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The importance of fiber/matrix adhesion and annealing process in water uptake of PLA/PMMA matrix composites reinforced with sisal fibers: The effect of coupling agent addition

With the aim to open new applications possibilities to novel biocomposites based on PLA/PMMA matrix and reinforced with sisal fibers, it was studied the effect of water immersion aging on biocomposite tensile properties. In the current study it was evidenced the importance of the annealing process and fiber/matrix adhesion on the mechanical performance of composites after immersing in water for around 7 months. The presence of the copolymer and the annealing process led to the minor extent of damage of mechanical properties of prepared biocomposites. Results obtained in the current study suggested that although the amount of copolymer incorporated in composites was low, the presence of copolymer is crucial to improve fiber/matrix adhesion and consequently the mechanical performance of composites after immersing in water. It was observed that even though the water uptake damaged the interfacial adhesion, leading to the tensile strength reduction, however, annealed composite with 30 wt% of fiber and modified with the copolymer showed a strength value of around 53.5 MPa. It must highlighted that even though water aged for 7 months, the annealed composite with copolymer showed yet a higher strength value than dried commercial mineral-filled PP composites reported in the literature.

Keywords: Sisal fibers; Polymer-matrix composites; Water uptake; Mechanical properties; Poly(lactic acid); Poly(methyl methacrylate).

1. Introduction

The research in lignocellulosic fiber-reinforced composite is promising due to its properties and environmental benefits. In a previous work (Orue et al. forthcoming a) it was compared the properties of new biocomposites based on PLA/PMMA matrix and sisal fiber bundles with literature data of thermoplastic composites that are commonly used in automotive applications. It was concluded that the specific tensile property values of composites based on PLA/PMMA matrix and treated sisal fibers were higher than those of mineral-filled PP systems. Unfortunately, the HDT values of prepared composites were low and an annealing process had to be carried out to increase the crystallinity of polymer matrix. Even though the estimated HDT value of composites increased considerably after the annealing process, the specific strength values of composites decreased noticeably because the fiber/polymer adhesion was damaged during the annealing process. With the aim to improve fiber/polymer adhesion, in another study (Orue et al. forthcoming b) it was studied the effect of the addition of a copolymer on the thermomechanical performance and tensile properties. It was concluded that it was crucial to form a strong adhesion between the fibers and polymeric matrix to improve both thermomechanical performance and tensile properties after annealing process. It was observed that the estimated heat deflection temperature (HDT) of annealed composite with 40 wt% of fiber and modified with a copolymer increased around 40 °C respect to commercial neat PLA and the tensile strength value increased around 50%. The results obtained previously suggested that novel composites based on PLA/PMMA matrix and sisal fibers with at least of 84 wt% of bio-based materials can be prepared with tensile and HDT properties adequate for automotive applications. However, in many applications, during servicing conditions, the composites reinforced with lignocellulosic fibers could be in contact with water. The

water can produce fiber swelling with the resultant changes in dimensional stability and mechanical properties (Saw et al. 2014). The absorbed water can result in mechanical properties reduction of composites (Rangaraj and Smith 2000; Dhakal, Zhang, and Richardson 2007; Gil-Castell et al. 2016; Chaudhary, Bajpai, and Maheshwari S 2020) due, partially, to the degradation fibre-matrix interfacial adhesion. The water absorption mechanism along the interface is very important when the fibre-matrix adhesion is poor or is damaged as consequence of water attack at the interface (Thomason 1995). The fiber/matrix adhesion is determined by the wettability of fiber with polymer matrix and the interfacial strength between fiber and matrix. One way to improve the fiber/matrix adhesion, and consequently improve the hydrolytic resistance of composites, could be the use of compatibilizer agent (Gaylord and Mehta 1998; Nabi Saheb and Jog 1999; Lu, Wu, and McNann 2000; Rozman et al. 2000; Kim et al. 2001; Gil-Castell et al. 2014). In the current work, it was studied the mechanical performance of PLA/PMMA sisal fiber composites after immersing in water for 7 months since the hydrolytic resistance of composites based on lignocellulosic fibers is crucial to expand the usage of these biocomposites.

2. Materials and methods

2.1. Materials

PLA was purchased from NatureWorks LLC (Ingeo™ 3051D, $M_n = 106000$ g/mol; PDI: 1.7; ≈ 4.6 % D-lactate) and PMMA from Evonik ROM GmbH (PLEXIGLAS® zk5BR, $M_n = 70000$ g/mol; PDI: 2.3), while P(S-co-GMA) copolymer ($M_n = 29000$ g/mol; PDI: 1.9) was kindly supplied by Macro-M (Kuo Group).

Sisal, *Agave sisalana*, fiber bundles cultivated in Africa were kindly supplied by Celulosa de Levante S.A. Sodium hydroxide pellets, supplied by Panreac, were used as

fiber surface modifier and NaOH treatment of fibers was carried out following the conditions described in a previous work (Orue et al. 2015).

2.2. Compounding and processing of materials

Previously dried PLA and PMMA pellets were melt-blended in a HAAKE Rheomix 600 internal mixer at 215 °C. Once PLA/PMMA (80/20 wt%) blend was melted, 3 pph of copolymer was added in the internal mixer and the blend was mixed during 5 min at 50 rpm after the torque value began to increase. Afterward, dried NaOH treated sisal fibers were added in the internal mixer and they were mixed during 5 min at 50 rpm. The fiber loading varied in the composites from 20 to 40 wt%.

All pelletized blends were dried in an oven prior to process by injection molding technique in a HAAKE Minijet II. Tensile test specimens (ASTM-D638-10, type V) were obtained. Some tensile specimens were annealed at 105 °C for 15 h.

2.3. Characterization

2.3.1. Water uptake test

The water absorption of the samples was carried out immersing tensile test specimens (ASTM-D638-10, type V) in distilled water at 30 ± 1 °C for a period of 220 days. The total absorbed water, Δm_t , during the immersion time was calculated by the Eq. (1):

$$\Delta m_t (\%) = \left(\frac{w_t - w_o}{w_o} \right) \times 100 \quad (1)$$

where w_t represents the sample weight after an immersion time t and w_o is the initial weight of the specimen before immersion.

The diffusion coefficient, D , was calculated assuming the hypothesis of a Fickian mechanism and one-dimension approach (Joseph et al. 2002). A correction for the effect

of diffusion through the edges can be made according to Eq. (2) for rectangular specimens (Karad, Jones, and Attwood, 2002):

$$D_c = D \left(1 + \frac{d}{h} + \frac{d}{w} \right)^{-2} \quad (2)$$

where D_c is the corrected diffusion coefficient and h and w are the length and width of the sample, respectively. For simplicity, tensile specimens were considered as rectangular with 9.53 mm width and 63.5 mm length, respectively.

2.3.2. Scanning electron microscopy

SEM micrographs were performed by JSM-6400 equipment. Fractured surfaces were previously coated with gold using Q150TES metallizer.

2.3.3. Tensile test

Tensile tests were performed according to ASTM D638 standard using Insight 10 testing system. Tensile tests were carried out at 1 mm/min deformation rate and tensile strength, modulus and deformation at break were calculated from stress-strain curves.

3. Results and discussion

3.1. Water uptake process of studied systems

Figure 1 a-b shows the evolution of water absorption profiles of systems with and without P(S-co-GMA) copolymer, before and after annealing process. Before the annealing process, unreinforced systems absorbed around 1 % of water content, probably because the ester polar groups presented in PLA and PMMA induced a little polarity (Bourmaud et al. 2009 Orue et al. 2016; Maurya et al. 2017). Nevertheless, after the addition of hydrophilic sisal fibers into the polymeric matrix, increased markedly the water uptake and corrected diffusion coefficient values (Table 1). The equilibrium water uptake and corrected diffusion coefficient values were higher for

composites prepared without copolymer than systems with copolymer. These facts can be ascribed to the stronger fiber/matrix adhesion in systems with copolymer that could reduce the amount of free -OH groups in the fiber surface (Ichazo et al. 2001). After the annealing process, Figure 1b, it was observed that the water uptake profile and diffusion coefficient values (Table 1) of unreinforced polymer blends were similar to non-annealed counterparts. Nevertheless, the equilibrium water uptake and diffusion coefficient values of composites without copolymer increased considerably after the annealing process.

[Figure 1 near here]

[Table 1 near here]

Conversely, it was observed that composites modified with copolymer showed slightly higher equilibrium water uptake value than non-annealed counterparts, being the diffusion coefficient increment more moderate than in systems without copolymer. The facts that equilibrium water uptake and diffusion coefficient values were influenced by the presence of the copolymer indicated that, in water absorption process, the fiber/matrix adhesion played a key role. Therefore, the results obtained in the current work suggested that the presence of the copolymer in composites improved fiber/matrix adhesion respect to composites without the copolymer. The improvement of fiber/matrix adhesion with the copolymer seemed to lead interfacial region with lower gaps than in composites without copolymer. This fact resulted in lower water accumulation in the interfacial voids, thus preventing the water entering through the natural fiber (Arbelaiz et al., 2005). Annealed composites reached more rapidly and a higher equilibrium water uptake value than non-annealed composites suggesting that annealing process could damage the fiber/matrix adhesion thus increasing the diffusion of water in composites. Although the sisal fiber/matrix adhesion was damaged by

annealing and water uptake processes, it seemed that fiber/matrix adhesion was damaged to a minor extent when the copolymer was added.

3.2. Fractured surface morphology of studied systems

Fractured surface SEM micrographs of non-annealed and annealed systems after the water uptake period are shown in Figure 2 a-f. Regarding the unreinforced polymer blends modified with copolymer, after the water uptake period, the fractured surface morphology was similar for non-annealed and annealed systems (Figure 2a and b). In non-annealed composites with 30 wt% fiber loading, Figure 2c and d, pulled-out fibers were observed in SEM micrographs. Moreover, the length of pulled-out fibers was longer for the composite without copolymer than composite with copolymer. This fact corroborated that the addition of copolymer improved the matrix/fiber adhesion being in accordance with water uptake values. In annealed composites, Figure 2e and f, the sisal fibers cannot be observed so clearly, probably the high amount of absorbed water degraded the sisal fibers to a great extent. However, a higher number of holes were observed in annealed composites than in non-annealed counterparts corroborating that fiber/matrix adhesion was damaged. Therefore, SEM micrographs indicated that water absorption damaged the fiber structure and fiber/matrix adhesion to a greater extent in annealed composites than in non-annealed counterparts. This fact caused that the annealed systems absorbed more water than non-annealed counterparts did.

[Figure 2 near here]

3.3. Tensile properties of studied systems

Figures 3-5 show the tensile properties of studied systems before and after water uptake process. The tensile strength of non-annealed unreinforced blends and the annealed polymer blend without copolymer hardly changed after the water uptake process.

Accordingly, Deroine et al. (2014) observed that the stress at break of PLA specimens remained constant during the ageing period of 7 months in distilled water.

[Figure 3 near here]

[Figure 4 near here]

[Figure 5 near here]

On the other hand, it can be observed in Figure 3b that annealed unreinforced polymer blend modified with copolymer showed around 22 % of strength increment after water uptake process. This increase in tensile strength value suggested that grafting/crosslinking could take place during the water uptake process enhancing the tensile strength. Similar observation was made in the literature by Dhakal, Zhang and Richardson (2007) when they studied the effect of water absorption on the mechanical properties of hemp fiber reinforced unsaturated polyester composites. According to Dhakal, Zhang and Richardson (2007), the tensile stress increment was due to the crosslinking or other mechanisms that occurred during water immersion.

It was observed in Figure 4 that the stiffness of unreinforced blends, especially in those annealed systems increased after the water uptake process. According to Le Duigou, Davies and Baley (2009), the reduction of PLA molecular weight may be compensated by structural reorganization (recrystallization) and this could be a reason for obtaining higher Young's modulus after water absorption process. On the other hand, the elongation at break of unreinforced systems decreased after water uptake process (Figure 5). Deroiné et al. (2014) observed for PLA that the strain at break increased significantly after 1 month of immersion at 30 °C but markedly dropped after 6 months. Regarding composites, after water uptake process (Figures 3-4) the strength and modulus values decreased since water molecules would change the structure and properties of fibers, matrix and interface. Kumar et al. (forthcoming) suggested that the

reduction of tensile strength in composites based on epoxy matrix and lignocellulosic fibers after water absorption was due to the breakage of H-bonds. Moreover, it was observed in Figures 3-4 that strength and modulus values of annealed composites decreased in a greater extent than non-annealed counterparts after ageing period. This fact was in agreement with SEM micrograph observations and water uptake analysis, corroborating that after annealing and water uptake processes, the fiber/matrix adhesion in composites was damaged more severely than in non-annealed counterparts.

Furthermore, it was observed that after water uptake process, annealed composites modified with copolymer showed higher tensile properties than those systems without copolymer. Obtained results suggested that the presence of copolymer improved the PLA/sisal fiber adhesion. Concerning the elongation at break values, Figure 5, all systems showed a reduction of deformation capability after the water uptake period.

Figure 6 shows the schematic drawings of the effect of annealing and water uptake processes on the fiber/matrix interphase of unmodified and modified composites with copolymer. Previously (Orue et al. forthcoming a and b) it was characterized mechanically composites with and without copolymer and the tensile strength values were similar, around 70 MPa with a fiber loading of 30 wt%, indicating that the fiber/matrix adhesion strength was similar. However, after annealing process in the presence of the copolymer the tensile strength increased until 75 MPa (Orue et al. forthcoming b) whereas for unmodified composite decreased until 28 MPa (Orue et al. forthcoming a). These results indicates that the fiber/matrix adhesion mechanism was not the same in both composites. Composite modified with copolymer, in addition to fiber/matrix mechanical interlocking adhesion mechanism that shows composite without copolymer, also presents chemical bonding between fiber and matrix through the copolymer. During the annealing process, the matrix can crystallize and the matrix

shrinkage in addition to create cracks within the matrix, also form gaps in the fiber/matrix interface.

[Figure 6 near here]

The presence of the copolymer in composites seemed to lead two favorable effects during annealing process. The toughness of PLA/PMMA matrix was increased (Anakabe et al. 2016, 2018) and it seemed that this reduced the cracks formation during the shrinkage. Besides, the copolymer seemed to create covalent linkages with both fiber and matrix that resulted in a minor extent of fiber/matrix adhesion damage. These covalent links could be the reason for the improvement of tensile strength after annealing process. The presence of the copolymer in composites improved fiber/matrix adhesion leading to fewer gaps formation during annealing process and reduced the water uptake respect to unmodified counterpart.

In table 2, the tensile strength and modulus values of PLA/PMMA based composites after water uptake process are reported and compared with similar lignocellulosic fiber reinforced systems. On the other hand, for comparison purposes, the tensile properties of commercial thermoplastic composites that are commonly used in automotive are included in the table. It is evident that the strength and modulus values of water immersed PLA/PMMA based systems are far from non water aged glass fiber reinforced polypropylene composites. Besides, Ghasemzadeh-Barvarz, Duchesne and Rodrigue (2015) for PP/glass fiber composites observed that the water uptake at equilibrium after 1000 h immersed in distilled water at 85 °C was only 1.4% and consequently the strength value slightly decreased after water immersion. Regarding

mineral filled composite water absorption capacity, Adeosun et al. (2013) studied the water absorption tendency of PP-CaCO₃ composites with different filler contents. They observed that the increment of composite weight due to water absorption after soaking in water for 168 h was lower than 0.2%. Comparing at the same water absorption time, the PLA/PMMA composites absorbed significantly higher amount of water, ranged between 2 and 8 wt%. This difference in the absorbed water amount could be ascribed to the hydrophilic character of sisal fibers.

Comparing lignocellulosic fiber reinforced composites tensile properties, except non-annealed PLA/PMMA composite without copolymer, other PLA/PMMA based composites showed similar even higher modulus and strength values than other water aged lignocellulosic fiber reinforced systems.

[Table 2 near here]

Comparing with commercial thermoplastic composites, it must be highlighted that except the composite without copolymer and without annealing treatment, in general, water immersed composites showed higher strength and modulus values than composites reinforced with mineral filler ones. Furthermore, in the presence of copolymer the annealed PLA/PMMA-treated sisal fiber showed a strength and modulus values of 53.9 and 4100 MPa, respectively, after water uptake process. The results obtained in the current work suggested that even though the water absorption damaged the mechanical properties of PLA/PMMA based composites, the presence of the copolymer and the annealing process led to minor extent of damage of mechanical properties.

In the literature, it was observed that the presence of a coupling agent is beneficial to improve the fiber/matrix adhesion and reduce the water uptake. For example, in PP-flax fibers composites it was observed that after water ageing process, the system with MAPP coupling agent showed 18% higher strength value than the system without copolymer (Arbelaiz et al., 2005). Similarly in the current work, the strength value is 129% higher for non- annealed composite with coupling agent than the counterpart without copolymer. Regarding annealed systems, the composite with copolymer showed about 15% higher strength value than the composite without copolymer.

4. Conclusions

The results obtained in the current work suggested that even though the water absorption damaged the mechanical properties of PLA/PMMA based composites, the presence of the copolymer and the annealing process led to minor extent of damage of mechanical properties. It must be highlighted that the reported values in the current study for annealed composites with coupling agent after water ageing, are higher than strength and modulus values than non water aged composites reinforced with mineral filler ones reported in the literature. In the presence of copolymer the annealed PLA/PMMA-treated sisal fiber showed a strength and modulus values of 53.9 and 4100 MPa, respectively, after water uptake process. The reported data in the current study highlighted the importance of the coupling agent presence and annealing process to improve hydrolytic resistance of PLA based biocomposites. The current study results open new possibilities to novel biocomposites based on PLA/PMMA matrix and reinforced with sisal fibers for new applications even in contact with water.

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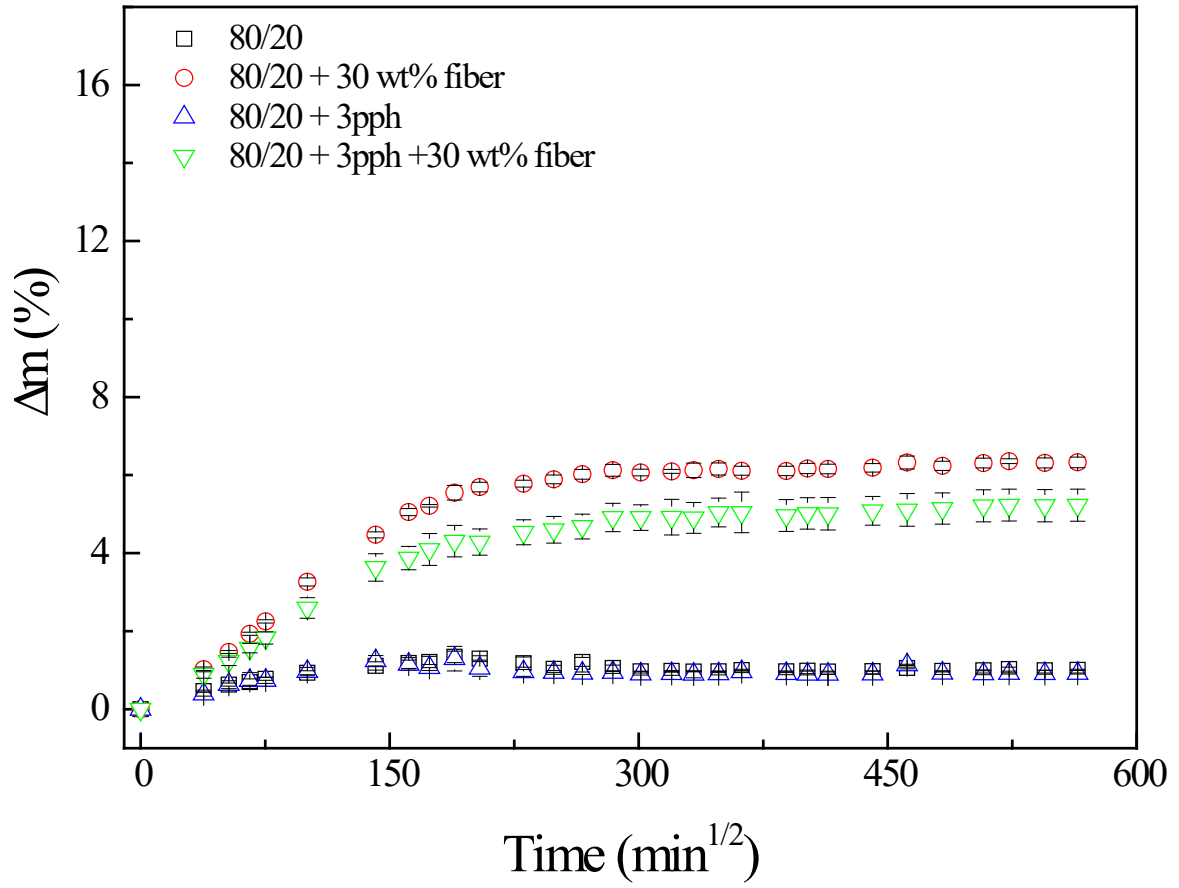


Figure 1a

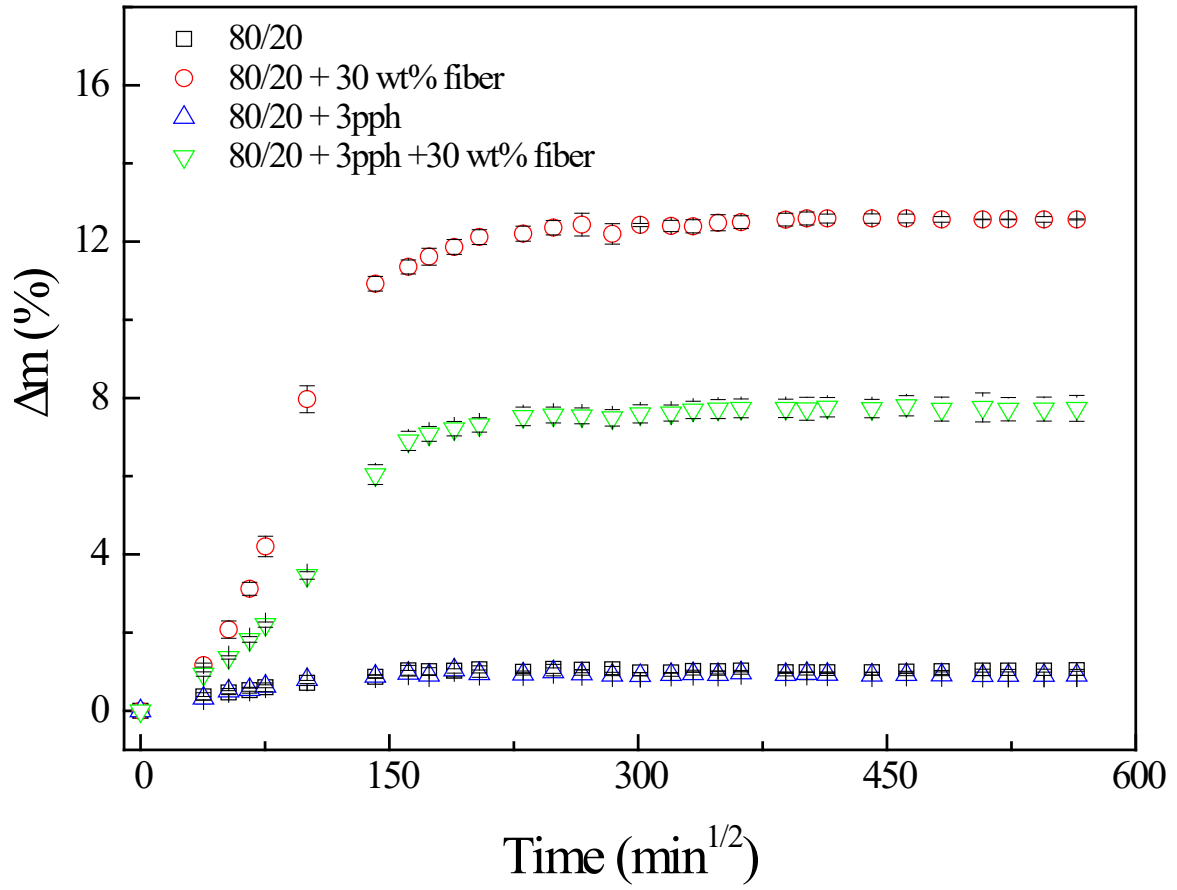


Figure 1b

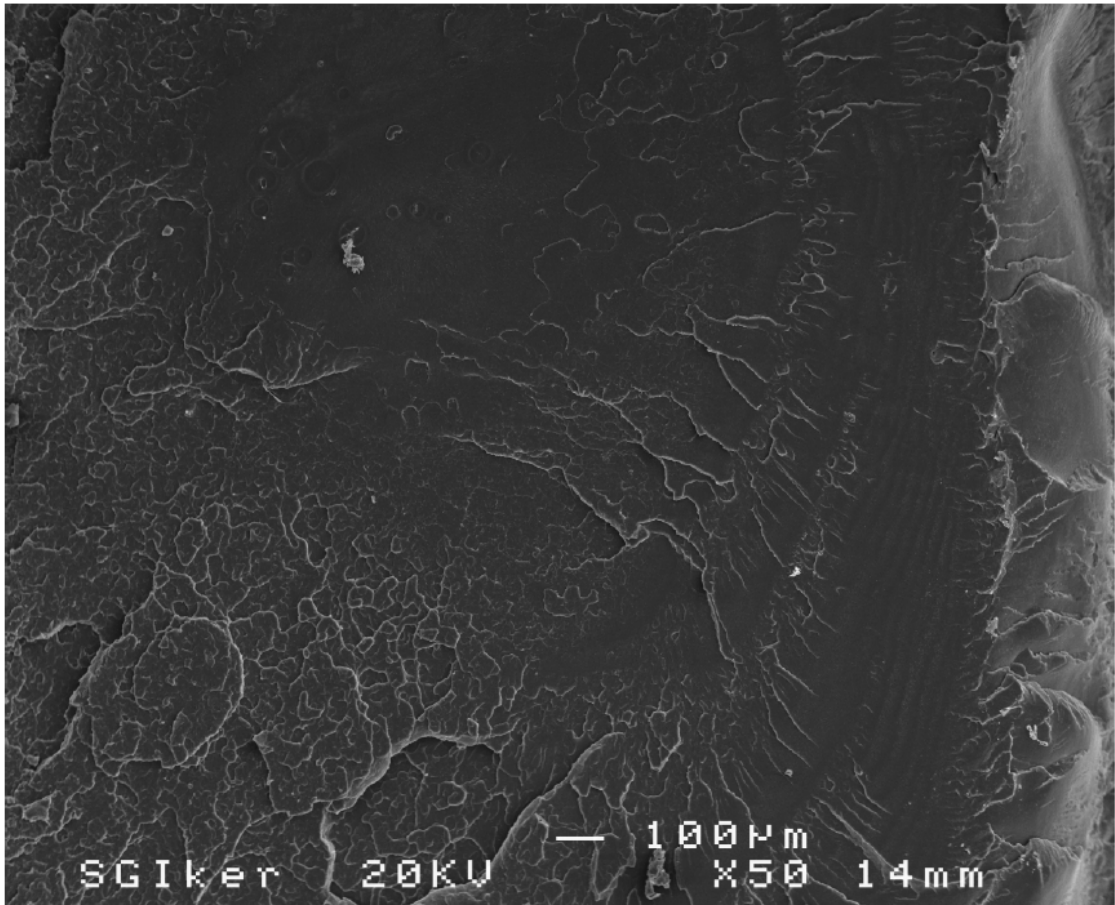


Figure 2a

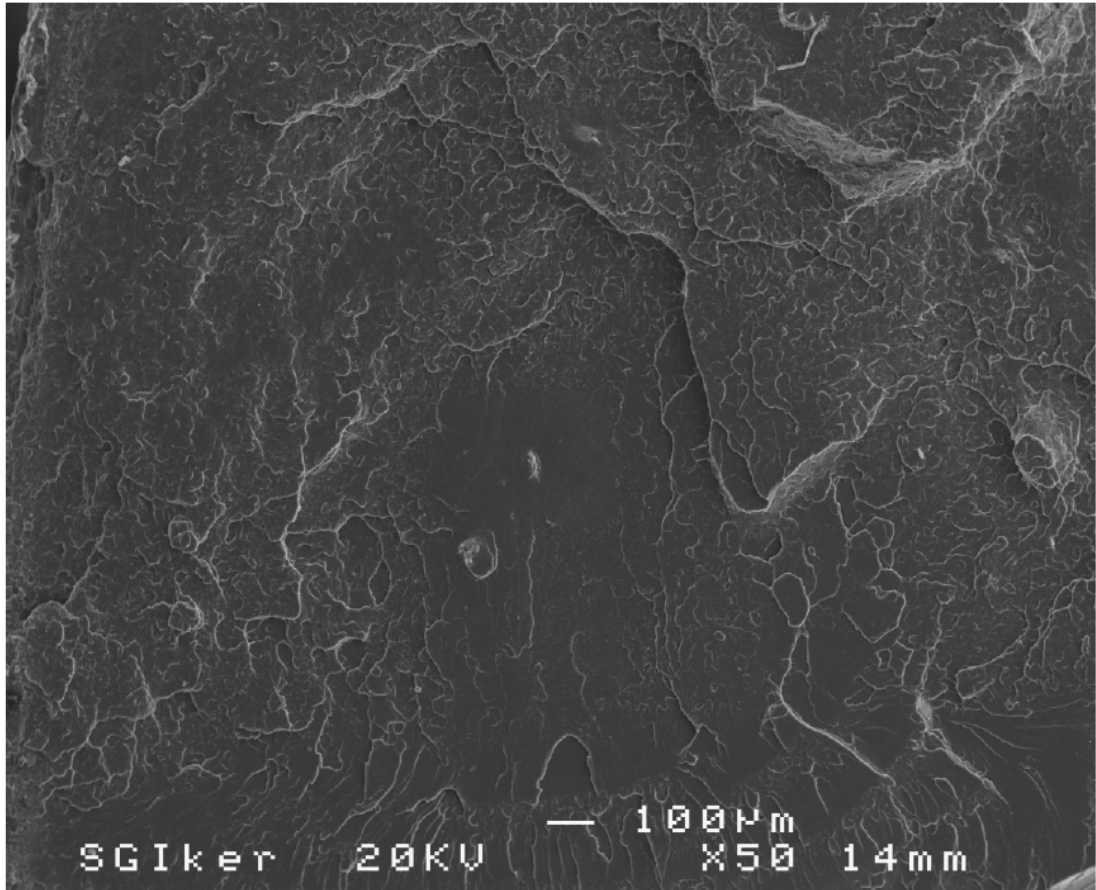


Figure 2b

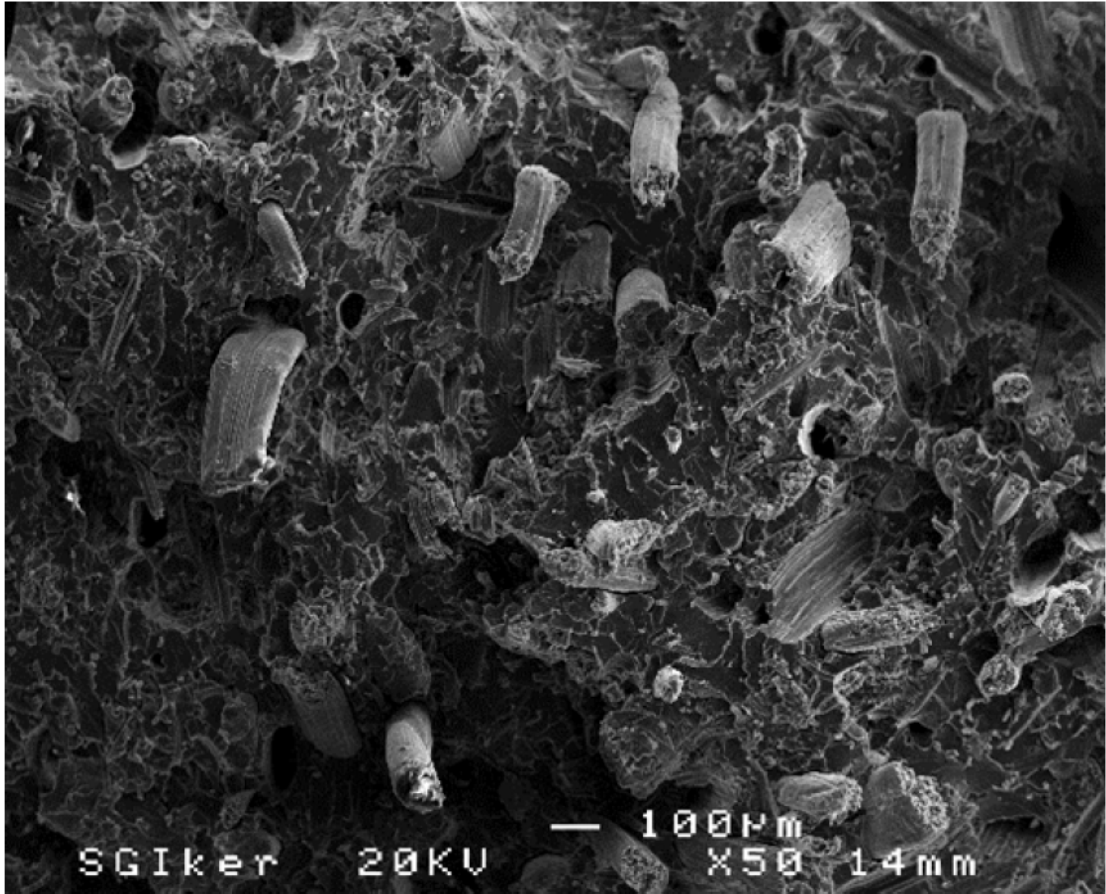


Figure 2c

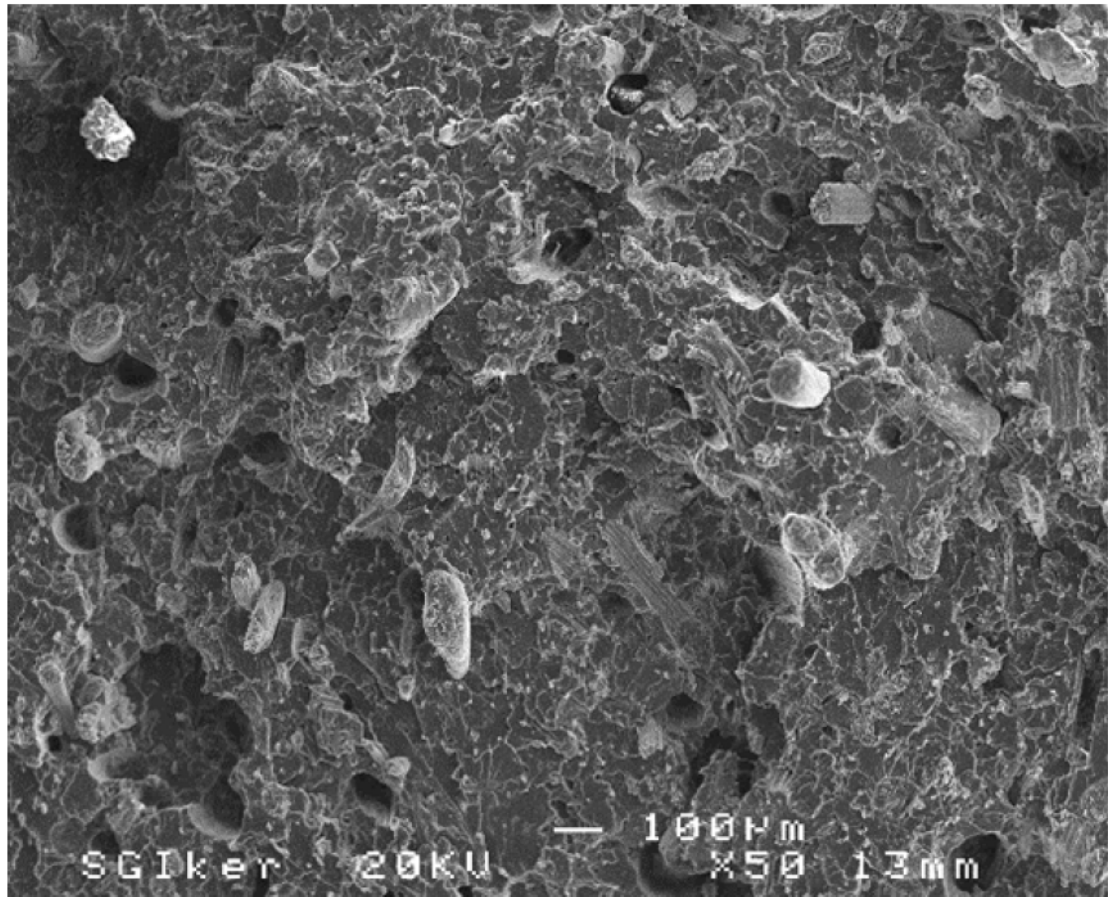


Figure 2d

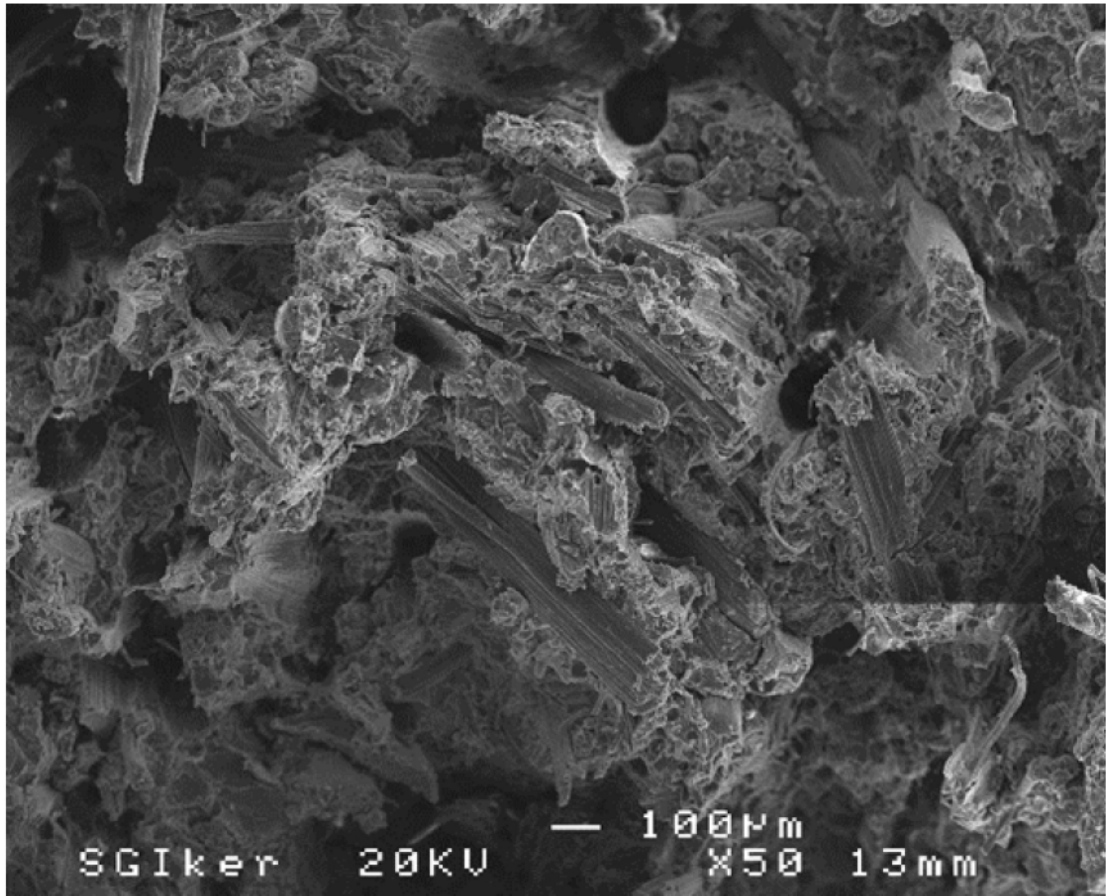


Figure 2e

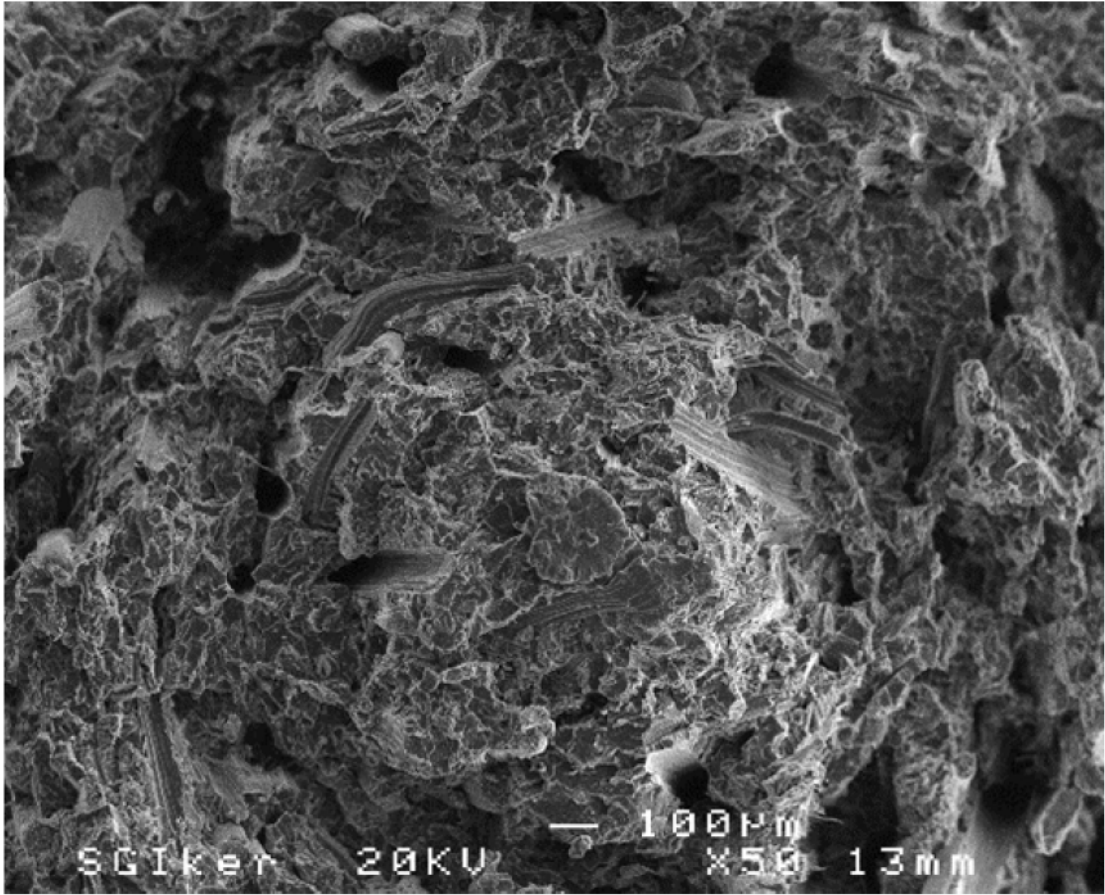


Figure 2f

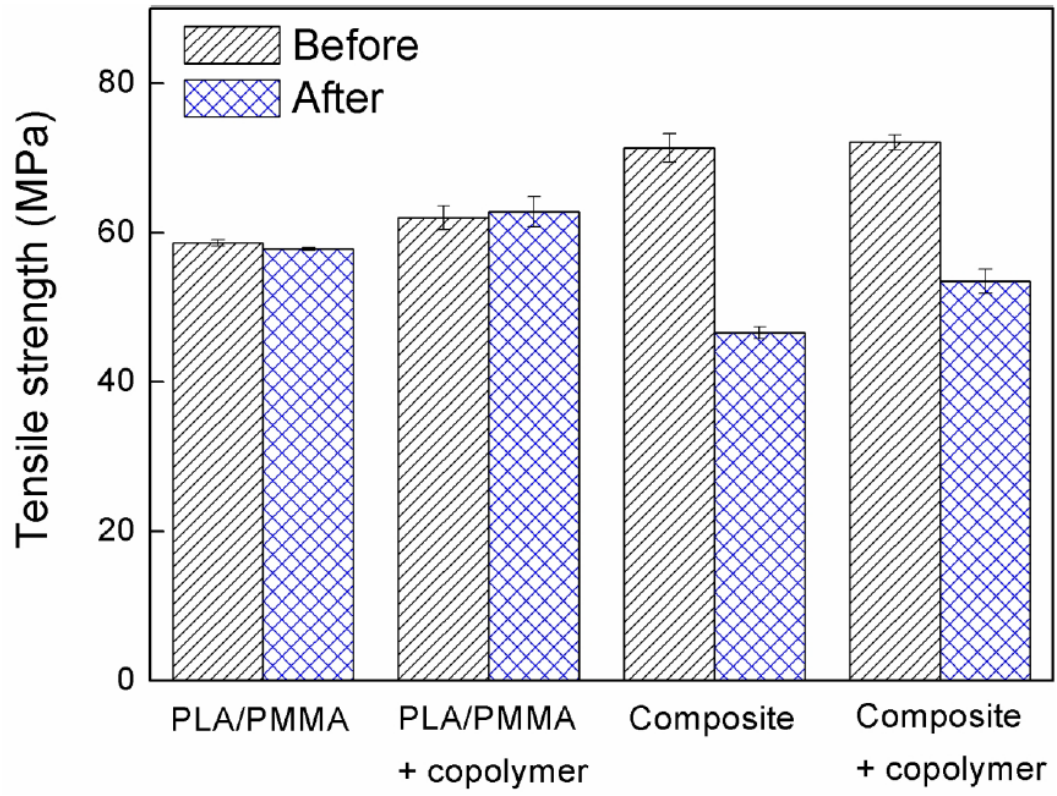


Figure 3a

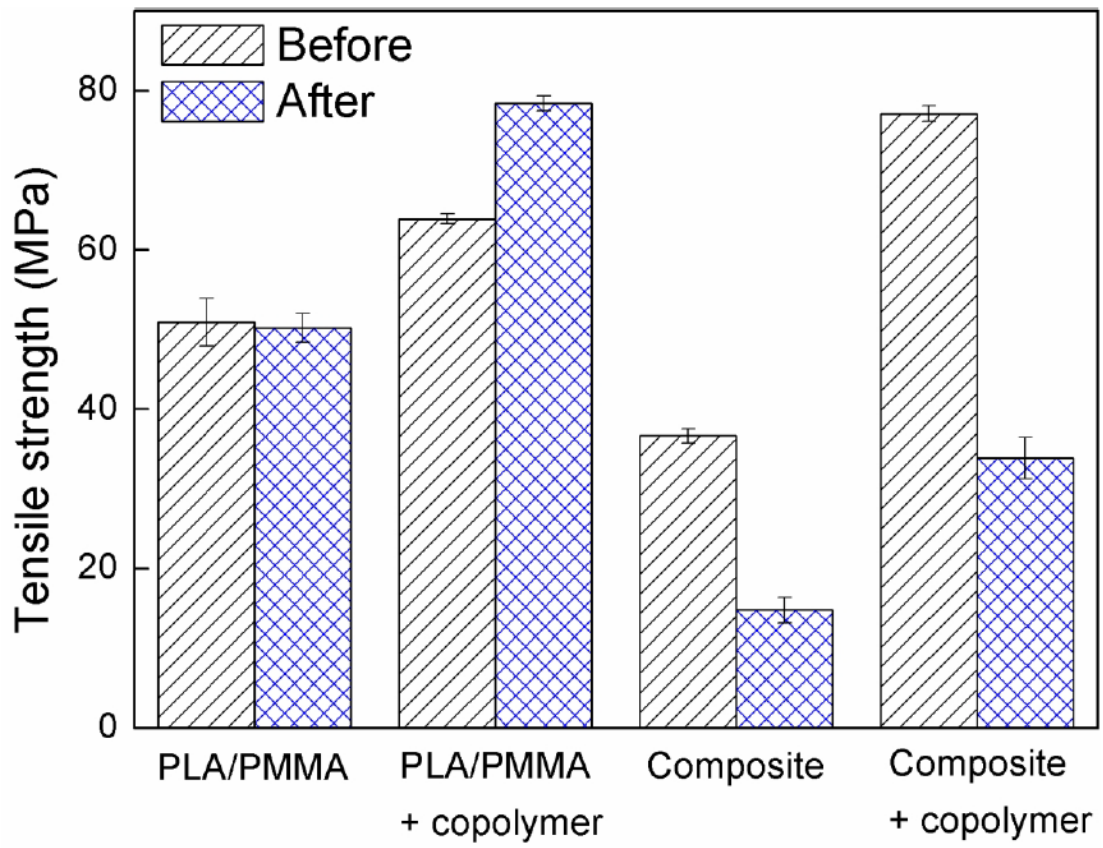


Figure 3b

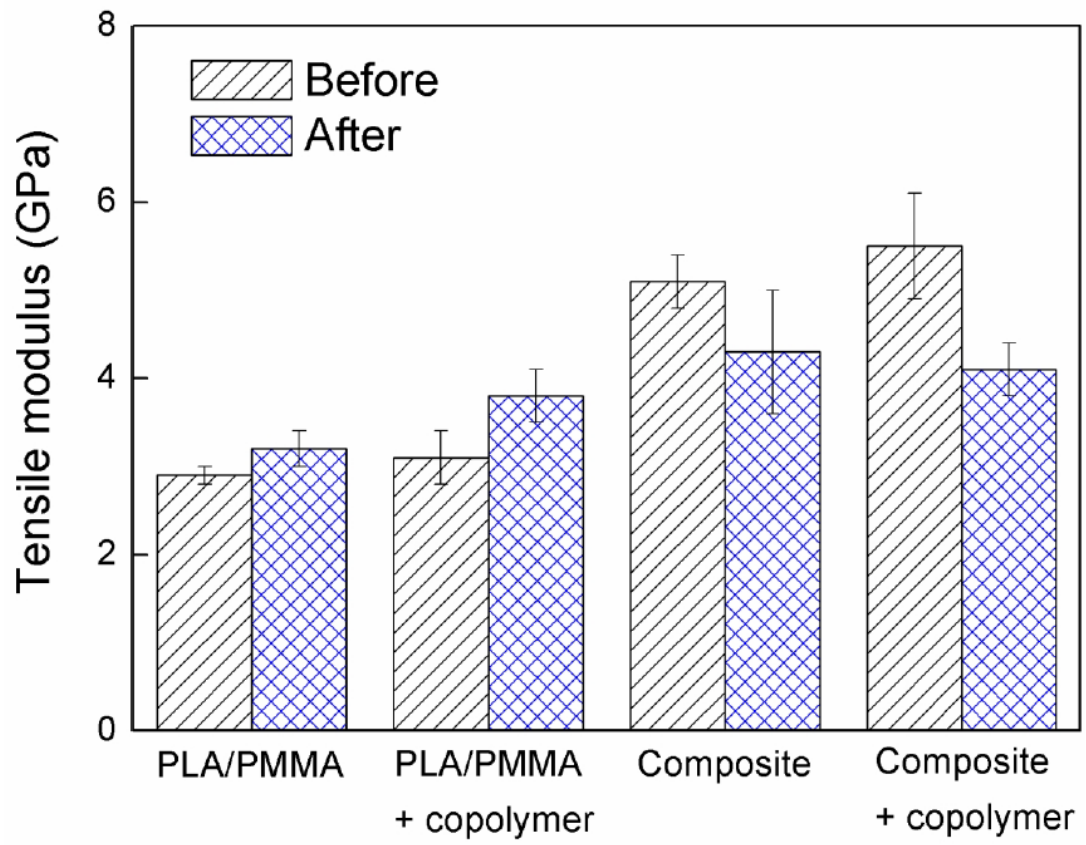


Figure 4a

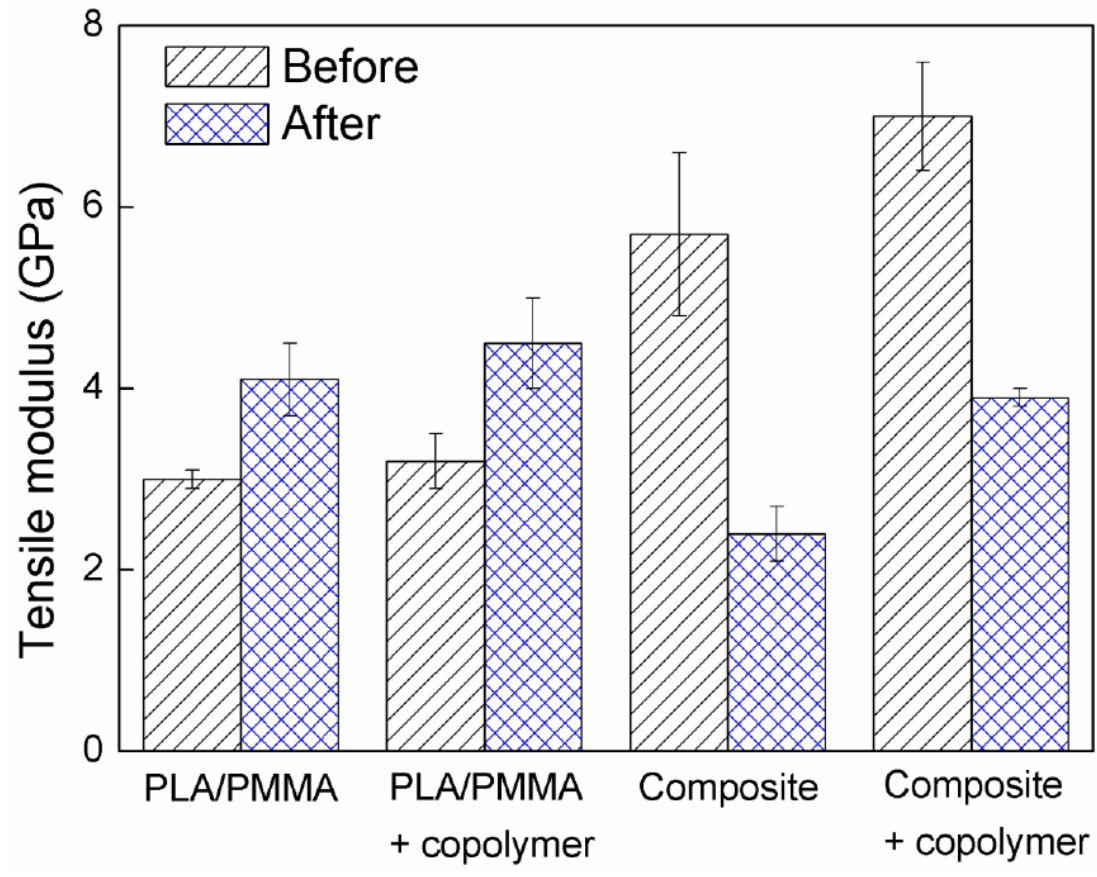


Figure 4b

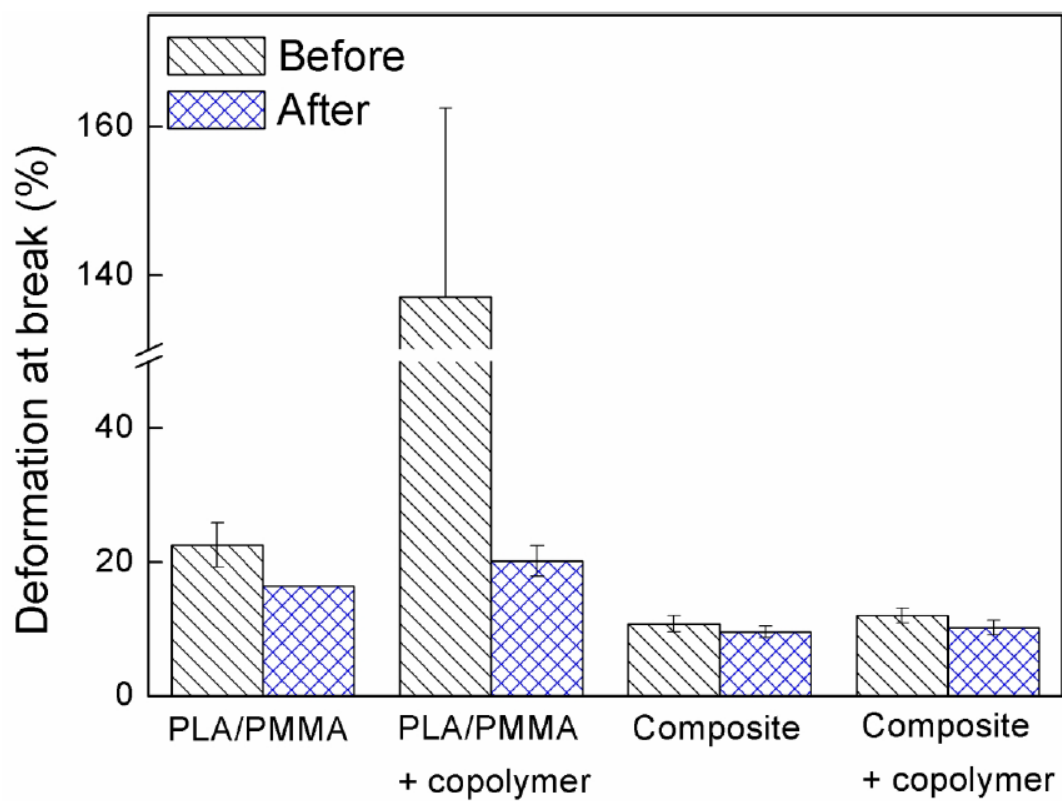


Figure 5a

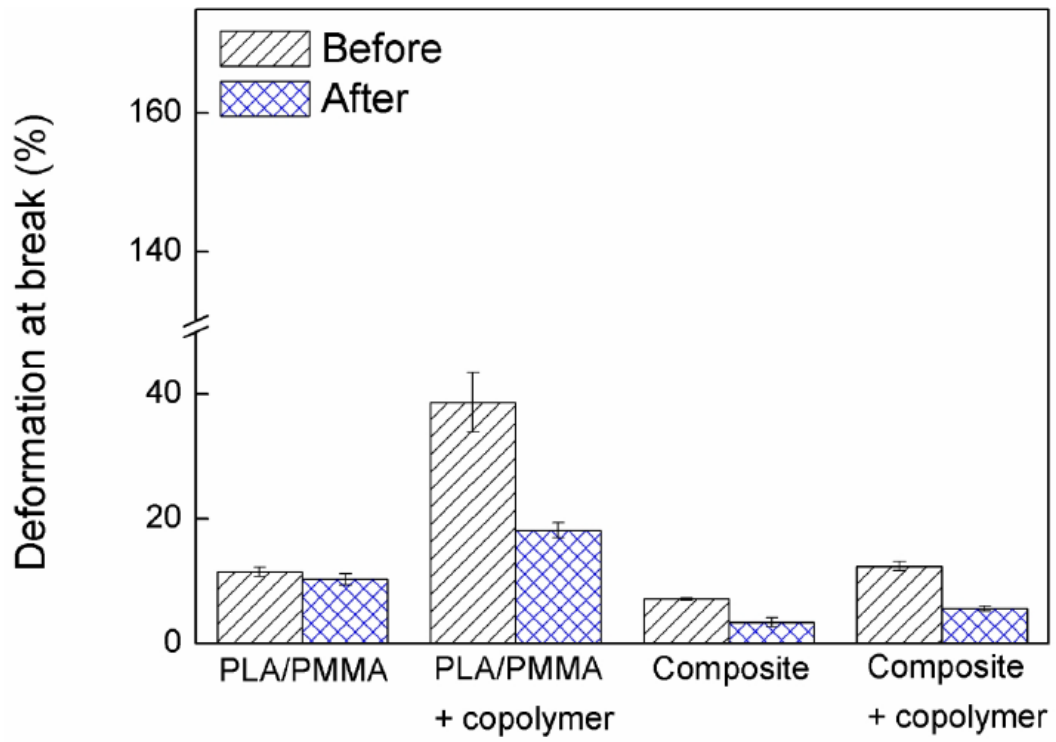


Figure 5b

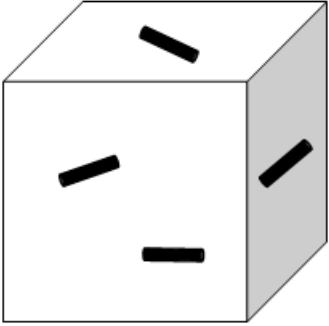
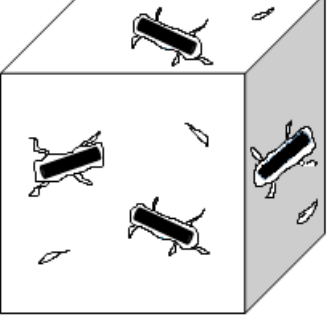
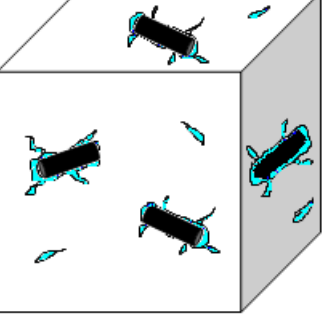
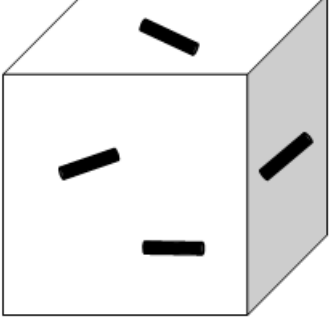
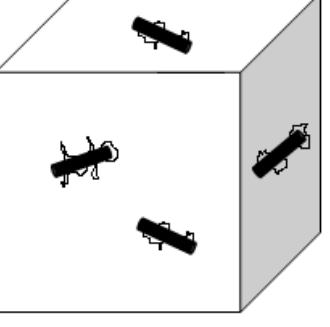
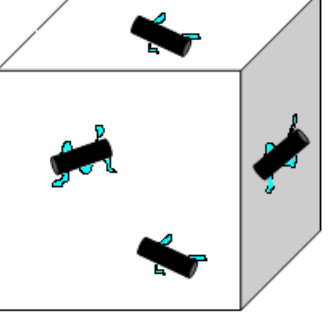
System	Initially	After annealing	After annealing + water uptake
Composite			
Composite with copolymer			

Figure 6

Table 1

System		$\Delta m(\infty)$ (%)	D_c (cm²/s)
Before	80/20	1.0	4.2
	80/20 + 30 wt% fiber	6.3	5.3
	80/20 + 3 pph	0.9	4.1
	80/20 + 3 pph + 30 wt% fiber	5.2	4.8
After	80/20	1.0	5.2
	80/20 + 30 wt% fiber	12.6	11.6
	80/20 + 3 pph	0.9	4.5
	80/20 + 3 pph + 30 wt% fiber	7.7	7.6

Table 2

System (<i>trade name</i>)	Reinforcement (wt. %)	Coupling agent	Annealing	Water immersion	Equilibrium water uptake (%)	Estimated density (g/cm ³)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Reference
PLA/PMMA-treated sisal fiber	30	none	No	Yes	6.3	1.3	14.8	2400	Current work
PLA/PMMA-treated sisal fiber	30	P(S-co-GMA)	No	Yes	5.2	1.3	33.9	3900	Current work
PLA/PMMA-treated sisal fiber	30	None	Yes	Yes	12.6	1.3	46.6	4300	Current work
PLA/PMMA-treated sisal fiber	30	P(S-co-GMA)	Yes	Yes	7.7	1.3	53.5	4100	Current work
PLA-sisal fiber	30	None	No	Yes	6.3	1.2	35.1	3000	Orue et al. 2016
PP-flax fibers	30	None	No	Yes	5.9	1.0	26.7	1175	Arbelaiz et al. 2005
PP-flax fibers	30	MAPP	No	Yes	--	1.0	32.0	1195	Arbelaiz et al. 2005
PP-CaCO ₃ (<i>RTP 143</i>)	30	None	No	No	--	1.1	26	2620	RTP company, 2021
PP-Talc (<i>RTP 132</i>)	30	None	No	No	--	1.1	32	3792	RTP company, 2021
PP-Mica (<i>RTP 149</i>)	25	None	No	No	--	1.1	30	4137	RTP company, 2021
PP-Glass Fiber (<i>RTP 105 CC</i>)	30	Yes	No	No	--	1.1	76	6206	RTP company, 2021