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An Overview Characterization Techniques for Starch Based Resin

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ABSTRACT: Starch films have been widely used in both food as well as non-food applications. Improvement of mechanical properties of starch-based materials is an ongoing challenge due to its poor mechanical performance, particularly tensile strength. To improve these mechanical properties, various blending and compositing techniques have been developed, such as blending with different biodegradable polyesters or reinforcing with mineral or natural fillers. Different compatibilizers or cross-linking agents have been utilized to improve the interface between starch and other components. However, incorporation of any additive is sensitive, in developing biomaterials or edible packaging films, due to its safety issue or toxic concern.

Starch is the most promising natural polymer because of its inherent biodegradability, overwhelming abundance and annual renewability. Starch-based polymers offer a very attractive low cost base for new biodegradable polymers due to their low material cost and ability to be processed with conventional plastic processing equipment. The development of biodegradable starch-based materials for general applications has been spurred by the oil shortage and the growing interest in easing the environmental burden due to extensive use of petrochemically-derived polymers.

Natural fibers and polysaccharide-based crystals, particularly at nano-scale, have attracted huge attention to optimizing the mechanical properties of starch-based biodegradable composites. It was found that both cellulose nano-crystals and starch nano-crystals can improve tensile strength as well as Young's modulus. Li et al. found that starch-based nanocomposite films filled with cellulose nano-fibrils could increase the creep resistance and reduce the creep recovery rate. Panaitescu et al. showed that starch films filled with 7% cellulose nano-crystals had strength and stiffness close to that of polyolefins, and were regarded as a low-cost "green" substitute for application in food packaging and conservation. Till date, most of these nano-crystals were synthesized in the laboratory and none of them have passed any food-safety regulation criteria of FDA.

KEYWORDS: starch, resin, characterization techniques, biodegradable, polymers, nanocomposite

I. INTRODUCTION

Starch and its derivatives have recently emerged as a sustainable and renewable alternative for petroleum-based expanded polystyrene (EPS) and expanded polypropylene (EPP) foam materials. In this study, biodegradable foam materials were prepared from cassava starch using a novel dual modification technique, combining microwave treatment and freeze-drying. The foam materials were prepared from starch solutions microwaved over different intervals. The starch-based foam materials were characterized using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), ¹³C nuclear magnetic resonance (¹³C-NMR) spectroscopy, and compression set test. Moreover, the water absorption capacities and density values of the foam materials were measured according to ASTM standards. [1,2] The biodegradability test was carried out according to the aerobic compost environment test. The lowest water absorption capacities of 65.56% and 70.83% were exhibited for the cassava starch foam sample (MWB) prepared at a 20 s microwave treatment time and immersed in distilled water for 2 and 24 h, respectively. Furthermore, the lightweight cassava starch-based foam materials displayed density ranging from 124 to 245 kg/m³. The biodegradation test exhibited significant biodegradation of over 50% after 15 days for all the foam materials prepared. These results suggest that the dual-modified cassava starch-based biodegradable foams show potential in sustainable packaging applications by replacing petroleum-based materials. [1,2]

Conventional methods such as casting and forming, injection, extrusion, compression molding, and novel techniques, including hot mold baking and reactive extrusion, have been employed for processing starch-based foam materials. In hot



mold baking, a baking technology is used to develop starch-based foam materials. This process involves placing a dough-like starch material with a high moisture content of 70–80% (w/w) in a heated mold. The steam produced from the moisture of the starch acts as the blowing agent, creating foam inside the mold. In the extrusion process, starch granules are converted into a homogeneous gelatinous solution. Usually, a co-rotating twin-screw extruder machine is used to produce starch foams. The extruded materials show comparable physical properties to commercial plastic foams. Therefore, starch foams are industrially manufactured via extrusion processes. Apart from the above two methods, the explosion puffing method is also employed to produce starch foam materials. The explosion puffing can produce low-density starch-based foam within several seconds, which is similar to the production process of popcorns. However, it is not suited for preparing molded products compared to extrusion processes.

Generally, starch-based foam materials have high water absorption and biodegradability. It has also been reported that mechanical properties such as tensile strength increase with increasing amylose content in starch. Moreover, the properties of starch foam materials are mainly dependent on the starch source. For example, tuber starch-based foam materials show low-density values compared to cereal starch-based foam materials.

To improve the water resistivity and mechanical properties of starch-based foams, other polymers such as cellulose, fiber, and natural rubber latex are incorporated as additives during foam production. Therefore, the physical, mechanical, and thermal properties of starch-based foams significantly depend on the additives added during the production process. Albeit starch foam materials are prepared by varying the amount of additive and extruder parameters, including temperature and moisture, this method possesses several setbacks. The drawbacks of the extruder methods include longer time requirement, high energy consumption, and generation of toxic chemicals. [3,4]

Recently, microwave techniques have been introduced as an alternative heating method during polymer processing, food processing, and nanomaterial synthesis. The application of microwave technology in foaming processes involves three main steps: mixing the material with blowing agents such as water, expanding the material by microwave radiation, and stabilizing the foam structure during drying. The microwave treatment helps reduce the heating time and facilitates homogeneous heating. Usually, microwaved starch-based foams are produced using extruded plasticized starch. For instance, Sjöqvist and Gatenholm, Chanvrier et al. Kraus et al. and López-Gil et al. prepared the starch-based foam materials with extruded thermoplastic starch (TPS) pellets using different conditions and additives, including blowing agents and plasticizers to obtain the optimum conditions.

The freeze-drying technique is used to remove moisture and prepare highly porous materials. During the freeze-drying process, the temperature of the particular solution is maintained at the freezing temperature of water, causing the separation of water from the solutes. The freeze-drying process is widely applied in tissue engineering applications to produce scaffolds and films using starch-based materials. Apart from the above, freeze-drying has been employed to prepare multiwall carbon nanotubes (MWCNTs). [5,6]

The current study presents the preparation and characterization of cassava starch-based foam materials using a combination of microwave radiation and freeze-drying techniques used as a novel approach. During this dual treatment, microwave energy promotes the generation of a significant amount of gelatinized starch quickly, saving time and energy, whereas the freeze-drying process facilitates foam formation. To the best of our knowledge, this is the first attempt to prepare and measure the properties of cassava starch-based foam materials produced using a combined method of microwave radiation and freeze-drying. Herein, we report the density, biodegradability, morphology, chemical, and thermal properties of the dual-modified cassava starch-based foam materials. Moreover, the prepared dual-modified cassava starch-based foam materials show potential in packing applications.

II.DISCUSSION

Native corn starch- and hydroxypropylated starch (HPS-) based plastic films were prepared using the short pulp fiber as the reinforcement and the glycerol as the plasticizer. Starch (or HPS) films showed different X-ray diffraction patterns with the A-type of native corn starch powder. The crystallinity of films increased with pulp content, but decreased with glycerol content and degree of substitution by hydroxypropylation. Also, the intensity of peaks at $2\theta = 15.3$ and 17.3° decreased with glycerol content and degree of substitution. The water uptake of films as a function of the relative humidity decreased with pulp content and degree of substitution by hydroxypropylation, but increased with glycerol content. Differential scanning



calorimetry (DSC) thermograms showed that the glass transition temperature of films decreased and the endothermic peaks at the melting temperature broadened due to the plasticizing effect and the decrease of the crystallinity, which were caused by the addition of glycerol and the hydroxypropylation. [5,6]

In recent years, the development of bioplastic composites from renewable resources has drawn significant attention due to the growing environmental concerns from petroleum-based plastics and the shortage of petroleum resources. Bioplastic composites developed from starch as low-cost and renewable materials have attracted much attention. Starch is one of the most abundant biopolymers in the world, along with chitin and cellulose. Comparatively, starch is the cheapest material for preparing the bioplastics, as compared to other sources, such as protein, chitosan, gelatin, and poly(lactic acid) (PLA). Sugarcane and corn are cultivated for animal feed and food purposes in Malaysia, while the main local sources of starch are cassava. Starch-based bioplastics comprise the largest production capacity (21.3%) in the bioplastic market, while the remaining production is based on PLA, poly(butylene adipate-co-terephthalate) (PBAT), bio-based polyethylene (PE), and others. Pure starch-based bioplastics are very brittle and need the incorporation of plasticizers such as glycerol or polyols to make them easier to handle. However, the application of these bioplastics has been hampered because of their great water sensitivity and low mechanical properties. Lignocellulosic fibers have a promising future as the reinforcements of bioplastic composites on account of their high strength, biodegradability, and low cost. Moreover, the fibers are miscible with starch potentially by forming hydrogen bonds. Though fibers could enhance the performance of starch-based bioplastics to a certain extent, both biopolymers and plasticizers are hydrophilic, resulting in a poor water resistance of the composites. [7,8]

In order to improve these properties, various strategies have been developed, including blending with other biodegradable polymers (e.g., poly(lactic acid) (PLA), polycaprolactone (PCL), and poly(butylene adipate-co-terephthalate) (PBAT)) or lipids (e.g., palmitic acid, stearic acid, beeswax, and plant oils), adding the crosslinking agents (e.g., sodium trimetaphosphate, epichlorohydrin, glutaraldehyde, and various poly(carboxylic acid)s, such as citric acid and 1,2,3,4-butane tetracarboxylic acid), and chemical modification of starch (e.g., esterification with carboxylic acid, acyl chloride and acid anhydride, acetylation with acetic anhydride, and oxidation with hydrogen peroxide).

Epoxidized oils (EOs) represent one of the most commercially important materials because they are cheap and can be produced in large scale. Currently, several studies have been conducted on the incorporation of EOs into biopolymer-based composites, to reduce their moisture sensitivity and enhance their mechanical properties. The addition of EOs could not only provide hydrophobicity to the composites, but also induce possible crosslinking effect with the biopolymers, to form a strong composite network. In addition, EOs can act as reactive plasticizers or compatibilizers to polymers, such as PLA, due to the reactivity of epoxy groups. However, the studies about the application of EO in the starch-based bioplastics are still rare. Epoxidized soybean oil (ESO) is one of the most widely utilized EOs throughout the world. Recently, few studies have applied it to modify the properties of starch-incorporated or -based composites. For example, Xiong, Yang, Feng, Zhang, Zhang, Tang, and Zhu fabricated a composite based on PLA and maleic anhydride grafted starch by melt-compounding with ESO. Furthermore, relevant studies have used ESO as the modifier for thermoplastic starch, by melt reactive blending. ESO has brought about a partial crosslinking of the epoxide ring with hydroxyl groups of starch. The tensile strength increased by 300% with the addition of 3 wt% ESO [11,12]

Palm oil is the cheapest and most abundant commodity oil in Malaysia. Developing new products from palm oil, such as epoxidized palm oil (EPO), has attracted considerable interest. EPO has been used as an additive in plastic, a starting material to make polyol, and a pre-polymer in surface coating. ESO has been established as a component in industrial production successfully, while EPO has just been developed as a potential modifier recently. Oxirane oxygen contents of EOs determine the number of reaction points and are suggested to be the key factor which affects the reaction efficiency of EOs and their performance in the composites. ESO shows higher oxirane oxygen percent and, thus, a greater possibility of reactions, as compared to EPO. Therefore, it is meaningful to compare the effect of EPO on the properties of biopolymer-based bioplastic composites with ESO and represent EPO as an alternative constituent for bioplastic composites. [9,10]



In palm oil plant, after the palm fruits have been detached for palm oil extraction, the rest is called oil-palm empty-fruit-bunch (EFB) fibers. EFB fibers are the most abundant wastes in Malaysia. They are a form of fibrous lignocellulosic residues and composed of cellulose, hemicellulose, and lignin. EFB fibers have a considerable potential as reinforcing fibers [29]. Therefore, to create a new market for the palm oil industry, it attracts great interest to investigate the effect of EPO on the properties of starch/EFB-based bioplastics.

Only few a research studies have been carried out on biopolymers, fillers, and oil modifiers blended composites. Tanrattanakul and Saithai prepared bioplastic-organoclay nanocomposites with ESO of different epoxide contents. Balart et al. processed the composites with PLA and hazelnut-shell flour plasticized by epoxidized linseed oil. Meng et al. compounded cellulose nanofibrils and ESO into PLA, to achieve high strength and toughness. In general terms, most of the studies were linked to PLA-based bio-composites. The interactions of EO and biopolymers/fillers led to the enhanced properties of the composites. However, as far as we know, no former study has proposed EO to modify starch/EFB-based composites.[15,16]

III.RESULTS

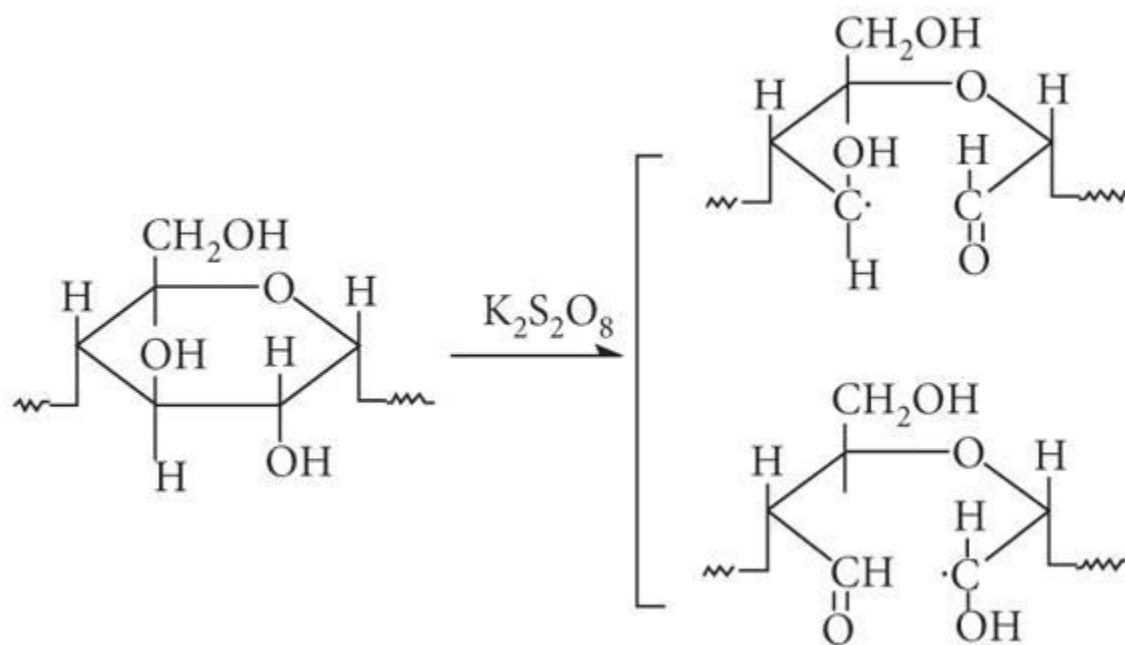
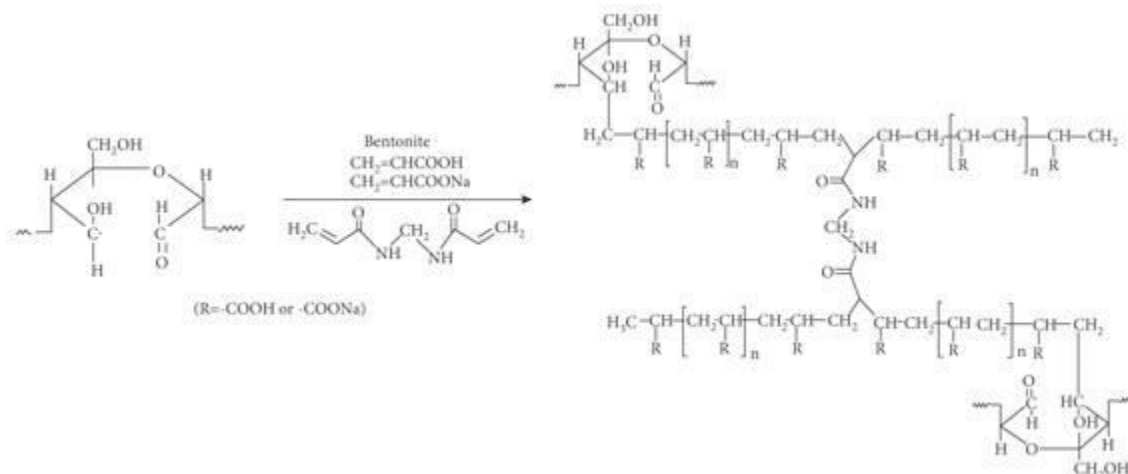
A superabsorbent resin (SAR) is a recently developed functional polymer material with strong hydrophilic groups, such as carboxyl and hydroxyl groups. It is soluble in neither inorganic nor organic solvents and has a specific crosslinking degree (CD) and network structure [2]. SARs have a good adsorption performance, water retention capacity, pressure resistance, and heat resistance and have been used widely used in agriculture, forestry, and horticulture, industry, health supplies, and other fields.

However, most traditional water absorbent resins have poor degradability and are expensive. To solve these problems, naturally available resources, such as polysaccharides and inorganic clay mineral, have been used recently as raw materials because of their renewability, biodegradability, and low cost. Introducing cheap mineral clay to modify SARs and synthesize composite SARs has become an important development direction. Kaolin, bentonite, attapulgite, and many other clays have been used to synthesize SARs. Besides, starch is an extremely abundant natural resource and is used widely to synthesize SARs.[17,18]

Traditionally, aqueous solution polymerization is commonly used to synthesize SARs, in which nitrogen and argon are essential to remove oxygen, and AA is purified before polymerization. Overall, these processes increase the complexity and cost of SAR synthesis. In this study, a novel SAR was investigated, which was based on potato starch, bentonite, and AA, with $K_2S_2O_8$ (potassium persulfate) as the initiator and N, N'-methylene-bis-acrylamide (MBA) as the cross-linker. The modified method has no nitrogen protection during the polymerization process, with raw AA and potato starch being used directly. Also, the optimal ratio of raw materials and main influences of the reaction conditions for the composite SAR were investigated, and its structure and properties were evaluated.

The composite SAR was synthesized using a free radical polymerization reaction. Firstly, after being heated with the starch, $K_2S_2O_8$ initiates starch to produce free radicals. Secondly, the free radicals initiate AA polymerization and form starch-acrylic free radicals, which continue to polymerize with AA and cause chain propagation, and then a mesh macromolecule is formed by the crosslinking action of MBA.[13,14]

With the increasing degree of neutralization of AA, the ionization of carboxyl groups in the polymer chain increases, resulting in an increase of repulsion, the network structure of the polymer product, and osmotic pressure; therefore, the water absorption of the SAR increases. However, when acrylic neutralization exceeds 50%, an excess of -COONa in the SAR results in an increase in water solubility of the resin, thereby decreasing the water absorption capacity of the resin [7,8]



IV. CONCLUSIONS

A novel composite SAR was synthesized by aqueous solution polymerization using potato starch, bentonite, and AA as raw materials. The optimum synthetic mass ratios of starch, bentonite, potassium persulfate ($K_2S_2O_8$), and N, N'-methylene-bisacrylamide to acrylic acid (AA) were 7.14%, 3.57%, 0.29%, and 0.057%, respectively, and the neutralization degree of AA was 50%. The SAR had a water absorbency of 1300 mL/g in distilled water. The results showed that the SAR synthesized using the modified method showed good water absorption, water retention, and moisturizing properties. The modified SAR synthetic method is characterized by a lack of nitrogen protection, the direct use of raw AA and potato starch, a simplified



synthesis process, substantially increased efficiency, and lower production costs. The FTIR and SEM results showed that potato starch, AA, and bentonite were graft polymerized well, and the ions in solution could affect the expansion of the network structure of the SAR. In the related literature, the humidity of the experimental environment is not considered when determining the water retention rate of the resin. [19,20]

REFERENCES

1. Y. Wang, C. Wang, Y. Zhao, and P. Wang, "Effects of a superabsorbent resin with boron on bacterial diversity of peat substrate and maize straw," *BioMed Research International*, vol. 2018, 2018.
View at: [Publisher Site](#) | [Google Scholar](#)
2. W. Kong, Q. Li, J. Liu et al., "Adsorption behavior and mechanism of heavy metal ions by chicken feather protein-based semi-interpenetrating polymer networks super absorbent resin," *RSC Advances*, vol. 6, no. 86, pp. 83234–83243, 2016.
View at: [Publisher Site](#) | [Google Scholar](#)
3. L. Li, H. Zhang, X. Zhou, M. Chen, L. Lu, and X. Cheng, "Effects of super absorbent polymer on scouring resistance and water retention performance of soil for growing plants in ecological concrete," *Ecological Engineering*, vol. 138, pp. 237–247, 2019.
View at: [Publisher Site](#) | [Google Scholar](#)
4. Y. Yang, J. Wu, S. Zhao et al., "Effects of long-term super absorbent polymer and organic manure on soil structure and organic carbon distribution in different soil layers," *Soil and Tillage Research*, vol. 206, Article ID 104781, 2021.
View at: [Publisher Site](#) | [Google Scholar](#)
5. D. Shen, J. Jiang, M. Zhang, P. Yao, and G. Jiang, "Tensile creep and cracking potential of high performance concrete internally cured with super absorbent polymers at early age," *Construction and Building Materials*, vol. 165, pp. 451–461, 2018.
View at: [Publisher Site](#) | [Google Scholar](#)
6. J. Yang, Y. Guo, A. Shen, Z. Chen, X. Qin, and M. Zhao, "Research on drying shrinkage deformation and cracking risk of pavement concrete internally cured by SAPs," *Construction and Building Materials*, vol. 227, Article ID 116705, 2019.
View at: [Publisher Site](#) | [Google Scholar](#)
7. Z. Jin, H. Chang, F. Du, T. Zhao, Y. Jiang, and Y. Chen, "Influence of SAP on the chloride penetration and corrosion behavior of steel bar in concrete," *Corrosion Science*, vol. 171, Article ID 108714, 2020.
View at: [Publisher Site](#) | [Google Scholar](#)
8. N. Peng, Y. Wang, Q. Ye et al., "Biocompatible cellulose-based superabsorbent hydrogels with antimicrobial activity," *Carbohydrate Polymers*, vol. 137, pp. 59–64, 2016.
View at: [Publisher Site](#) | [Google Scholar](#)
9. Y. Tang, X. Wang, and L. Zhu, "Removal of methyl orange from aqueous solutions with poly(acrylic acid-co-acrylamide) superabsorbent resin," *Polymer Bulletin*, vol. 70, no. 3, pp. 905–918, 2013.
View at: [Publisher Site](#) | [Google Scholar](#)
10. L. Li, Z. Lin, L. Yu, W. Li, and G. Yang, "Self-assembling solid-state hydrogen source for drylands photocatalytic hydrogen production," *Journal of Materials Chemistry*, vol. 4, no. 41, pp. 15920–15928, 2016.
View at: [Publisher Site](#) | [Google Scholar](#)
11. A. Roshani, M. Fall, and K. Kennedy, "Impact of drying on geo-environmental properties of mature fine tailings pre-dewatered with super absorbent polymer," *International journal of Environmental Science and Technology*, vol. 14, no. 3, pp. 453–462, 2016.
View at: [Publisher Site](#) | [Google Scholar](#)
12. J. Geng, M. Chen, T. Shang, X. Li, Y. R. Kim, and D. Kuang, "The performance of super absorbent polymer (SAP) water-retaining asphalt mixture," *Materials*, vol. 12, no. 12, p. 1964, 2019.
View at: [Publisher Site](#) | [Google Scholar](#)
13. I. Anastopoulos, J. V. Milojković, K. Tsigkou et al., "A nappies management by-product for the treatment of uranium-contaminated waters," *Journal of Hazardous Materials*, vol. 404, Article ID 124147, 2021.
View at: [Publisher Site](#) | [Google Scholar](#)
14. T. Zou, T. Xu, H. Cui et al., "Super absorbent polymer as support for shape-stabilized composite phase change material containing $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ - $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ eutectic hydrated salt," *Solar Energy Materials and Solar Cells*, vol. 231, Article ID 111334, 2021.
View at: [Publisher Site](#) | [Google Scholar](#)



15. J. Xi and P. Zhang, "Application of super absorbent polymer in the Research of water-retaining and slow-release fertilizer," IOP Conference Series: Earth and Environmental Science, vol. 651, no. 4, Article ID 042066, 2021.
View at: [Publisher Site](#) | [Google Scholar](#)
16. Z. Ma, Q. Li, Q. Yue, B. Gao, X. Xu, and Q. Zhong, "Synthesis and characterization of a novel super-absorbent based on wheat straw," Bioresource Technology, vol. 102, no. 3, pp. 2853–2858, 2011.
View at: [Publisher Site](#) | [Google Scholar](#)
17. Y. Zhuo, J. Liu, F. Yang, Q. Li, and G. Xing, "Preparation and characterization of PVA/P(AA-AM) super absorbent polymer," Integrated Ferroelectrics, vol. 179, no. 1, pp. 166–172, 2017.
View at: [Publisher Site](#) | [Google Scholar](#)
18. R. J. Wang, L. W. Yang, H. D. Zhang, and T. J. Geng, "Synthesis of super absorbent resin from starch/bentonite," Advanced Materials Research, vol. 873, pp. 708–712, 2013.
View at: [Publisher Site](#) | [Google Scholar](#)
19. G. Lan, M. Zhang, Y. Liu et al., "Synthesis and swelling behavior of super-absorbent soluble starch-g -poly(AM-co -NaAMC₁₄ S) through graft copolymerization and hydrolysis," Starch - Stärke, vol. 71, Article ID 1800272, 2019.
View at: [Publisher Site](#) | [Google Scholar](#)
20. Y. Chen, Y.-f. Liu, H.-m. Tan, and J.-x. Jiang, "Synthesis and characterization of a novel superabsorbent polymer of N,O-carboxymethyl chitosan graft copolymerized with vinyl monomers," Carbohydrate Polymers, vol. 75, no. 2, pp. 287–292, 2009.
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