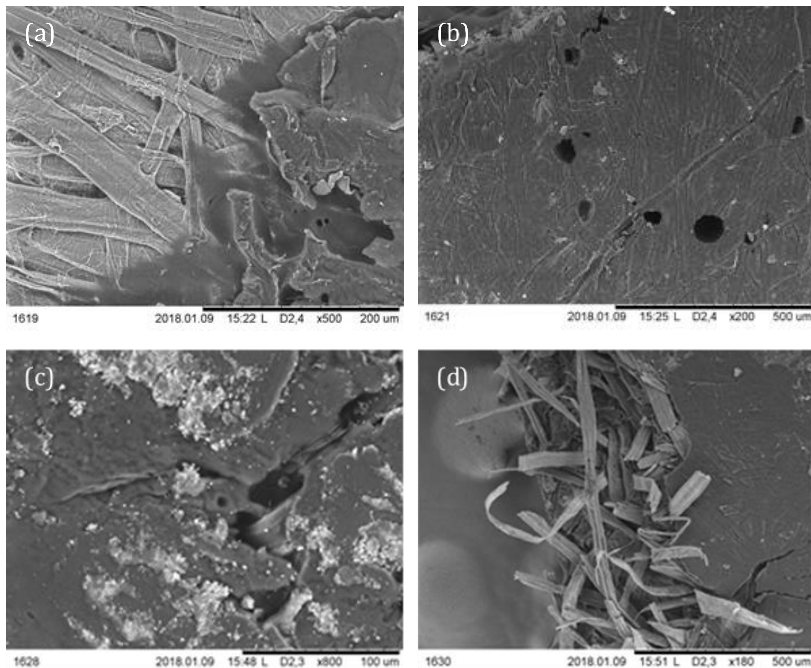


Fig. 5. SEM images of PRPP and PUPP, (a) PRPP image showing a peeled off layer of PP, (b) PRPP image showing pores in the matrix, (c) PUPP top side image, (d) PUPP cutting zone image

Further study of the SEM images in Figure 6 shows uneven distribution of polymer structure within all the composite and plain polymer sheets. This shows the importance of standardization and urge for the development in the manufacturing method.

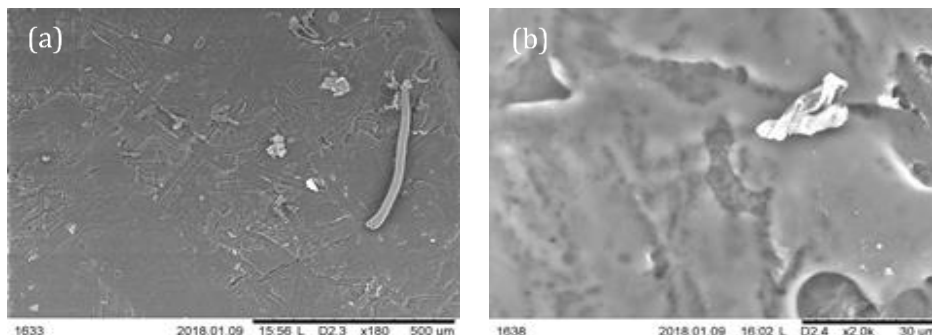


Fig. 6. SEM images of PP, with (a) 180x and (b) 2000x magnification

4. Conclusion

The present study was conducted to understand the effect of inherent incompatibility of hydrophilic natural fibers and hydrophobic thermoplastics on the mechanical and thermal behavior of their composites. Both the mechanical and thermal measurements exhibited a lot of variation and the chosen manufacturing method was deduced to produce unsatisfactory properties due to weak bonding between the constituents and existence of material defects such as pores, which can be clearly seen in the captured SEM images. This shows the necessity of compatibilizer use, which provides the retention and uniform mixing in case of constituent incompatibility.

Since the hot-pressing process was the mere option for the composite handsheet formation without damaging the fibers in the present facilities, another major challenge was the melting behavior of the PP during the process to get an interconnected and even matrix between the fibers. The hot pressing with the used parameters was not able to fulfil this task and fiber network was deduced to be dense for a uniform PP flow through. As seen in Figure 7(a), warping effect was experienced with most of the composite handsheets after hot pressing, which was an evidence of the nonuniform PP flow over the layered structure. When cutting the samples, the sheets had to be straightened as depicted in Figure 7(b), which caused residual strains as the aftermath.

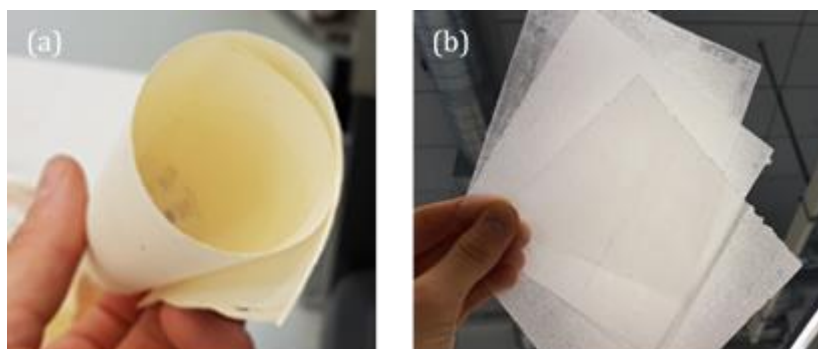


Fig. 7. Composite handsheets: (a) warping after hot pressing and conditioning to standard air moisture, and (b) handsheets to be used for test specimens

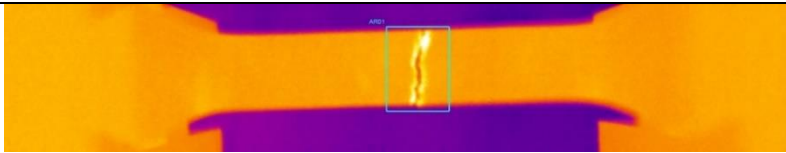
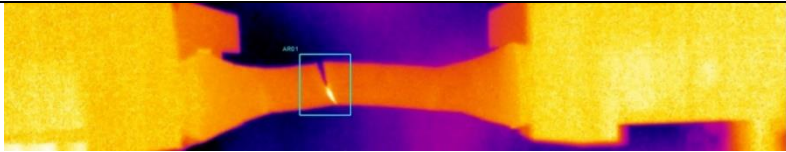
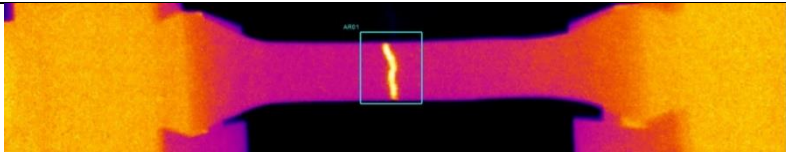
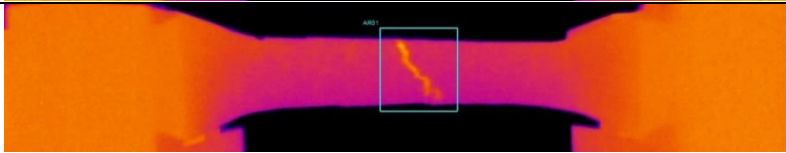
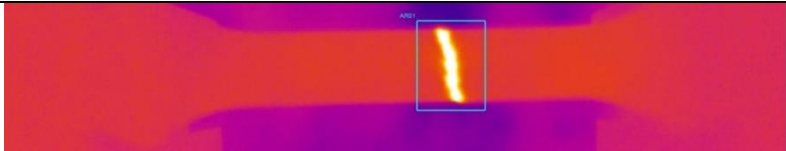
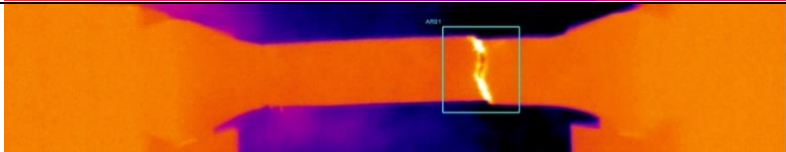
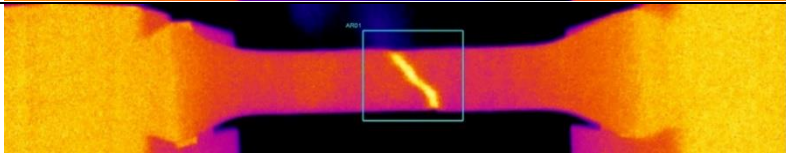
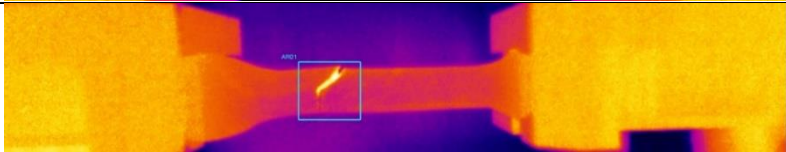
All these manufacturing-based defects and constituent incompatibility were detrimental and resulted in low mechanical characteristics with high variations. Therefore, use of ply structure with low grammage and thin layers of fiber network with polymer stacked on top of each other in multiple layers could be a potential solution to this issue. In addition, increase in the pressure and process time would be also beneficial. Alternatives to hot pressing could also be considered, as long as the other methods do not damage the fibers. As a summary, the present study, which investigated the interactions between the reinforcement and the matrix without a compatibilizer, paved a way for improved natural fiber polymer composite manufacturing methods.

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Appendix

ID	Thermal Image (camera: FLIR A655SC)	
BR		
BRPP		
BU		
BUPP		
PR		
PRPP		
PU		
PUPP		
PP	