

NATURAL FIBRE REINFORCED BIODEGRADABLE POLYMER COMPOSITES

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Abstract. Currently, numerous research groups have explored the production and properties of biocomposites where the polymer matrices are derived from renewable resources such as poly lactide (PLA), thermoplastic starch (TPS), cellulose and polyhydroxyalkanoates (PHAs). This review is carried out to evaluate the development and properties of natural fibre reinforced biodegradable polymer composites. They are the materials that have the capability to fully degrade and compatible with the environment.

1. INTRODUCTION

Of late, product made from natural fibre reinforced biodegradable polymer composites are yet to be seen in high magnitude. The depletion of petroleum resources coupled with awareness of global environmental problem provides the alternatives for new green materials that are compatible with the environment and their development is independent of petroleum based resources. The development of natural fibre reinforced biodegradable polymer composites promotes the use of environmentally friendly materials. The use of green materials provides alternative way to solve the problems associated with agriculture residues.

Agricultural crop residues such as oil palm, pineapple leaf, banana, and sugar palm produced in billion of tons around the world. They can be obtained in abundance, low cost, and they are also renewable sources of biomass. Among this large amount of residues, only a small quantity of the residues was applied as household fuel or fertilizer and the

rest which is the major portion of the residues is burned in the field. As a result, it gives a negative effect on the environment due to the air pollution [1]. The vital alternative to solve this problem is to use the agriculture residues as reinforcement in the development of polymer composites [2]. A viable solution is to use the entire residues as natural fibres and combine them with polymer matrix derived from petroleum or renewable resources to produce a useful product for our daily applications as shown in Fig. 1.

2. BIOCOSITES

2.1. Poly Lactide (PLA) - natural fibre composites

In recent years, due to concerns about disposal of plastics, polymer scientists have been strongly encouraged to develop new biodegradable polymer composite materials from renewable resources [3]. However, research on biodegradable polymers as

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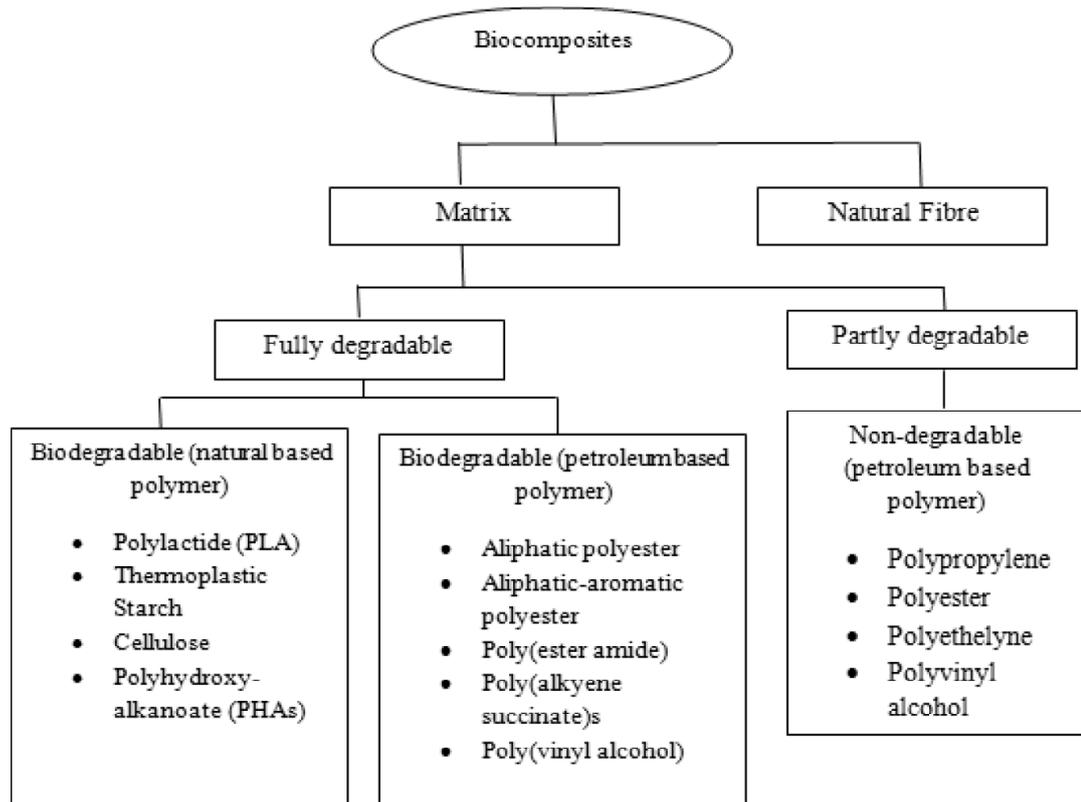


Fig. 1. Classifications of biocomposites (adapted from Mohanty et al. [2]).

composite matrices are limited in comparison with research on thermoplastic and thermoset polymers because of the relatively poor availability and high price of biodegradable polymers. The research focused more on the influence of natural fibres on the mechanical properties of petroleum based polymers rather than using biopolymer like PLA as a matrix. Many advantages are associated with the use of natural fibers, including low cost, abundance, low density, high specific properties and lack of residues upon incineration [4-8]. Thus, the combination of natural fibre with PLA offers an answer to maintaining the sustainable development of economical and ecological technology.

A recent study on PLA composite was carried out by Ochi [9] where in his investigation, the unidirectional biodegradable composite materials were fabricated from kenaf fibres and PLA which showed that tensile and flexural strengths of 223 MPa and 254 MPa respectively were achieved. He also evaluated the biodegradability of kenaf/PLA composites for four weeks using a garbage-processing machine and the experimental results showed that the weight of composites decreased by 38% after four weeks of composting. The SEM photomicrographs of kenaf/PLA composites shown in Fig. 2.

Oksman et al. [10] reported the work on manufacture of PLA/flax composites and compared them to more commonly used polypropylene (PP) flax fibre composites (PP/flax). Preliminary results show that the mechanical properties of PLA and flax fibre composites about 50% higher compared to PP/flax fibre composites; which are used today in automotive panels (Fig. 3).

Meanwhile, van den Oever et al. [11] examined the different types of agrofibres such as ramie, flax and cotton and they reinforced PLA to form composites. In their finding, flexural stiffness of composites increase linearly with fibre contents for all types of fibres (ramie, flax and cotton) while the impact strength reduces with increasing fibre content. This reduction of impact strength trend is similar for the composites of these three fibre sources investigated and for the other natural fibres reported earlier [12-15] except for composites with rayon [15-17] and long kenaf [13].

2.2. Thermoplastic starch - natural fibre composites

In late 1980s, the development of biocomposites had been intensified and polymer matrices reinforced with natural fibres had gained more attention among

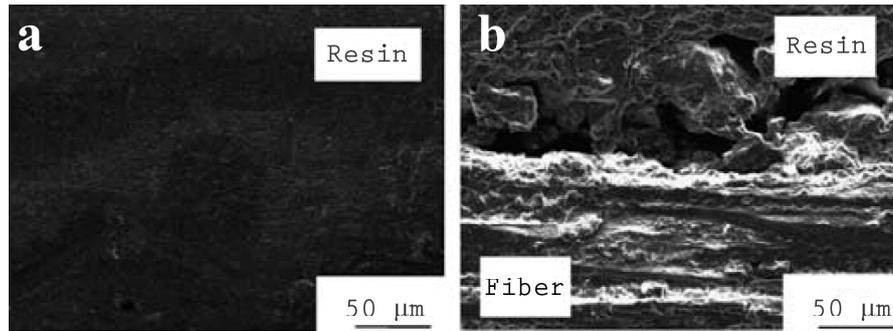


Fig. 2. SEM photomicrographs of kenaf/PLA composites: (a) before composting test and (b) after composting test for four weeks, replotted from [9].

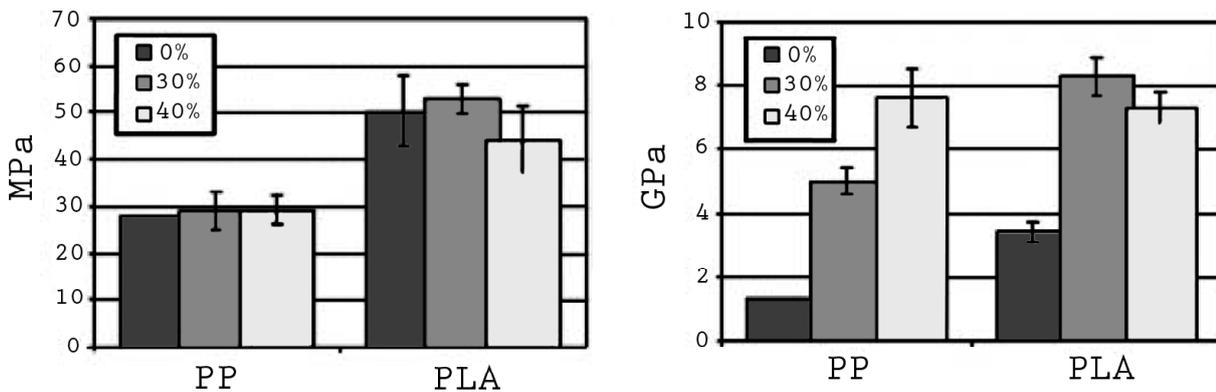


Fig. 3. Tensile stress and tensile modulus of PLA/flax composite compared to PP/flax, data from [10].

the researchers [18]. Biocomposite with starch used as a matrix is one of the most popular biodegradable biocomposite and is highly investigated by researchers [19, 20]. Biodegradable matrices were reinforced with natural fibres to improve the composites properties [21–25] and these composites provide positive environmental advantages, good mechanical properties and light weight [26–28].

In the recent years, some researchers have studied the properties of biodegradable composites made from plasticized starch reinforced with natural fibres. Vilaseca et al. [18] have developed composite materials from biodegradable starch and jute strands fabricated using injection moulding process. Mechanical properties of starch-based polymer and its composites with different percentages of untreated jute strands and alkali treated jute strands were determined. The tensile strength of untreated jute reinforced starch-based biopolymer composites increased for fibre contents of 10, 20, and 30% (w/w) respectively. The increase of the strength and stiffness were also observed for alkali treated jute strand/starch composites. Moisture absorption of the composites was also studied by leaving in open air the untreated jute-starch composites for 72 days. The humidity absorbed was very low and they

claimed that the increase in the percentage of reinforcement did not affect substantially the moisture absorption as shown in Fig. 4.

Averous and Boquillon [23] studied thermal and mechanical behaviour of composites made from thermoplastic starch (TPS) reinforced with agro-materials (cellulose and lignocellulose fibres). It was observed that decreases of both storage and loss moduli against temperature for various composites and moduli increase with the increase in fibre content as shown in Fig. 5. TPS composites modulus displays a regular behaviour where reinforcement effect increases with the fibre length from short length fibre (SF) to medium length fibre (MF) and fibre content while elongation at break decreased with the increase in fibre contents and length (Fig. 6). But, the result of elongation at break is clearly in contrast to the results obtained by Soykeabkaew [26] shown in Fig. 7 where the elongation at break increases with the increase of fibre content.

Averous et al. [30] produced TPS composites by the introduction of leafwood cellulose fibres into a matrix derived from water/glycerol plasticization of wheat starch. The work revealed an increase in the main transition temperature (Dynamic Mechanical Thermal Analysis (DMTA)) of about 30 °C by the introduction of fibres and fibre-matrix

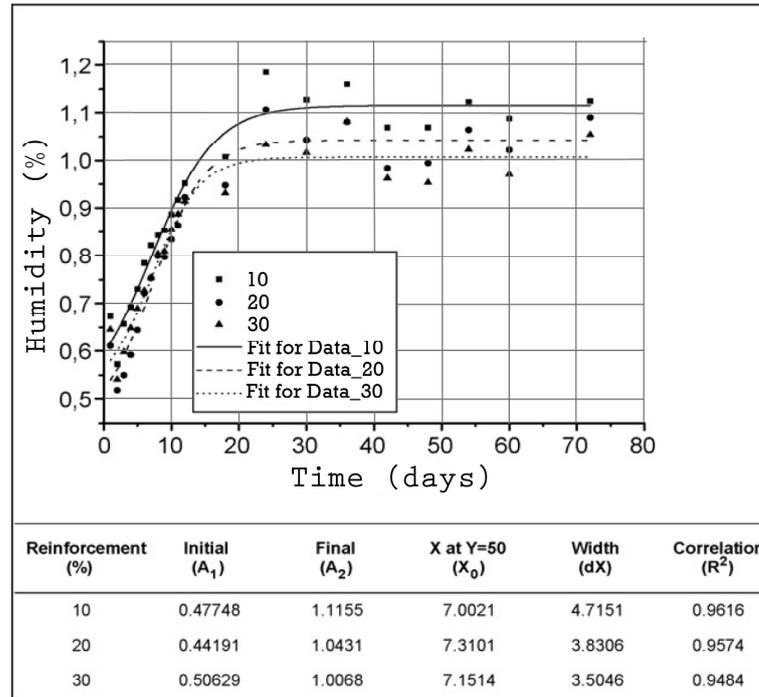


Fig. 4. Boltzmann parameters and quadratic coefficient of the Boltzmann curve for the moisture absorption of untreated jute strand/starch composites at 10, 20, and 30 wt.% of reinforcement, replotted from [18].

interaction improved the mechanical properties of TPS composites. Recently, Vallejos et al. [31] studied the potential use of fibrous materials obtained from ethanol–water fractionation of bagasse as reinforcements of TPS in order to improve mechanical properties of TPS and it was also claimed that there were significant improvements due to fibre treatment and fibre loading on mechanical properties of the composites. In general, it has been shown that there is high compatibility between TPS and natural fibres in composites [32].

2.3. Cellulose - natural fibre composites

The technological development in the recent years has created the problem of global warming with

carbon dioxide emission and caused the shortage of fossil fuels. Therefore, new materials derived from biodegradable renewable sources are considered as partial solution to these problems. New materials such as cellulose derivatives have been foreseen to use as the potential matrices in composites. In the past, limited studies have carried out use of cellulose esters as matrices in biocomposites [33-37]. These cellulose esters are very well suited for use as matrices in natural fibre-based composites. The composites can be processed using injection moulding, extrusion, blow and rotation moulding to form structural components. Typical processing temperatures for cellulose ester are between 180 ° and 240°C and glass transition temperature (*T_g*) values for the cellulose esters achieved in common

Table 1. Single fiber fragmentation test [38].

Fiber matrix	Ramie CAB	Flax CAB	Flax CAP
Fiber diameter (μm)	25	24.3	23.4
Single fiber tensile strength (MPa)	180	580	580
Average fiber fragment length (mm)	0.74	0.51	0.59
Standard deviation (mm)	0.27 (36%)	0.16 (31%)	0.27 (46%)
Critical fiber length, <i>l_c</i> (mm)	0.99	0.68	0.79
Interfacial shear strength, τ (MPa)	2.32	9.98	8.59

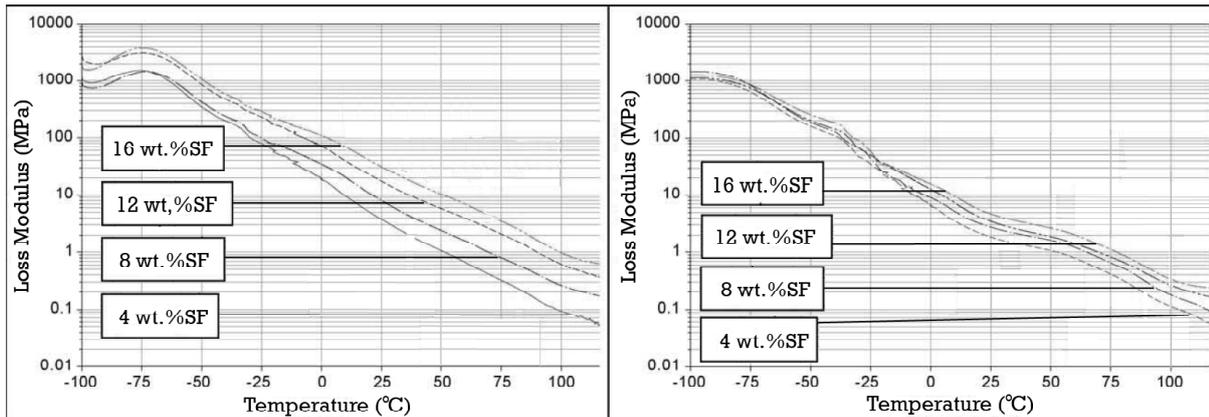


Fig. 5. TPS/SF (short fibre) composites with different filler contents. Variations of loss and storage modulus vs. temperature, replotted from [23].

Table 2. Tensile properties of CAB or CAP sisal/wood fibers at 30% fiber content [38].

	Tensile Modulus (GPa)	Stddev(±)	Stress at Break (MPa)	Stddev(±)	Max Strain (%)	Stddev(±)
CAB	1.3	0.2	25.2	0.3	-	-
CAB/15/15 ^a	3.4	0.06	26.0	0.6	2.6	0.3
CAP	1.5	0.1	26.7	0.4	-	-
CAP/15/15 ^a	4.1	0.06	41.5	0.4	2.1	0.2

^a – composites prepared with 15 wt.%sisal/15 wt.% wood fibers.

Table 3. Flexural properties of CAB or CAP sisal/flax fibers at 50% fiber content [38].

CAB/fiber	Breaking Strength		Elongation		Flexural Modulus	
	MPa	Std	%	Std	Gpa	Std (MPa)
Neat	70.3	12.5	4.9	0.1	1.35	50
Flax	82.3	16.5	3.6	0.3	5.71	1613
Sisal	87.6	27.9	2.5	0.7	7.85	1553

Table 4. Impact strength of CAB or CAP sisal/wood fibers at 30% fiber content [38].

Composite	Impact Strength (kJ/m ²)	Stddev(±)
CAB	80.2	9.2
CAB/15/15 ^a	11.4	1.5
CAP	83.5	6.2
CAP/15/15 ^a	10.4	1.8

^a – composites prepared with 15 wt.% of wood fibers and 15 wt.% sisal fibers.

plastic applications fall in the range of ~140 °C “190 °C [38].

Toriz et al. [38] have carried out a study on single fibre fragmentation testing for composites made

from cellulose acetate butyrates (CAB) and cellulose acetate propionate (CAP) as matrices combined with single fibres of flax and ramie by using hot press at 210 °C It was shown that flax fibres provide better adhesion to CAB compared to ramie fibres as shown in Table 1. Furthermore, the results shown in Tables 2 and 3 revealed that reinforcement of the fibres is clearly seen to improve the tensile and flexural properties of the biocomposites as well as for their shear storage modulus (Fig. 8) but, it is found that the impact strength of biocomposites was dramatically reduced as shown in Table 4.

Seavey et al. [35] prepared thermoplastic composites using high modulus lyocell fibres produced by solutions of N-methyl morpholine-N oxide (NMMO)/water as reinforcement and CAB as matrix. From their analysis, it was revealed that at

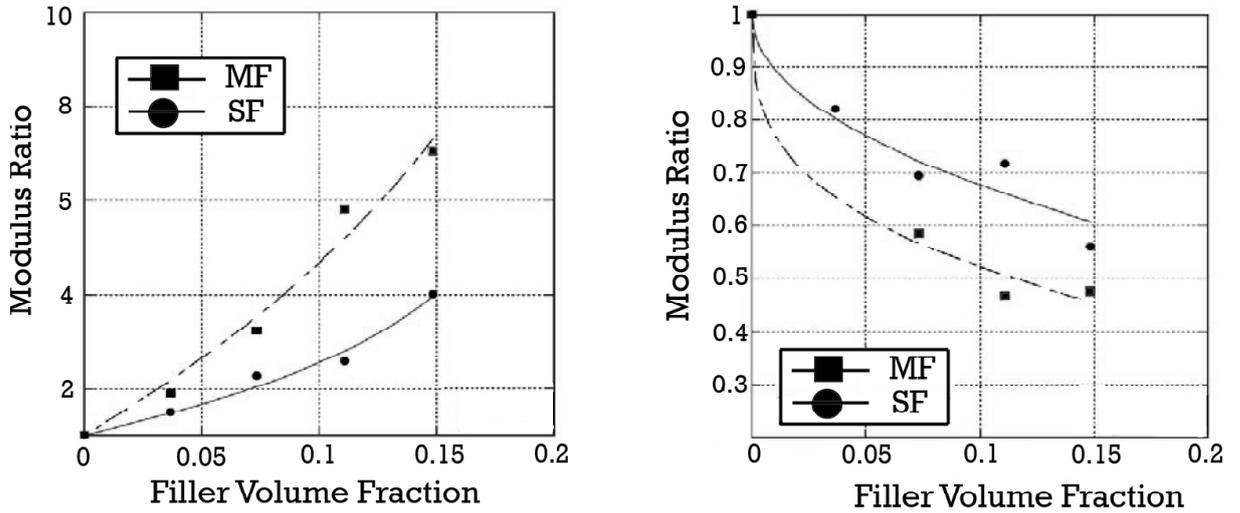


Fig. 6. TPS/ SF (short fibre) and MF (medium fibre) composites. Variation of modulus and elongation at break ratios, replotted from [23].

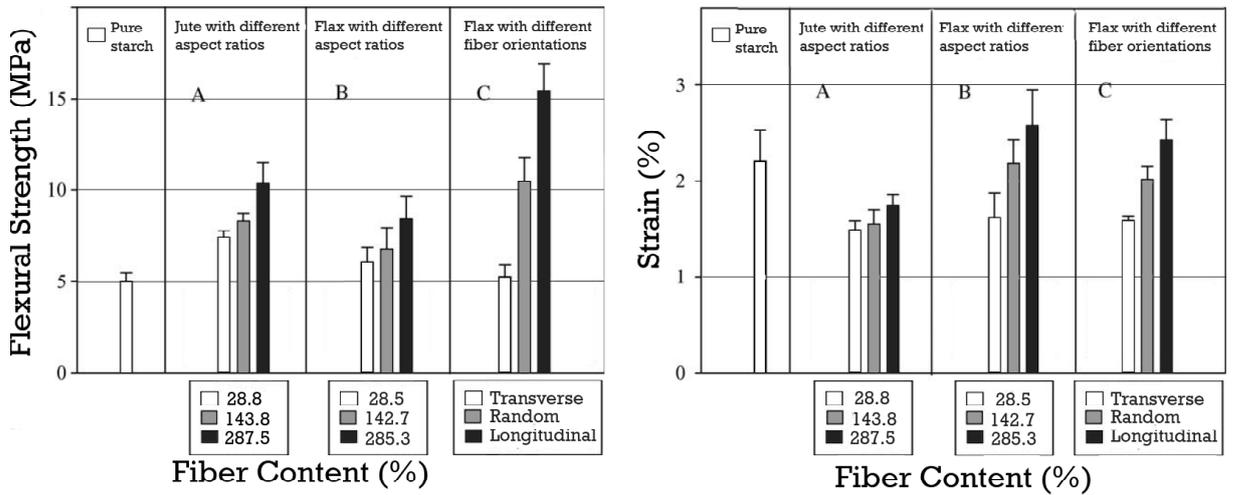


Fig. 7. Effects of flexural strength and strain for starch-based composite foams reinforced with (A) jute and (B) flax fibers of different aspect ratios, and for (C) starch-based composite foams reinforced with flax fibers of different fiber orientations, replotted from [29].

fibre volume contents of approximately 60%, the tensile strength, modulus, and strain at failure values are approximately 250 MPa, >20 GPa and 3–4%, respectively. Meanwhile, Gindl, and Keckes [39] investigated biocomposites of CAB reinforced with cellulose sheets synthesised by *Gluconacetobacter xylinus* by solvent evaporation casting method. In their study, bacterial cellulose was applied as the reinforcement of CAB composite sheets, in order to investigate the potential of a bacterial cellulose network as reinforcement in polymer composites, and its usefulness as a model system for cellulose fibre reinforced composites in general. At the end of their work, it was found that the composites contained 10% (composite A) and 32% (composites B) by volume of cellulose showed a Young's modulus of 3.2 and 5.8 GPa, and a tensile strength of 52.6 and 128.9 MPa, respectively. The stress-strain behaviours shown in Fig. 9 for the

biocomposites tend to give better performances than unreinforced CAB.

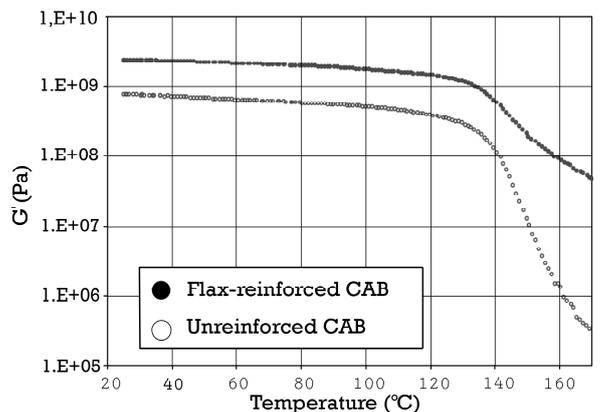


Fig. 8. Shear storage moduli of neat CAB and CAB"flax biocomposites, data from [38].

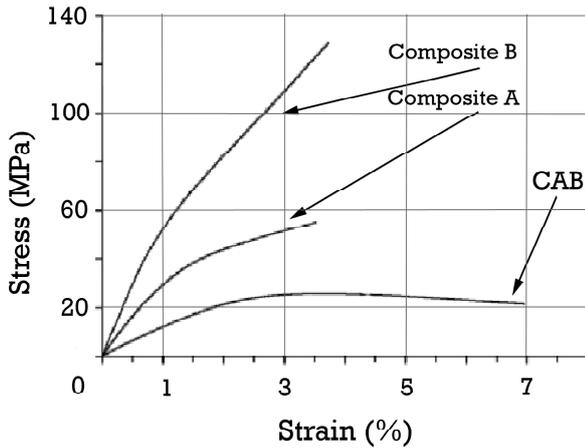


Fig. 9. Stress–strain curves of tensile tests of cellulose acetate butyrate (CAB) and its composites, replotted from [39].

2.4. Polyhydroxyalkanoates (PHAs) - natural fibre composites

Due to the abundance of plastic wastes over last few decades, biodegradable ‘green’ plastics are regarded as possible substitutes to petroleum-based plastics. Polyhydroxyalkanoates (PHAs) are a family of biodegradable polyesters which are synthesized via various bacteria and these polymers differ from petroleum based synthetic polymers with regard to their being renewable resource and biodegradability [40]. Therefore, PHAs have attracted the attention of many researchers and recently their composites with natural fibres have been studied extensively [41-43].

Singh and Mohanty [44] developed ‘green’ composites using natural bamboo fibre and bacterial polyester i.e., poly(hydroxybutyrate-co-valerate) (PHBV) which is member of the family of PHAs. The fabrication of the biocomposites was carried

out using injection moulding following the extrusion compounding of PHBV and bamboo fibre with 30 or 40 wt.% fibre. The main objective of their study was to investigate the fundamental prospects of bamboo/PHBV biocomposites such as mechanical, thermo-mechanical and morphological properties. From their experiment, it was found that tensile modulus of the PHBV composites increased steadily with the increase in fibre loading where at 30 wt.% fibre loading it increased by 67% and at 40 wt.% the increase was 175% (Fig. 10). Meanwhile, the tensile strength of PHBV decreased with the addition of bamboo fibre and they claimed that this phenomenon can be attributed to the lack of sufficient interfacial interaction between the fibre and matrix (Fig. 11). In comparison to the results obtained previously, the tensile and flexural modulus of PHBV based biocomposites reinforced with 40 wt.% of wood fibre was improved by 167% compared with neat PHBV [44]. For the thermo-mechanical behaviour, it is shown that the storage modulus of PHBV increased with the increase in fibre loading up to 40 wt. % as depicted in Fig 12.

3. CONCLUSIONS

Natural fibre reinforced biodegradable polymer composites appear to have very bright future for wide range of applications. These biocomposite materials with various interesting properties may soon be competitive with the existing fossil plastic materials. However, the present low level of production and high cost restrict them for to be applied in industrial application. In addition, its hydrophilic properties makes the real challenge to design the product which can can be good candidate for outdoor applications. Thus, further research and improvement should be conducted so that these fully

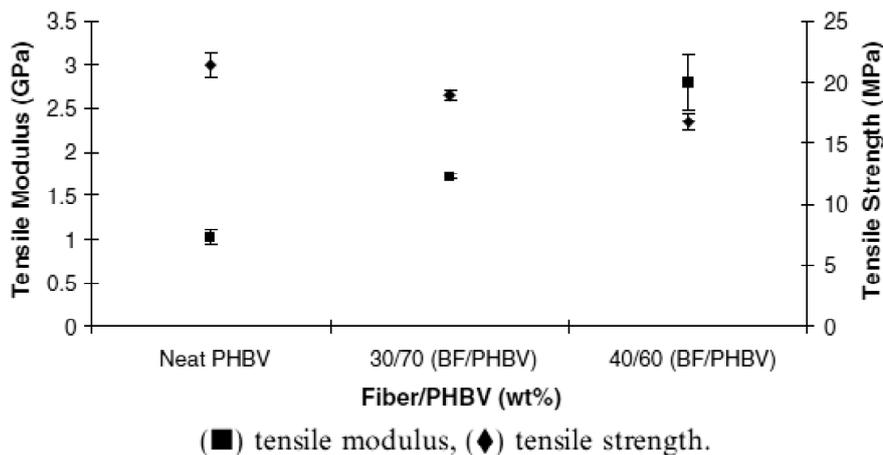


Fig. 10. Tensile properties of bamboo/PHBV composites, data from [44].

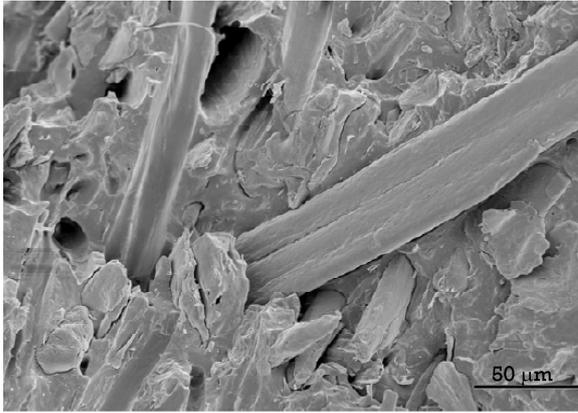


Fig. 11. SEM photomicrographs of impact fractured samples of bamboo/PHBV (70:30) composite, replotted from [44].

degraded composites can easily be manipulated and can give benefit to all mankind and environmental issues.

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REFERENCES

- [1] H.P.S. Abdul Khalil, M. Siti Alwani, R. Rizuan, H. Kamarudin and A. Khairul // *Polym. Plas. Tech. Eng.* **47** (2008) 237
- [2] A.K. Mohanty, M. Misra, L.T. Drzal, S.E. Selke, B.R. Harte and G. Hinrichsen, *Natural Fibres, Biopolymers and Biocomposites* (CRC Press, Boca Raton, 2005)
- [3] D. Plackett and A. Södergard, In: *Natural Fibres, Biopolymers and Biocomposites*, edited by A.K. Mohanty, M. Misra, L. T. Drzal, S.E. Selke, B.R. Harte and G. Hinrichsen (CRC Press, Boca Raton, 2005), p. 569
- [4] A.K. Bledzki, V.E. Sperber and O. Faruk // *RAPRA Rev Rep* **13** (2002) 152
- [5] W.J. Evans, D.H. Isaac, B.C. Suddell and A. Crosky, In: *Natural Fibres and Their Composites: A Global Perspective, Proceedings of the 23rd Risø International Symposium on Materials Science: Sustainable Natural and Polymeric Composites—Science and Technology*, edited by H. Lilholt et al., (Risø National Laboratory, Roskilde, Denmark, 2002), p. 1.
- [6] S.M. Sapuan and M.A. Maleque // *Mat. Des.* **26** (2005) 65
- [7] Z. Leman, S.M. Sapuan, A.M. Saifol, M.A. Maleque and M. Hamdan // *Mat. Des.* **29** (2008) 1666
- [8] E.S. Zainudin, S.M. Sapuan, K. Abdan and M.T.M. Mohamad // *Polym. Polym. Comp.* **17** (2009) 55

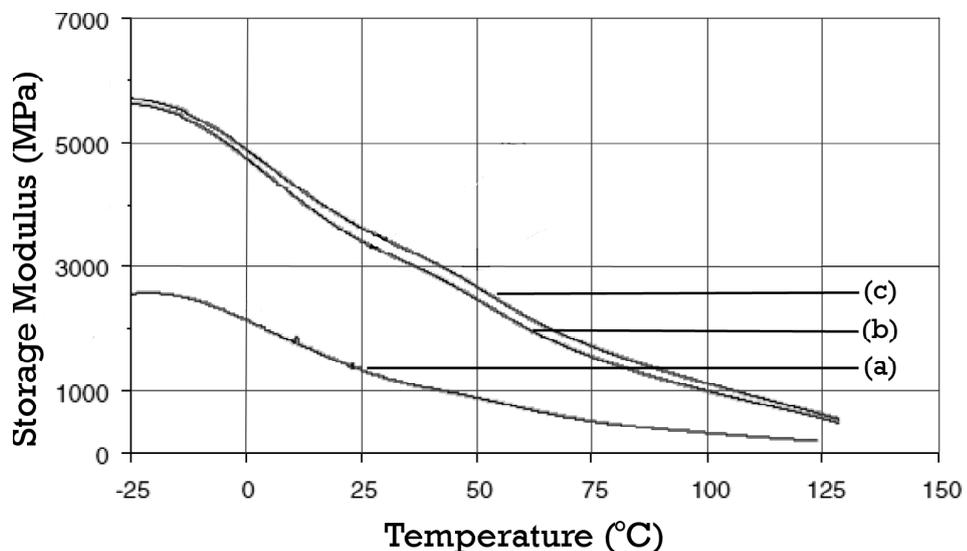


Fig. 12. Storage modulus versus temperature of PHBV with varying loading level of fibre (a) PHBV, (b) PHBV/bamboo fibre (70:30) wt.% and (c) PHBV/bamboo fibre (60:40) wt.%, replotted from [44].

- [9] Shinji Ochi // *Mech. Mat.* **40** (2008) 446
- [10] K. Oksman, M. Skrifvars and J.F. Selin // *Comp. Sci. Tech* **63** (2003) 1317
- [11] M.J.A. van den Oever, B. Beck and J. Müssig // *Comp. Part A* **41** (2010) 1628
- [12] M.S. Huda, L.T. Drzal, M. Misra, A.K. Mohanty, K. Williams and D.F. Mielewski // *Ind. Eng. Chem. Res.* **44** (2005) 5593.
- [13] M.S. Huda, L.T. Drzal, M. Misra and A.K. Mohanty // *J. Appl. Polym. Sci.* **102** (2006) 4856
- [14] S. Serizawa, K. Inoue and M. Iji // *J. Appl. Polym. Sci.* **100** (2006) 618.
- [15] B. Bax and J. Müssig // *Comp. Sci. Tech.* **68** (2008) 1601.
- [16] J. Ganster and H.P. Fink // *Comp. Part A* **37** (2006) 1796.
- [17] M. Shibata, K. Ozawa, N. Teramoto, R. Yosomiya and H. Takeishi // *Macromol. Mater. Eng.* **288** (2003) 35.
- [18] F. Vilaseca, J.A. Mendez, A. Pelach, M. Llop, N. Canigüeral, J. Girones, X. Turon and P. Mutje // *Pro Biochem* **42** (2007) 329.
- [19] A.S. Hermann, J. Nickel and U. Riedel // *Polym. Degrad. Stab.* **59** (1998) 251.
- [20] C. Bastioli // *Macromol. Symp.* **130** (1998) 379.
- [21] M. Wollerdorfer and H. Bader // *Ind. Crops. Prod.* **8** (1998) 105.
- [22] X.F. Ma, J.G. Yu and J.F. Kennedy // *Carbohydr. Polym.* **62** (2005) 19.
- [23] L. Averous and N. Boquillon // *Carbohydr. Polym.* **56** (2004) 111.
- [24] N. Soykeabkaew, P. Supaphol and R. Rujiravanit // *Carbohydr. Polym.* **58** (2004) 53.
- [25] V. Tserki, P. Matzinos, N.E. Zafeiropoulos and C. Panayiotou // *J. Appl. Polym. Sci.* **100** (2006) 4703.
- [26] R. Narayan // *ACS. Symp. Ser.* **476** (1992) 1.
- [27] A.K. Rana and K. Jayachandran // *Mol. Cryst. Liq. Cryst.* **353** (2000) 35.
- [28] A.K. Mohanty and M. Misra // *Polym. Plas. Tech. Eng.* **34** (1995) 729.
- [29] S. Nattakan, S. Pitt and R. Ratana // *Carbohydr. Polym.* **58** (2004) 53.
- [30] L. Averous, C. Fringant and L. Moro // *Polym.* **42** (2001) 6565.
- [31] M.E. Vallejosa, A.A.S. Curveloc, E.M. Teixeira, F.M. Mendesc, A.J.F. Carvalhoe, F.E. Felissia and M.C. Area // *Ind. Crops Prod.* **33** (2011) 739
- [32] L. Averous and P.J. Halley // *Biofuel Bioprod. Bior.* **3** (2009) 329.
- [33] G. Toriz, R. Arvidsson, M. Westin and P. Gatenholm // *J. Appl. Polym. Sci.* **88** (2003) 337.
- [34] H. Matsumura, J. Sugiyama and W.G. Glasser // *J. Appl. Polym. Sci.* **78** (2000) 2242
- [35] K.C. Seavey, I. Ghosh, R.M. Davis and W.G. Glasser // *Cellulose* **8** (2001) 149.
- [36] K.C. Seavey and W.G. Glasser // *Cellulose* **8** (2001) 161
- [37] A. Franko, K.C. Seavey, J. Gumaer and W.G. Glasser // *Cellulose* **8** (2001) 171.
- [38] G. Toriz, P. Gatenholm, B.D. Seiler and D. Tindall, In: *Natural Fibres, Biopolymers and Biocomposites*, ed. by A.K. Mohanty, M. Misra, L. T. Drzal, S.E. Selke, B.R. Harte and G. Hinrichsen (CRC Press, Boca Raton, 2005), p. 617
- [39] W. Gindl and J. Keckes // *Comp. Sci. Tech.* **64** (2004) 2407
- [40] S. Singh, A.K. Mohanty, T. Sugie, Y. Takai and H. Hamada // *Comp. Part A* **39** (2008) 875.
- [41] A.K. Bledzki and A. Jaszkiwicz // *Comp. Sci. Tech.* **70** (2010) 1687.
- [42] E. Zini, M.L. Focarete, I. Noda and M. Scandola // *Comp. Sci. Tech.* **67** (2007) 2085.
- [43] E.R. Coats, F.J. Loge, M.P. Wolcott, K. Englund and A.G. McDonald // *Bior. Tech.* **99** (2008) 2680.
- [44] S. Singh and A.K. Mohanty // *Comp. Sci. Tech.* **67** (2007) 1753.