Green Composites:
Challenges to reach high performance components

S. Lloret Pertegás[1*], A. Anusic[2], K. Resch[2], R. Schledjewski[(1,3)]

[1]Christian Doppler Laboratory for High Efficient Composite Processing, Department Polymer Engineering and Science, Montanuniversitaet Leoben, Otto Gloeckel-Strasse 2, A-8700 Leoben,
Email: silvia.lloret-pertegas@unileoben.ac.at, Web Page: http://www.kunststofftechnik.at/lvv-cdl-en/
[2]Chair of Materials Science and Testing of Polymers, Department Polymer Engineering and Science, Montanuniversitaet Leoben, Otto Gloeckel-Strasse 2, A-8700 Leoben, Austria
Email: katharina.resch@unileoben.ac.at, Web Page: http://www.kunststofftechnik.at/
[3]Chair of processing of composites, Department Polymer Engineering and Science, Montanuniversitaet Leoben, Otto Gloeckel-Strasse 2, A-8700 Leoben,
Email: Ralf.Schledjewski@unileoben.ac.at, Web Page: http://www.kunststofftechnik.at/composites/

Keywords: Bio-based thermoset resins, natural fibers, press moulding

Abstract

Due to the limitation of fossil resources interest in bio-based composite materials is rising [1]. Besides the wide selection of thermoplastic polymers made of renewable resources, also some potential thermoset resin systems are available [2]. Regarding reinforcing materials a wide variety of different natural fibers are available. In frame of the Green2Green-project (Green Composites for Green Technologies) a 100% bio-based composite component is aimed. In the present paper challenge in green composite manufacturing methods will be presented. Beside the use of a newly developed epoxy resin based on hempseed oil and other bio-based thermoset resin systems in combination with hemp fibers the use of a vacuum chamber when press molding and the effect of using aligned fibers are studied. The major focus is on processability and reaching void free composite components. Process-structure-property relationship is analyzed and the final performance of the bio-based composite materials is compared with conventional systems, i.e. epoxy-glass fiber.

1. Introduction

Nowadays natural fibers from different renewable resources have increased its interest not only due to properties such as biodegradability, availability, flexibility or easy processing but also because of their promising mechanical properties. Bio based materials are finding their applications in different fields as automotive industry or construction, reducing structural weight and manufacturing costs. Natural fibers have been frequently used as the reinforcement component in polymers. In this study the processing of bio renewable natural fibers and different strategies to prepare fully green polymer composites is studied. The aim is to find an eco-friendly product that can compete and be a feasible alternative to glass fibre composite based on petroleum feedstock.

Manufacturing fully green thermoset resins is still a challenging topic, due to the fact that the final mechanical properties of the composite will depend on the plant harvesting and the hemp oil manufacturing. The reason is that all the natural reinforcing fibers are lingno-cellu-losic and the content of cellulose and lignin vary from one biofiber to another [3].

Excerpt from ISBN 978-3-00-053387-7

Our research, has the purpose of find an innovative approach to develope components for the Green Energy like a small wind turbine consequently produced from Green Composites (Green2Green). Following points will be needed to achieve the objective of the project:

- Synthesis, characterization and evaluation of suitable hemp oil-based resins and curing agent.
- Preparation of various technical fabrics of hemp yarn.
- Processing, characterization, and evaluation of different samples of green composites from hemp oil-based thermosets and technical hemp fabrics.
- Testing of the green composites. (This topic, will not be discuss in this study)

1.2. Natural fibers used as reinforcement

In last decades typical fibers like glass or carbon have been replaced by fibers such as flax, hemp, kenaf, sisal or jute. The advantages of using these fibers are low cost, low density, biodegradability and acceptable mechanical properties (strength and stiffness) [4]. Natural fibers classification is based on their origin (Fig. 1), according to the research from Biaggioti et. al. In this study we are focus on bast fibres, hemp in particular.

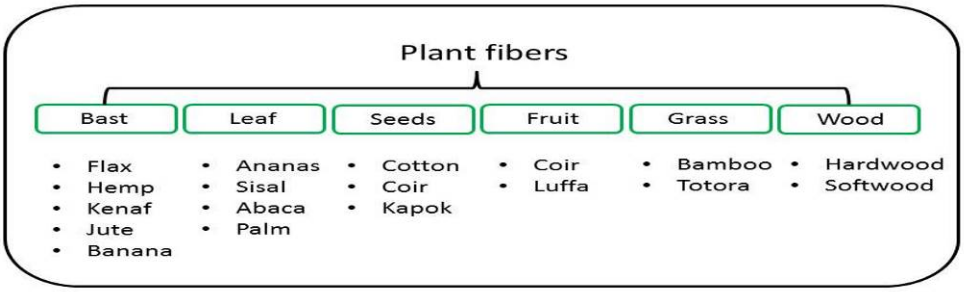

Figure 1: Schema of the natural fibre classification [5]

1.3. Matrix

High performance of the epoxidized hemp oil is still a challenge it lies in the fact that they should be stable during storage and usage. This is still an ongoing work. Different epoxidation methods have been studied before, also different feedstocks were used specially soy bean oil. In Fig. 2. the hemp oil epoxidation route is shown.

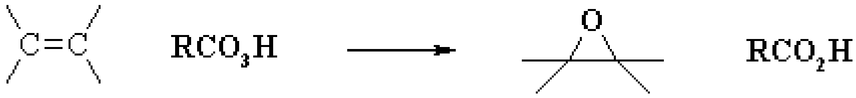

Figure 2: Mechanism of epoxidation using peracidic method

However the principal product for the resin production is the oil used as a renewal source, we should always keep in mind that for the production of the epoxy resins not only the oil is used, also curing agents and in some cases catalyst are employed.

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For comparaison reasons "green" resins commercially available i.e. GREENPOXY 56 (Sicomin Epoxy Systems), SUPER SAP® CPM (Entropy Resins Inc.), and a standard epoxy resin system EPIKOTE™ RIMR 135 (Hexion Inc.) were used in order to find suitable parameter, which accomplish the requirements for the industrial production.

2. Experimental Work

The epoxidized hemp oil is mixed with a hardener with a specific mixing ratio which needs to be maintained to ensure optimum hardening. Often, also a catalyst/accelerator is necessary to allow for a reaction of resin and hardening agent. Despite the aim of the study is manufacture a green composite we have to keep in mind the fact that we have to deal with the harmfulness of the curing agent and sometimes the toxicity of the catalysts.

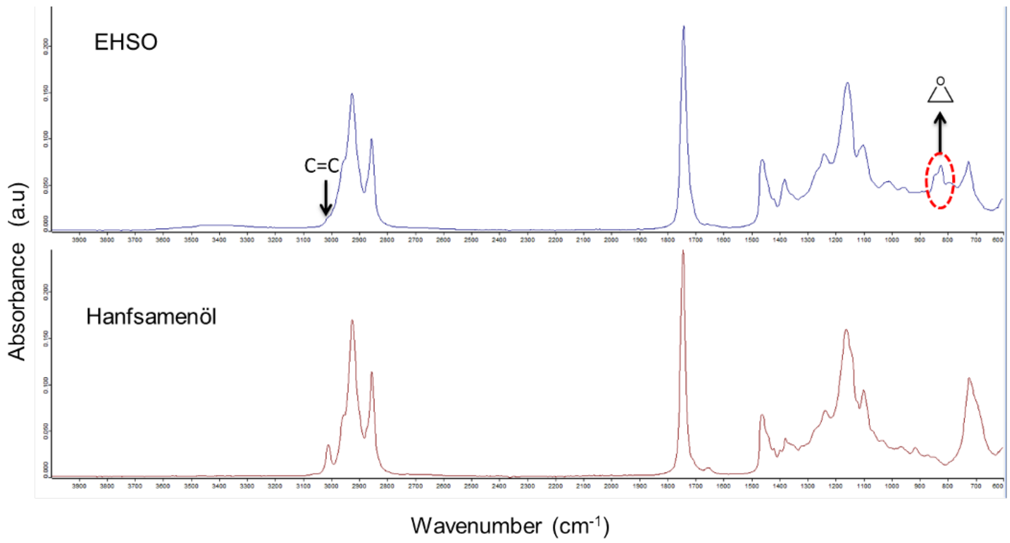

Figure 3: FTIR spectrum of the Hemp seed oil and epoxidized Hemp seed oil (control sample before distillation)

The hemp seeds which are cultivated in the Lower Austria region was cold pressed and used without further distillation. The epoxidation was carried out in a 5 L laboratory reactor and for that hemp seed oil was charged initially into the reactor. The ion exchange resins in the form of small beads were added to the hempseed oil and then the reactor was heated to 55 °C. The acetic acid was added next and stirred well with the above mixture. Finally hydrogen peroxide was added to the mixture in the interval of every 30 min and the whole epoxidation reaction was carried out at the temperature between 65-75 °C for the duration of 3-6 hrs. The change in chemical structure was characterized using FTIR. The conversion of double bonds in the fatty acid chains to an oxirane ring (epoxy) was first confirmed in the FTIR before purification (Fig. 3). The ion-exchange catalyst (beads) was removed through filtration and the whole mixture was neutralized using bicarbonate. The water molecules were separated from the oil through gravity and once if it is undisturbed then water gets deposited on bottom.

Different processing methods such as vacuum infusion and compression moulding were used for prosessing composite samples. Manufacturing set up is shown in Fig. 4, and manufactured plate using hemp fiber and epoxidized hemp seed oil are shown in Fig. 5.

A comparison from the point of view of manufacturing was done, with the different resins mentioned above.

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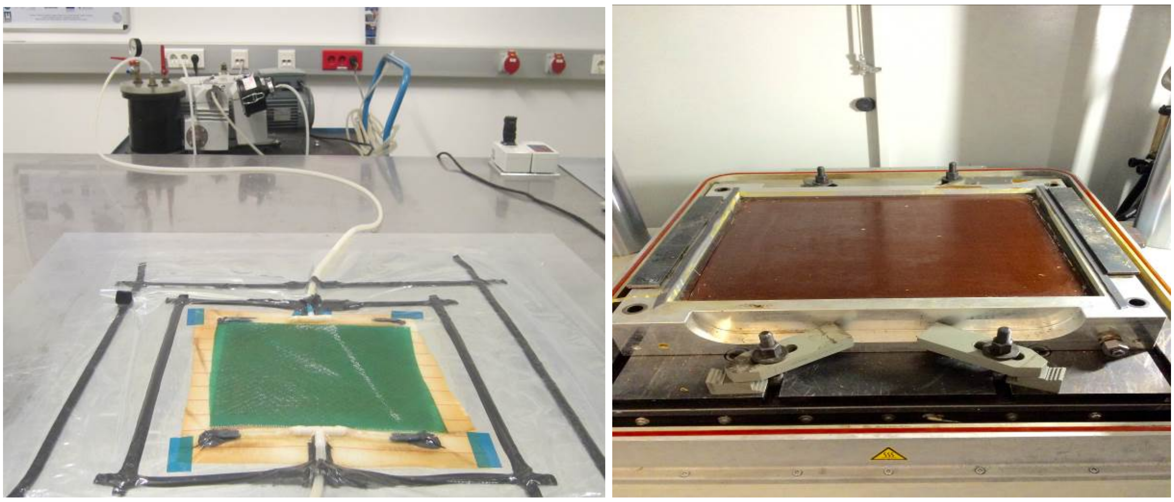

Figure 4: Vacuum Infusion and Press Moulding set up

Figure 5: Manufactured plate by Pressing Moulding

3.Challenges in manufacturing

Generally, epoxidized vegetable oils are used in the plastics industry as plasticizers. As previously mentioned not only natural products are used for the resin procution, we should keep in mind that curing agent and sometimes catalyst is request. Usually ratio 1:1 is needed to achieve a value of 100% of curing degree. Unfortunately, anhydrides are not generally bio-based and they are often are harmful, not only for humans, also for the environment. And in this case, the use of catalysts is essential. After an extensive research of catalyst which fulfill the requirements of the project, imidazole showed good mechanical properties, but is classified toxic and was therefore discarded for the production of a green resin. Therefore, other options had to be taken into account.

Summarizing, the problem of using anhydrides for obtaining epoxy resins is based on three basic aspects: First, the limited availability of biological products, second harmfulness of anhydrides and finally the toxicity catalysts when required.

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4. Results

In order to do our system as green as possible, Tetrahydro-4-methylphthalic anhydride and 2-Ethylimidazole (mixing ration 100:100:4) were chosen as curing agent and catalyst, respectively. With the aim to find the right parameters for the procedure, thermal characterization was studied and the parameter influence is analyzed by DMA (Dynamic mechanical analysis) curves. In Fig. 6 is shown the E-Modulus determined by DMA measurment. It can be seen that the glass transition temperature increases with increasing postcure time and temperature, which usually leads to better mechanical properties. The storage modulus also increases proportionally and simultaneously, the loss modulus, decreases. In addition, it can be observed in Fig. 7 that by increasing the curing time from 24h to 48h the glass temperature not rises significantly and thus the cure can be reduced from 48h to 24h.

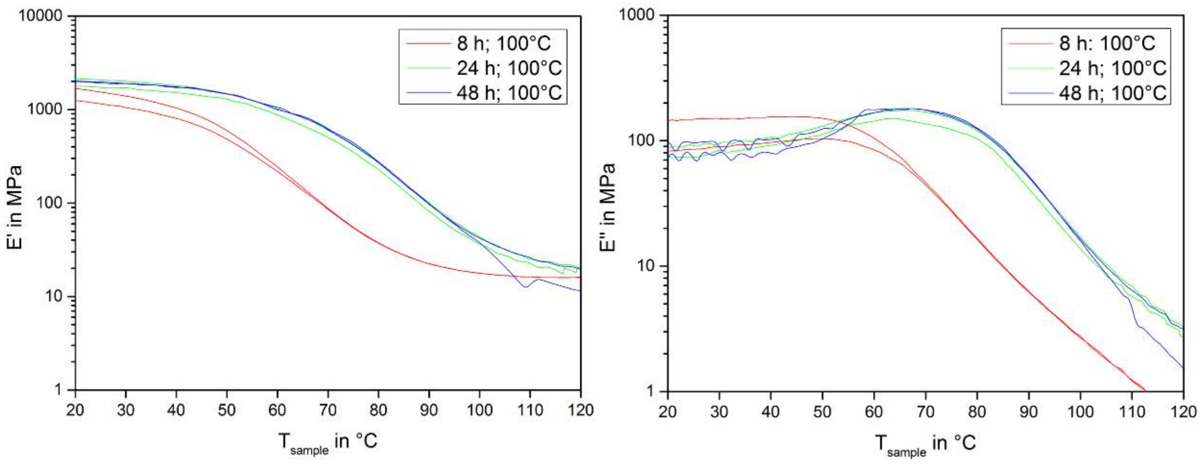

Figure 6: Storage modulus and loss modulus determined by DMA

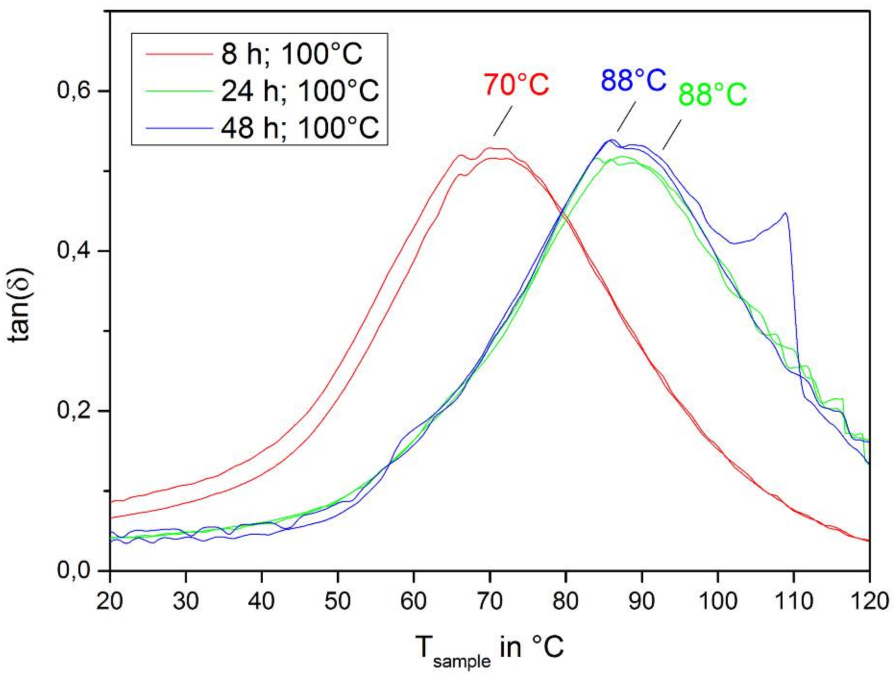

Figure 7: Loss Tangent determined by DMA

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5. Conclusions

The most important limitation in the manufacturing of the bio-composites is the thermoset resin system production due to several issues related to the harvesting of the hempseeds, harmful curing agent, the commercial availability, and toxicity of the catalyst. Bio composites are not only used in the automotive field only, also they are gaining interest in the application of green energies. They are an interesting alternative to replace conventional composites, and we can expect in the future that the interest in such materials will increase. Technological advantages of composites from classical synthetic fibers and polymers are undisputed, however, are the production, processing and above all disposal from the viewpoint of environmental problematic classified. In this study it was find out that the system should be improved. Compared with the new system the other commercially available products and the standard resin EPIKOTE™ have lower T_g and shorter curing cycles. Extremely long curing time around 64h and 2 steps curing cycle are the most important disadvantage of our system not being comparable with other systems already available in the market.

Acknowledgments

Hemp seed oil was generously given by Waldland Naturstoffe GmbH and epoxidized by Kompetenzzentrum Holz GmbH. A major part of the work presented was financially supported by the Austrian Ministry for Transport, Innovation and Technology in frame of the program “Produktion der Zukunft” under contract no. 848668, project “Green Composites for Green Technologies”.

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