Manufacturing Process of a Novel Biomass Composite Inspired from Cellular Structure of Wood

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Abstract—A novel biomass composite inspired from wood porous structure was manufactured by impregnating vinyl monomer into wood cellular structure under vacuum conditions, and initiating the monomer for in situ polymerization through a thermal treatment. The vacuum condition was studied, and the mechanical properties of the composite were also tested. SEM observation shows that polymer generated in the wood porous structure, and strongly interacted with wood matrix; and the polymer content increased with vacuum value increasing. FTIR indicates that polymer grafted onto wood matrix, resulting chemical complex between them. The rate of monomer loading increased with increasing vacuum value and time, accordance with rate of polymer loading. The compression strength and modulus of elasticity linearly increased with the increasing rate of polymer loading. Results indicate that the novel biomass composite possesses good mechanical properties capable of applying in the fields of construction, traffic and so forth.

Keywords—Biomass composite, manufacture, vinyl monomer, wood cellular structure.

I. INTRODUCTION

ONE direction of new composite manufacture is focusing On bionic fabrication inspiring from the special structure of natural bioresource [1]. Wood as a natural material of biological origin has been an essential material for human survival, which can be used for shelter, tool, fuel, furniture and so on, because of its special structure, renewability and almost universal availability [2]. Wood possesses a special structure featuring porous structure consisting of various cell walls, which are mainly composed of biopolymers, i.e., carbohydrate polymers of cellulose and hemicelluloses and phenolic polymers of lignin. The special cellular structure of wood endows it with high strength-to-weight ratio, so that wood often

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has good mechanical properties. However, wood is easy to be degraded by organisms and vulnerable to be deformed by water, which limit its value-added applications [3]. So the authors put forward a new thought inspired from the cellular structure of wood to generate a novel biomass composite by thermoforming polymer from vinyl monomers in wood porous structure. The resultant composite, called wood-polymer composite, both having the advantages of wood and polymer, may be a promising novel composite capable of being widely used in fields of construction, traffic and sport, as well as weapons.

The key of successfully manufacturing the novel composite with good performance mainly focused on the content of in situ generated polymer loading in wood cellular structure. So this study discussed the main factors of influencing the manufacturing process of the novel composite, and characterized the compounding style of wood and the resultant polymer with SEM and FTIR. Finally, the method was further verified by testing some mechanical properties of the composite.

II. MATERIAL AND METHODS

A. Material

Analytical grade methyl methacrylate (MMA), was obtained from Nanjing Jiulong Chemical Industry, Co., Ltd. which was cleaned with sodium hydroxide, followed by a drying procedure with anhydrous CaCl₂, and then distilled under a vacuum pressure for further purification before use. AIBN is recrystallized before use. Wood samples selected for this study are cut from Poplar panels, named Populus ussuriensis Kom. The impregnating equipment is self-made.

B. Methods

MMA and AIBN as an initiator were mixed for first. AIBN accounts for 1% of weight of MMA. Then, the wood samples in different sizes were immerged in the mixed solution under different vacuum conditions for different time. After the impregnated samples wrapped in aluminum foils, they were further heated to 80 for 8h. The wood-polymer composites were eventually obtained through the above procedure.

C. Analytical Techniques

ESEM was used to observe the degree of polymer loading

filling in the cellular structure, and the compounding style of polymer and wood matrix. FTIR was used to analyze the reaction mechanism of the vinyl monomer and wood matrix. The samples for FTIR analysis were made by grounding solid samples into powders with a disintegrator and passing a 100-mesh screen, followed by extracting with acetone for 24 hrs, and toluene for 24 hrs, and then subsequently drying to constant weight.

D. Performance Evaluations

Compression strength and modulus of elasticity for each sample were tested. And the relationships between rate of monomer loading in wood and impregnating craft, as well as rate of polymer loading and some mechanical properties (compression strength and modulus of elasticity) were analyzed, respectively. Rate of monomer loading is calculated according to the following equation 1:

$$R_m = \frac{G_i - G_0}{G_0} \times 100\%$$
 (1)

Where: R_m represents rate of monomer loading; G_i represents weight of impregnated samples after immersing in monomers under vacuum condition; G_0 represents weight of samples before any treatment.

Rate of polymer loading is calculated according to the following equation 2:

$$R_{p} = \frac{P_{i} - P_{0}}{P_{0}} \times 100\%$$
⁽²⁾

Where: R_p represents rate of polymer loading; P_i represents weight of resultant wood-polymer composite; P_0 represents weight of wood samples before any treatment.

III. RESULTS AND DISCUSSION

A. Analysis of Factors Influencing Impregnation Craft

As we know, under a certain heating craft, the more monomer loading, the higher polymer loading, as well as higher performance. So, the study tested each rate of monomer loading under different vacuum and time. The results were shown in Fig.1. As a whole, under same vacuum, the rate of monomer loading increased with vacuum time; and under same vacuum time, rate of polymer loading increased with the increasing of vacuum value. For each vacuum, the relationship of rate of monomer loading and time was described by data fitting shown in Fig.1. There's a linear positive correlation between rate of monomer loading and vacuum time for each -0.01MPa, -0.02MPa, -0.03MPa, and -0.04MPa, respectively y=2.188x+4.809. described by y=1.72x+2.333, y=2.765x+5.761, y=3.382x+7.047; while there's a quadratic equation for each -0.05MPa and -0.06MPa, respectively described $y=-0.0008x^{4}+0.052x^{3}-1.31x^{2}+17.0643x+0.0714,y=-0.0006x^{4}+$ $0.0384x^{3}-0.9169x^{2}+12.9656x+0.1151$. The adopted optimum impregnation craft is vacuum value of -0.06MPa, and time of 25min.



Fig. 1 Relationship of rate of monomer loading and impregnating crafts

B. Characterization for Microstructure of Composite with SEM



(a) 500×Untreated Wood
(b) 500×PMMA-Wood Composite (vacuum of -0.02MPa)
(c) 500×PMMA-Wood Composite (vacuum of -0.04MPa)
(d) 500×PMMA-Wood Composite (vacuum of -0.06MPa)
Fig. 2 SEM morphologies of untreated wood and wood-polymer composite with different preparing conditions

Fig.2 shows SEM morphologies of untreated wood and PMMA-Wood Composite prepared under different vacuums for same time of 25min. From Fig.2a, it can be known that untreated wood possesses a porous structure with different-size pores, and the interspace is called wood cell lumen, and the matrix is called wood cell walls; while from Fig.2b, it can be clearly shown that some solid polymer filled in small wood porous structure (i.e. wood cell lumen), and the big wood cell lumens are still empty, indicating lower content of polymer loading in wood cellular structure under the vacuum of -0.02MPa for 25min. Fig.2c clearly show that lots of polymer filled in wood cell lumens, although some big interspaces were empty, indicating good polymer loading under the impregnating

condition with vacuum of -0.04MPa for 25min. Fig.2d illustrates that under vacuum of -0.06MPa for 25min, the resultant polymer fully filled in wood porous structure, indicating largest polymer loading and optimum vacuum condition among the above impregnating conditions. Furthermore, from Fig.2b,c,d, it can be also observed that polymer strongly interacted with wood matrix for no obvious gaps being observed between them, despite of content of polymer loading, indicating strong interaction between them generated.

C. Analysis of reaction mechanism with FTIR



Fig. 3 FTIR Spectrum of untreated wood and PMMA-Wood Composite (vacuum of -0.06MPa)

Fig.3 shows that compared with untreated wood, there was an obvious new peak for carbonyl group appearing at 1732cm⁻¹ in PMMA-Wood composite, indicating polymer containing carbonyl groups grafted onto wood matrix, thus a chemical complex generated between wood matrix and polymer, agreement with the results of strong interaction between them from SEM observation in Fig.2d. And the band intensity of peak at 3429cm⁻¹ was lower than that of untreated wood, which indicates that amount of hydroxyl groups reduced in PMMA-Wood composite. These can be attributed to vinyl monomer, MMA, both bearing an ester group and an unsaturated carbon-carbon double bond, reacted with hydroxyl groups on wood matrix by its ester group, when it polymerizing into polymer, PMMA, through free radical polymerization. Consequently, amount of hydroxyl groups reduced, resulting lower band intensity of peak at 3429cm⁻¹ in PMMA-Wood composite; and PMMA grafted onto wood matrix, resulting chemical compounding between polymer and wood matrix. The reaction mechanism can be described according to the following scheme 1:



D. Mechanical Properties of the Biomass Composite

Fig.4 shows the variable trend of compression strength according to rate of polymer loading, as well as variable trend of modulus of elasticity according to rate of polymer loading, respectively. For compression strength, it can be described by a function, y=0.456x+51.86, where x represents rate of polymer loading. It indicates that there is a linear positive correlation between compression strength and rate of polymer loading, and compression strength increases to about 80MPa when rate of polymer loading is 59%. The variable trend for modulus of elasticity is similar to that of compression strength. The function for modulus of elasticity can be described by y=62.35x+4192, where x represents rate of polymer loading. When rate of polymer loading reached to 59%, modulus of elasticity approached 7989MPa.

In conclusion, both compression strength and modulus of elasticity linearly increased with rate of polymer loading.



Fig. 4 Relationship of mechanical properties and rate of polymer loading

IV. CONCLUSION

1) Vinyl monomer can be quickly immersed into wood porous structure under a vacuum condition. Rate of monomer loading in wood respectively increased with the increasing of vacuum value and vacuum time. The optimum impregnating craft among the adopted conditions is vacuum value of -0.06MPa and vacuum time of 25min.

2) Vinyl monomer can be in situ polymerized into polymer through a thermal process, which chemical grafted onto wood matrix, resulting chemical complex between polymer and wood matrix with strong interaction.

3) Both compression strength and modulus of elasticity linearly increased with rate of polymer loading. And compression strength and modulus of elasticity reached 79.3MPa and 7989MPa, respectively, when rate of polymer loading was 59%, which represented the biomass composite possessing high mechanical properties capable of applying in fields of construction and traffic etc.

4) The method by impregnating vinyl monomer into wood cellular structure and initiating them for in situ polymerization through a thermal process seems to be a promising way for manufacturing a novel biomass composite with good mechanical properties.

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