

Influence of Plant Natural Fibers on Polymer Hydrogel Properties: A Short Review

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ABSTRACT: The effects of plant natural fibers (PHFs) on polymer hydrogels (PHGs) properties in terms of swelling ratio, biodegradation, thermal and mechanical properties were encompassed in this review. The Swelling ratio of PHGs is enhanced by using plant natural fibers (PNFs) up to an optimum point and decline with further content of fibers. PNFs have positive effect on the biodegradation of PHG materials. There is no clear picture in the previous research describing the effect of PNFs on thermal stability and mechanical properties of PHGs.

Keyword: Hydrogels, polymer hydrogels, plant natural fibers, swelling ratio, thermal properties

I. INTRODUCTION

Polymer hydrogels (PHGs) are visco-elastic, loosely crosslinked, hydrophilic, and three-dimensional networks of flexible polymer chains with dissociated ionic functional groups, that can absorb large amount of water or other biological fluid in a short time and retain them under pressure [7, 8, 22, 27, 28]. PHGs have been abundantly used in disposable diaper industry for the past 35 years; their applications are still being expanded to many fields including agriculture, horticulture, sealing composites, artificial snow, drilling fluid additives, medicine for drug delivery system and more. Recently, the preparation of polymer hydrogels composites (PHGCs) received great attention because of their relatively low production cost and high water absorbency. There is a wide range of organic and inorganic materials available for preparation of PHGCs such as kaolinite, montmorillonite (MMT), hecrite, saponite, synthetic mica, used paper (UP), oil palm empty fruit bunch (OPEFB), and wheat strew (WS). Some of these materials are used in Nanosize to prepare Nanocomposite of PHGs such as fabrication of silver or zinc nanoparticles. PHGC materials find many new applications beyond those of PHG such as catalysis, optics, electronics, bio-medicals and quantum-sized domain applications. Also, there are some potential applications of SAPC in water treatments that have been described [11, 34]. The main raw materials that are normally needed to synthesis PHGs are; polymer or monomers repeating unit, crosslinking agent, and initiator. Several polymerization methods have been used to synthesize and prepare PHGC such as solution polymerization or aqueous polymer solution [17], radiation polymerization [26] or photopolymerization [4, 39], suspension polymerization [24], reversible addition-fragmentation chain transfer (RAFT) polymerization [43], and free radical polymerization [4, 36, 42]. Natural fibers are materials extracted from substances made naturally in nature. Natural fibers have been used for textile applications long before the first polymer was synthesized. Natural fibers are divided into three categories; vegetable (plant fibers), animal and minerals as seen in Figure 1.

Vegetables or plant fibers are classified into three subdivisions; leaf fiber such as oil palm, pineapple, and abaca leaf; bast fiber such as kenaf, jute and flax; seed fibers such as rice husk kapok, and coir [1]. In view of recent global environmental issues and inadequate fiber resources, scientists worldwide have shown interest in exploiting the full potential of plant fiber [2]. Natural fibers have been attracted by many scientists for last decades and it considered as genuine alternative to glass fibers. The advantages of natural fiber over glass reinforced fiber are that the first is lower cost, lower density, recyclable and very good biodegradation [14, 15]. Table 1 indicated that cellulose is the main component of natural fibers. Cellulose is a semicrystalline polysaccharide made up of β -D-glucopyranose units linked together by β -(1-4)-glucosidic bonds Cellulose was extracted first time in the eighteenth century in a crystalline form. It has very long chain of one repeating unit that called cellobiose. It is considered as one of the most natural biodegradable materials that can be consumed

by aerobic and anaerobic bacteria. The microorganisms will primary degrade the cellulose to glucose and cellodextrins and then they provide enzymes to degrade the cellodextrins to glucose. Produced glucose will be fully utilized by the microorganisms as food. The final products of aerobic biodegradation are CO₂ and water. Un likely in anaerobic degradation the final products are CO₂, hydrogen, hydrogen sulphide, methane, and ammonia [5]. For the reasons above the cellulose or any fiber with acceptable percentage of cellulose can be used for enhancing the biodegradation of synthesized polymers.

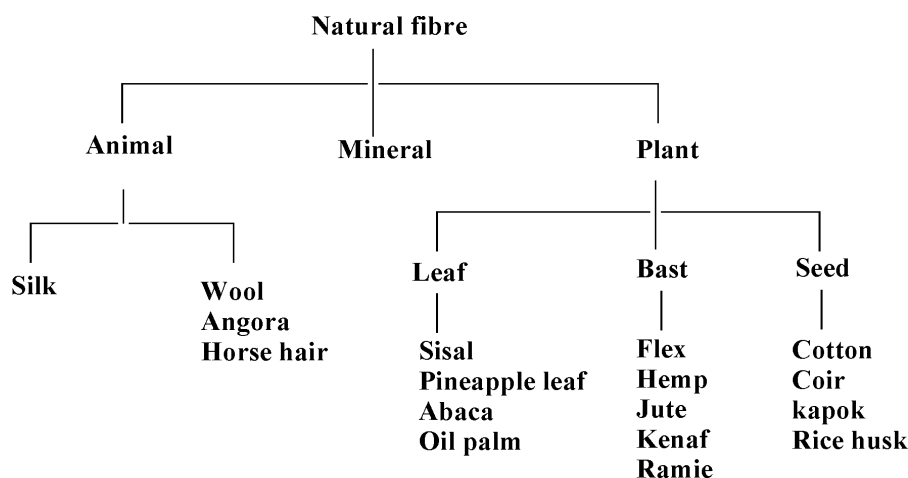


Figure 1: Classification of nature fibers

Table 1: Chemical composition of some natural fibres

Fiber	Cellulose %	Lignin %	Pentosan %	Ash %
Cotton	85-96	0.7-1.6	1-3	0.8-2
Oil palm	42-65	15-23	22-32	1-3.8
Kenaf	44-47	15-19	22-23	2-5
Jute	41-48	21-24	18-22	0.8
Esparto	33-38	17-19	27-32	6-8
Bagasse	32-48	19-23	27-32	1.5-5
Bamboo	26-43	21-32	15-26	1.7-5
Wheat	29-51	16-21	26-32	3-7
Oat	31-48	16-19	27-38	6-8
Rice	28-48	12-16	23-28	9-14
Hemp	57-77	9-13	14-17	0.8
Abaca	56-63	7-9	15-17	1-3
Sisal	43-62	7-9	21-24	0.6-1
Rye	33-50	16-19	27-30	2-5

II. THE EFFECT OF PNFs ON SWELLING RATIO OF PHG

Swelling behavior and absorption capacity (AC) of PHGs are the most important properties that give PHG materials wide applications. Swelling and absorption properties are attributed to the presence of hydrophilic groups such as -OH-, CONH-, -CONH₂-, and -SO₃H in the network [12]. The ratio of the weight of sample at swelling and de-swelling behaviors is called swelling ratio (SR) [20, 35, 44]. There are many factors affecting SR and AC of PHGs such as chemical structure of the repeating unit or chemical compositions [10, 18, 21], network structure [29], solvent concentration, quality of solvent, cross-linking ratio, and the specific stimuli or the surrounding medium Also, SR and AC of PHGs are affected by polymers molecular weight. The swelling process of PHGs can be explained as following:

The fluid tries to penetrate into polymer networks to produce 3D-molecular network at the same time expanding the molecule chain between the cross-linked points thus decreasing the configuration enthalpy value. The molecule network has an elastic contractive force that tries to make the networks contract. When these opposing forces reach equilibrium, the expansion and contraction also reach a balance. In this process, the

osmotic pressure is the driving force for the expansion of swelling, and the network elastic force is the driving force of the contraction of the gel. There are many methods used to measure AC “a standard is yet to be established” such as volumetric, gravimetric, spectroscopic and microwave method. Absorbed water in the network of PHGs can exist in three states; bound, half-bound and free water. Free water shows freezing point when the environment temperature is around 0°C. However, this freezing point cannot be seen with bound water. The half-bound water shows property between them. Bounded water in PHG usually is 0.39-1.18 g/g. The principles of PHGs absorbency can be illustrated by the Flory theory of ionic network [9].

$$q_m^{5/3} = \frac{\left[\left(\frac{1}{2} \times \frac{i}{v} \times \frac{1}{s+1/2} \right)^2 + \left(\frac{1}{2} - x \right) / V_1 \right]}{(v/V_0)} \quad (1)$$

Where q_m stand for the swelling ratio, v/V_0 is the number of effectively cross-linked chains in unit volume, S^* is the ionic strength of the swollen liquid, i/v_u is the concentration of fixed charge referred to the unswollen network, x is the molar volume of water. Flory equation shows that the water absorption power mainly depend on network cross linking density, initiator content, degree of neutralization, chemical composition of raw materials and solvent quality.

Swelling ratio of PHG is highly affected by chemical composition and content of used fibers. Hydrophilicity of the plant natural fibers is the most property that has direct effect on swelling properties of polymer hydrogel materials. Fiber hydrophilic groups are contributing to improve network affinity of the cross-linked polymer hydrogels. Previous work on sodium alginate (Na-AG) grafted with carboxymethylcellulose (CMC) showed that SR of polymer hydrogels increase gradually with increase in Na-Ag content and the maximum absorption capacity (AC) is achieved at 0.5 weight ratio of Na-Ag/CMC [32, 40]. Another work used Kappa-carrageenan (kC) as a fiber showed that the water absorption capacity (WAC) of PHGs is increased with increase in kC content. Same result has been obtained using CMC grafted with polyacrylonitril (PAN), and starch-poly (sodium acrylate-co- acrylamide)[31]. The influence of wheat straw (WS) content on water absorption capacity of poly acrylic acid hydrogel was investigated by Rui Liang and coworker. The finding of this study indicated that the content WS fiber has remarkable effect on the absorbency of WS/PAA composite in distilled water and 0.92 wt% NaCl solution as can be seen in Figure 2[23].

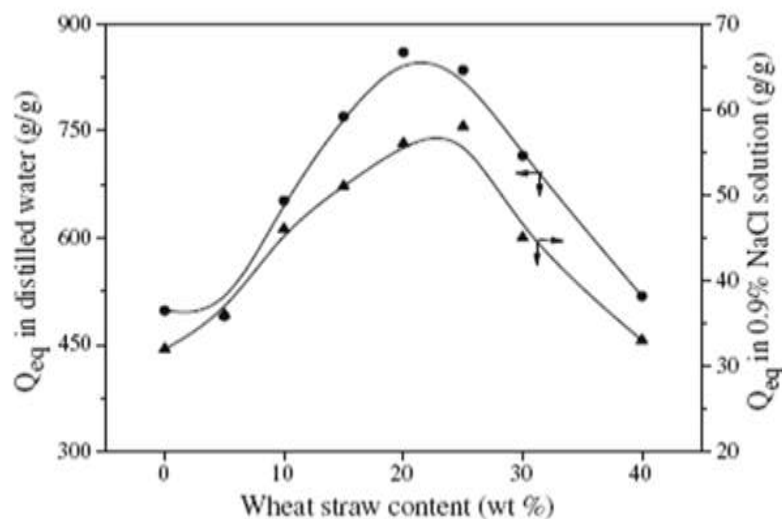


Figure 2: Influence of wheat straw content on the absorbency of WS/PAA composite

The reason behind the absorbency improvement of the polymer hydrogel composite based plant natural fibers is that, the reactions between the polymer chains and –OH groups of the cellulose of the fibers. Cellulose based natural fiber proposed to enhance the network structure of PHG at optimum content. High content of plant natural fiber seems to have negative effect of water absorbency due to generation of high cross linking hydrogels and this might lead to reduce the elasticity of the network. Using plant natural fiber of low hydrophilic content might lead to decrease the final hydrophilic groups of the network and thus decrease the hydrogels affinity and water absorption capacity[23, 37, 41].

III. THE EFFECT OF PNFS ON BIODEGRADATION OF PHGS

Biodegradability is defined as decomposition or deformation of the materials by microorganism's attack such as fungi, bacteria, yeasts and their enzymes. These microorganisms consume the substance as a food under appropriate condition [5]. The biodegradation of synthesized polymer is mainly depended on the polymer molecular weight (MW). High MW prevents the polymer to pass through the plasma membrane of microbial cells. There is one way to enhance the biodegradation of synthesized polymer of high MW and that is to insert highly biodegradable components into the main polymer backbone [6, 25]. Plant natural fibers of high percentage of cellulose are highly biodegradable materials therefore they have the possibility to be used for enhancing the biodegradability of polymer hydrogels. Toshio Yoshimura and his colleagues have synthesized polymer hydrogel from cotton fiber and succinic anhydride without using cross linker via esterification process. This study stated that the hydrogel derived from cotton cellulose is biodegraded almost completely after 25 days in contrast to 10% degrade of conventional sodium polyacrylate hydrogel by using biological oxygen demand (BOD) testing as illustrated in Figure 3. They describe the different in biodegradation of the hydrogels as a result of different networks chemical bonding. Sodium polyacrylate hydrogel has an ether linkage that is more stable and hard to degrade in contrast to ester linkage of cotton hydrogels [41].

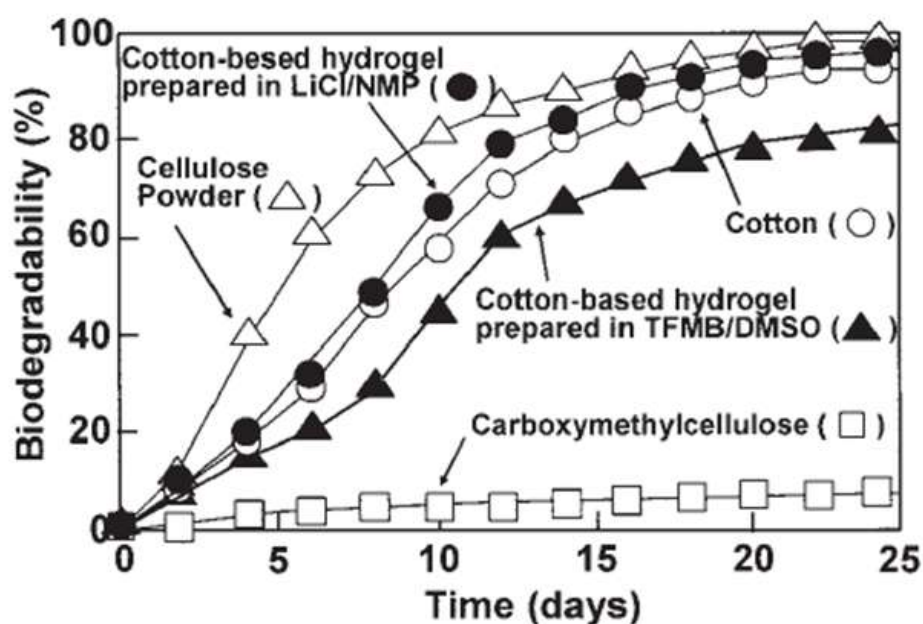


Figure 3: Biodegradability of various materials evaluated at 25 °C

IV. THE EFFECT OF PNFS ON THERMAL STABILITY OF PHGS

Thermal stability is one of the tests that have been used to characterize polymer hydrogel materials and polymer hydrogel composites using thermogravimetric analysis (TGA). Most of the earlier works on thermal stability of PHGC have been done on polymer hydrogel filled with minerals and a very few studies on thermal stability of PHGC based plant natural fibers were conducted. The effect of microfibril of sodium humate (SH) of thermal stability of guar gum-g-polysodium acrylate (GG-g-PNaA) has been studied. The work has reported that SH has positive effect on thermal stability due to the formation of chemical bonds between SH and GG-g-PNaA polymer network [38]. The effect of cotton fiber on thermal stability of poly acrylic acid (PAA) has been investigated by Sunil K. Bajpai using TGA. The result of this work indicated that, cotton fiber has higher thermal stability than PAA-g-cotton fiber. In addition, the work described that biphasic decomposition of grafted fiber in contrast to one phase in plain cellulose fiber [3]. Another study has reported the effect of wheat straw (WS) on thermal stability of PAA and TGA graph shows decreasing in thermal stability of PAA via grafted with WS as shown in Figure 4.

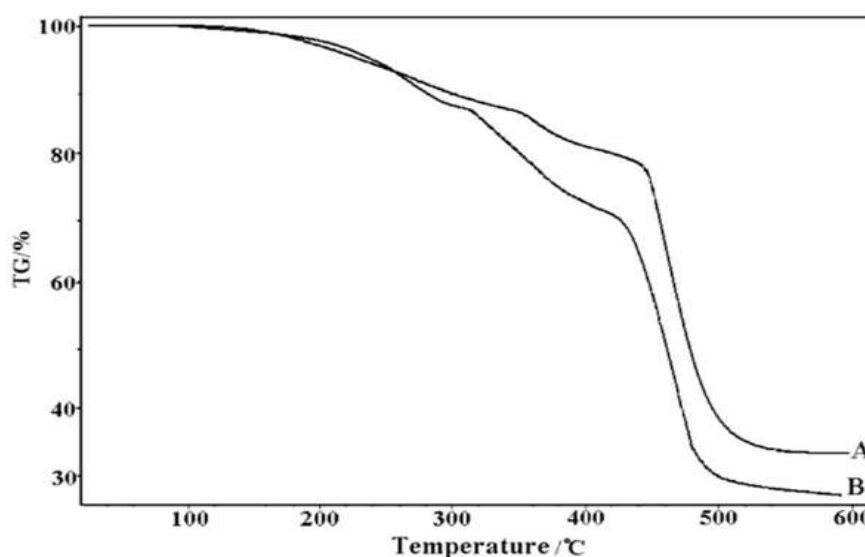


Figure 4: TGA curves of PAA (A) and WS/PAA (B) superabsorbent composite at a heating rate of 10 °C/min

V. THE EFFECT OF PNFS ON MECHANICAL PROPERTIES OF PHGS

Mechanical properties of polymer hydrogels are very important in several applications, such as drug delivery system. Mechanical properties of hydrogels related directly with cross-linking degree, it can be accomplished by changing degree of cross linking of the system. Increasing in cross linking degree leads to more stronger gels, which more brittle structure [30]. Therefore, degree of cross-linking has to be optimized to achieve a relatively strong and yet elastic property hydrogels. Also mechanical properties can be affected via main monomers that used to synthesize PHG which means copolymerization of two type of repeating unit (hydrophilic-hydrophobic) or monomers of different hydrophilicity [19]. Introducing a co-monomer, which can contribute to hydrogen bonding increased hydrogels strength [13]. Mechanical properties can be improved by using Nano filler materials such as, inorganic nanoclay and carbon nanotubes to produce nanocomposites of hydrogels [16, 33]. Till the date, the effects of plant natural fiber of mechanical properties of polymer hydrogel have not been reported. According to our primary result the absorption under load (AUL) of polymer hydrogel was improved in the similar way with swelling rate and absorption capacity via using cotton and oil balm empty fruit fibers.

VI. CONCLUSION

In general, a few studies have been done on polymer hydrogel composite based plant natural fibers, which this is an invitation for the researches to study the effect of plant natural fiber on PHG properties. Plant natural fibers can be used to enhance the properties of polymer hydrogels to replace the mineral and synthesis fibers. This review can be considered an invitation for the researches to focus of using plant natural fiber for improving the main properties of polymer hydrogels mainly in terms of production cost.

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