

BIOCOMPOSITES FROM CANOLA OIL BASED RESINS AND HEMP AND FLAX FIBERS

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ABSTRACT

Canola oil (CO) was modified through a number of chemical pathways to yield a variety of monomers namely, Acrylated Epoxidized CO (AECO), Maleinized Acrylated Epoxidized CO (MAECO), Maleinated Hydroxylated CO, and Maleinated CO Monoglyceride. Two of these, namely AECO and MAECO, were evaluated for their potential as a matrix for manufacturing thermoset hemp and flax fiber composites using VARTM (Vacuum Assisted Resin Transfer Molding). The monomers were polymerized and cross-linked with styrene as the co-monomer. Needle punched hemp and flax mats were manufactured and used in manufacturing biocomposites. Results of cure optimization, manufacturing, and property characterization, for both canola oil based resins and their biocomposites, are presented and discussed in this paper.

KEYWORDS: Modified Canola Oil, Biocomposites, Natural Fiber, Hemp, Flax, Renewable, Biopolymer, Composites

1. INTRODUCTION

The environmental concerns, including dwindling crude oil resources, high oil prices, pollution, greenhouse CO₂ emissions, and toxicity in the environment, married to societal pressures towards sustainable development are currently making countries around the world turn to biomass as a renewable resource for a variety of products: fuels, lubricants, chemicals, polymers, fibers, etc. Currently, there is a concentrated effort around the world to develop biocomposites, using synthetic- or bio polymers derived from agricultural resources and natural fibers. Injection, compression, and thermoformable grade bio-composites, made from natural fibers and polypropylene, have been increasingly used in automotive industry [1-2]. Thermoset resins synthesized from soybean oil have been shown to have a great potential as matrix in composites manufacturing with VARTM and SMC (Sheet molding compound) [3, 4]. Extending this study to manufacturing of thermoset biocomposites, for semi-structural and structural applications using Canola oil based resin and natural fibers, is the focus of this study.

Triglycerides are the main component of plant oils such as soybean oil, corn oil, linseed oil, sun flower oil, and canola oil. Triglyceride molecules have unsaturated bonds which can be chemically modified and used as polymers. Triglyceride-based polymers have been used in various different industrial products such as pressure sensitive adhesives, inks and coatings [2]. They have multiple functional sites per molecule, which enable them to copolymerize and cross-link with low molecular weight monomers like styrene. Addition of styrene decreases the viscosity of the triglycerides, which makes them

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suitable for inexpensive composite manufacturing processes like VARTM [3,4] while enhancing the mechanical properties of the cured polymer.

Among plant based oils, canola oil contains relatively lower amount of saturated fatty acids that do not polymerize and this is likely to lead to better properties. However, the un-saturation level (number of double bonds per triglyceride) in canola oils is relatively less than that in soy bean or linseed oils. The overall properties of the canola oil based resins would depend on both un-saturation and saturation levels. Additionally, the level of chemical modification of these unsaturated sites would influence the property of the canola oil based thermoset resins and their viscosity, which would in turn influence the wettability and successful impregnability of the natural fiber mats during VARTM. Current knowledge in this area is very limited in general and non-existent with respect to canola oil based resins.

Owing to their potential to offer comparable properties and cost advantages, hemp and flax are currently being explored as an alternative to glass fibers in polymer composites used in building products, automotive parts, etc. in Europe and North America. In other parts of the world, locally grown fibers such as jute, baggasse, kenaf are currently being studied as replacements for glass fibers. Various issues related to the use of natural fibers such as fiber treatment to enhance fiber-matrix bonding [6-8], and moisture absorption [9] have been studied in the past. However, the current knowledge on design and manufacture of natural fiber mats and their influence on manufacturability of thermoset biocomposites using VARTM is very limited.

Hence, a comprehensive research program was pursued by the authors to develop a comprehensive understanding of issues related to successful manufacturing and application of semi-structural and structural biocomposites using VARTM, Canola oil, and hemp / flax fibers. Canola Oil (CO) based resins were synthesized through chemical modification of triglycerides using various chemical pathways developed for soy bean oil [3-5]. Based on these results, two resins - Acrylated Epoxidized CO (AECO) and Maleinized Acrylated Epoxidized CO (MAECO) - were chosen for further studies on manufacturing of biocomposites using VARTM. Needle-punched hemp and flax fiber mats were manufactured and their impregnability by the canola oil based resins has been studied. Mat manufacturing parameters were varied to understand their impact on the impregnability by the canola oil based resins during VARTM. Finally, the properties of the biocomposites were compared, with synthetic polyester – natural fiber and polyester – glass fiber composites, and evaluated to understand their potential for use in semi-structural and structural applications.

An overview of the preliminary results from this research program is presented and discussed in this paper.

2. EXPERIMENTAL DETAILS

2.1. Materials

Canola oil was purchased from a local grocery store. Initiators (Arkema's Luperox LP and Luperox 26, Akzo-Nobel's Trigonox C), styrene, and accelerator (cobalt naphthenate) were purchased from Sigma Aldrich (St.Louis, MO). CCP's (Cook Composites and Polymers) Stypol 8086 unsaturated polyester resin was used for comparative evaluation of the canola oil based resins. It was cured with 1.5% Luperox 22. Acrylated epoxidized canola oil (AECO) was synthesized by reacting acrylic acid with epoxidized canola oil (ECO). In addition, epoxidized Linseed oil was purchased from Arkema. Subsequently, it was acrylated and mixed with AECO to optimize the mechanical properties. This 1:1 mixture was used in the manufacture of composites and is referred to as AECLO in this study. Maleinized acrylated epoxidized canola oil (MAECO) was synthesized by reaction of hydroxyl groups (HCO) with maleic acid. Detailed chemical pathways can be found in reference 5. Mechanically decorticated hemp fibers were supplied by Stemergy Inc. Needle punched non-woven mats were manufactured using the facilities at North Carolina State University, USA.

2.2. Cure Optimization

Prior to manufacturing of composites, the matrix cure formulation was optimized by studying the effect of the type and amount of initiator, amount of styrene, and cure temperature on the cure and mechanical / rheological properties of resin. TA Instrument's 2910 MDSC and 2980 DMA were used to characterize the cure and mechanical/rheological properties.

2.3. Composite Manufacturing

Hemp and flax mats with two needle-punch densities – 2.6 and 30 p/cm² (punches / cm²) - were used in this study. Additionally, a hybrid mat consisting of hemp and flax in 1:1 ratio was manufactured and used in this study. The details on mat are tabulated in Table 1. The volume fraction was estimated using a hemp fiber density of 1.475 g/cc and flax fiber density of 1.5 g/cc. These values were taken from literature. However, the diameter of the fibers were found to vary by a large margin and hence, the density is expected to vary. Experiments to characterize variation of density with diameter of the fibers are currently underway. All mats were dried at 70 °C for 24 hours prior to impregnation by the matrix. The mats were cut to 10 inch by 10 inch size and placed on molds prepared with a gel coat. A flow assist medium was placed under each mat. The mats were vacuum-bagged and impregnated with three resins, STYPOL 8086 polyester, MAECO and AECLO as shown in Figure 1. Resin fill rate were recorded to understand the influence of mat manufacturing parameters on mat impregnation and quality of the laminates. Mats impregnated with AECLO and MAECO were cured under the vacuum at 70 °C, after impregnation, for about 6 hours. While mats impregnated with STYPOL 8086 were cured at ambient temperature after impregnation.

Mat	Thickness(mm)	Mat weight / unit area (g/m ²)	Thickness under vacuum (mm)	Mat Density after consolidation (g/cc)	Estimated Fiber Volume Fraction in consolidated mat	In-plane permeability 10E-6 sq.cm
Hemp(2.6p/sq.cm)	8.07	1132	4.735	0.2391	16.20%	4.6
Hemp(30p/sq.cm)	4.94	878	3.658	0.24	16.30%	5.08
Flax(2.6 p/sq.cm)	7.7	974	3.878	0.2512	16.70%	
Flax(30 p/sq.cm)	4.38	887	2.918	0.3039	20.26%	5.08
50% Hemp+ 50% Flax (2.6 p/sq.cm)	6.1	924	3.61	0.256	17.21%	

Table1- Natural fiber mat properties

Rectangular samples were cut from the composite panels and their edges were polished. Samples were subsequently tested in the 2980 DMA using a dual cantilever clamp at a frequency of 1Hz and in the temperature range of -30 °C to 200 °C .

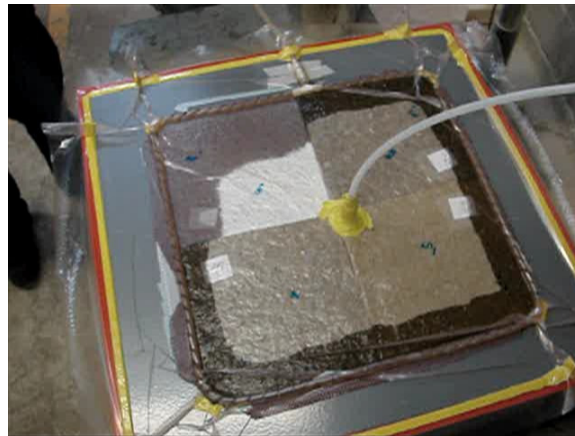


Figure 1- Impregnation of natural fiber mats in a VARTM mold

3. RESULTS AND DISCUSSION

3.1. Cure Optimization

Total heat of reaction, measured using MDSC, was monitored for various amounts of initiator and was found to reach a plateau value for 3 weight % initiator. Hence, 3% initiator was used for subsequent tests. Multiple peaks were observed during cure kinetics studies depending on the cure temperature, which also influenced the properties. Higher cure temperature resulted in higher modulus and T_g (Glass to Rubber Transition temperature) as shown in Figure 2. Based on these results, AECO and MAECO resins were cured at 100 °C and post-cured at 150 °C. Styrene was added to the canola oil based

resins to reduce its viscosity to a level conducive for manufacturing biocomposites through VARTM. The modulus of the resins increased with styrene content while decreasing the viscosity as shown in Figure 3. Based on these results, 33 weight % styrene was used for subsequent tests.

The efficiency of various initiators – Luperox 26, Trigonox C, Luperox LP, and MEKP – in initiating and sustaining the cure of the AECO and MAECO were evaluated. MEKP did not result in complete curing and hence was dropped. The moduli and T_g obtained for resins cured with the three initiators are compared in Figures 4 and 5 respectively. The plotted T_g values correspond to $\tan\delta_{\max}$. Since Luperox LP resulted in the best properties for both resins it was chosen for subsequent studies. The modulus and T_g for AECO are about 400 MPa and 50 °C respectively while the modulus and T_g for MAECO was about 800 MPa and 70 °C respectively.

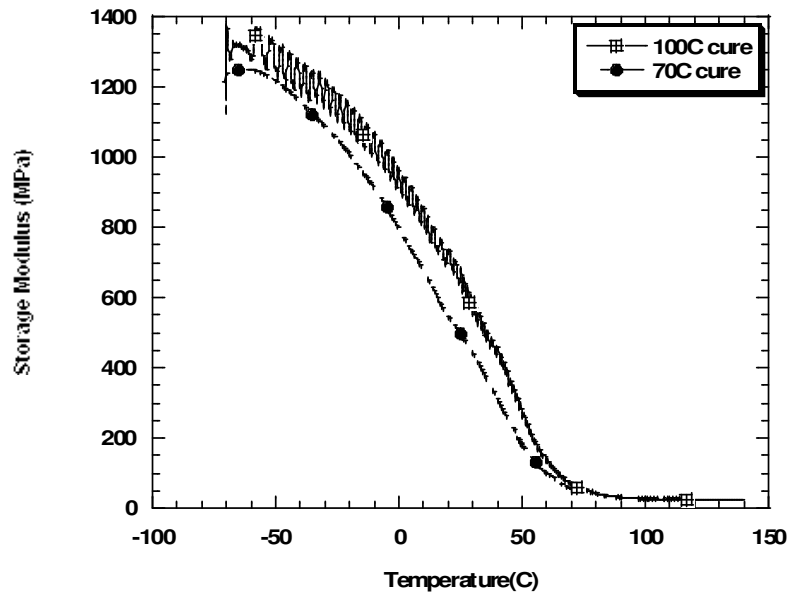


Figure 2. Effect of cure temperature on storage modulus of MAECO cured with Trigonox C

This is almost of half of the values obtained for AESO and MAESO based on soy bean oil [3]. The T_g of soy bean oil based resins was more than 50 °C. Subsequent NMR (Nuclear Magnetic Resonance) investigation revealed that the synthesis was not efficient enough. For example, the number of acrylates per triglyceride present in soy-bean based resins was about 3.8 – 4 whereas those present in the AECO and MAECO synthesized by the pilot plant were 1.9 and 1.5 respectively.

The modulus of MAECO and AECO were much lower than the modulus of unsaturated polyesters (2.8 -3.5 GPa) and vinyl ester (3.5 – 4GPa). In order to improve the properties of AECO, expoxidized linseed oil (with higher levels of un-saturation) was purchased,

acrylated and mixed with AECO in 1: 1 ratio to obtain AECLO, which was used to manufacture composites.

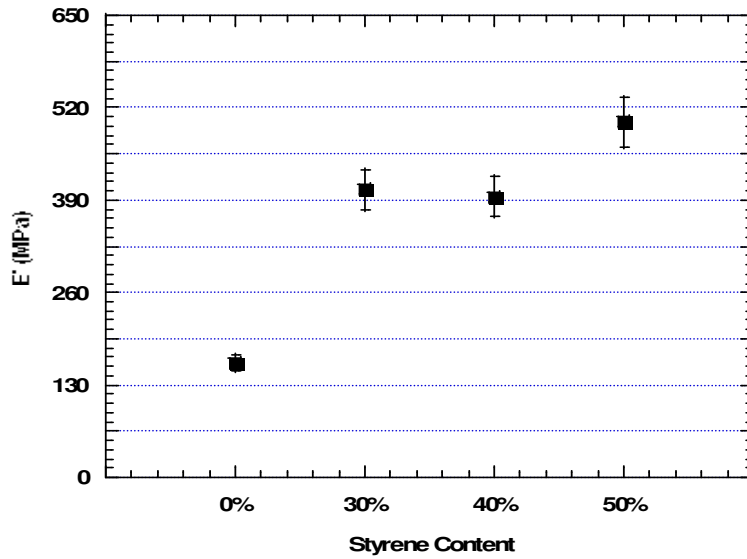


Figure 3- Effect of styrene on the modulus of AECO

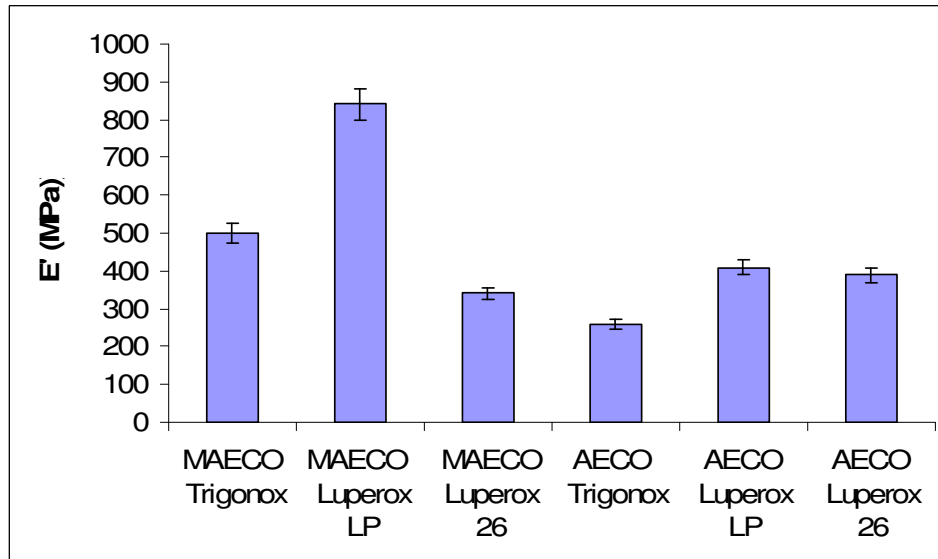


Figure 4. Storage modulus of AECO and MAECO at 25 °C

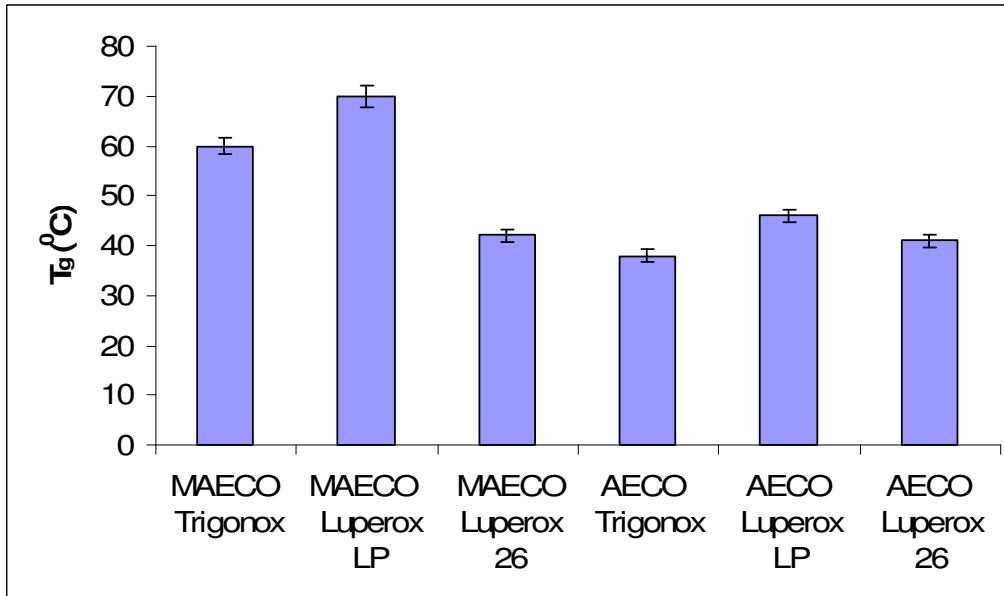


Figure 5 -Glass transition temperature of AECO and MAECO cured with different initiators

3.2. Composite Manufacturing and Properties

Separate experiments were pursued to determine the rate of impregnation of natural fiber mats. The in-plane mat permeability of the various mats determined using this data is shown in Table 1. It can be observed that the permeability of the natural fiber mats, manufactured as a part of this research, did not vary with fiber type and needle punch density. Due to lower viscosity, AECLO impregnated the mat completely in about 1 minute while MAECO impregnated the mat in about 18 minutes. The impregnation rate by synthetic STYPOL 8086 was comparable to that of AECLO, highlighting the suitability of AECLO for biocomposite manufacturing using VARTM.

Nine panels were manufactured using 3 resins and 5 types of natural fiber mats. The average values of storage modulus and glass transition temperature, measured using the DMA, are presented in Figure 6 and 7 respectively for the nine panels. The hemp fiber biocomposites exhibited higher modulus than that for the flax fiber biocomposites due to higher modulus of hemp fibers. Bicomposites manufactured with AECLO as the matrix exhibited higher modulus than biocomposites manufactured with MAECO as the matrix, for both natural fibers. This is unexpected since MAECO resin exhibited better properties than AECO and AECLO. The reason for this is currently under investigation. Composites from natural fibers and STYPOL 8086 have higher modulus than that of MAECO and AECLO biocomposites. This is to be expected due to higher modulus of the polyester resin. The modulus values for AECLO composites are slightly lower than that of soy bean oil based AESO-hemp composite (4.4 GPa) and AESO-flax composite (≈ 3 GPa) [4]. This difference is thought to be due to better modulus of AESO by a factor of 2.

The data in Figures 6 and 7 clearly show the reinforcement effect of natural fibers on the modulus of the canola oil based resins. Biocomposites have a modulus in the range of 2.5 to 3 GPa that is 3.5 to 4 times that of the MAECO or AECLO resin for a fiber volume fraction of 17%. For similar volume fraction of glass fibers, the modulus of polyester composite would be in the range of 6.6 – 7.3 GPa [10], which will be about 2.5 times the modulus of the polyester resin. However, such an effect is not apparent with natural fiber – STYPOL 8086 composite since the modulus of the unsaturated polyester would be in the range of 3 GPa. Further investigation of this is currently underway.

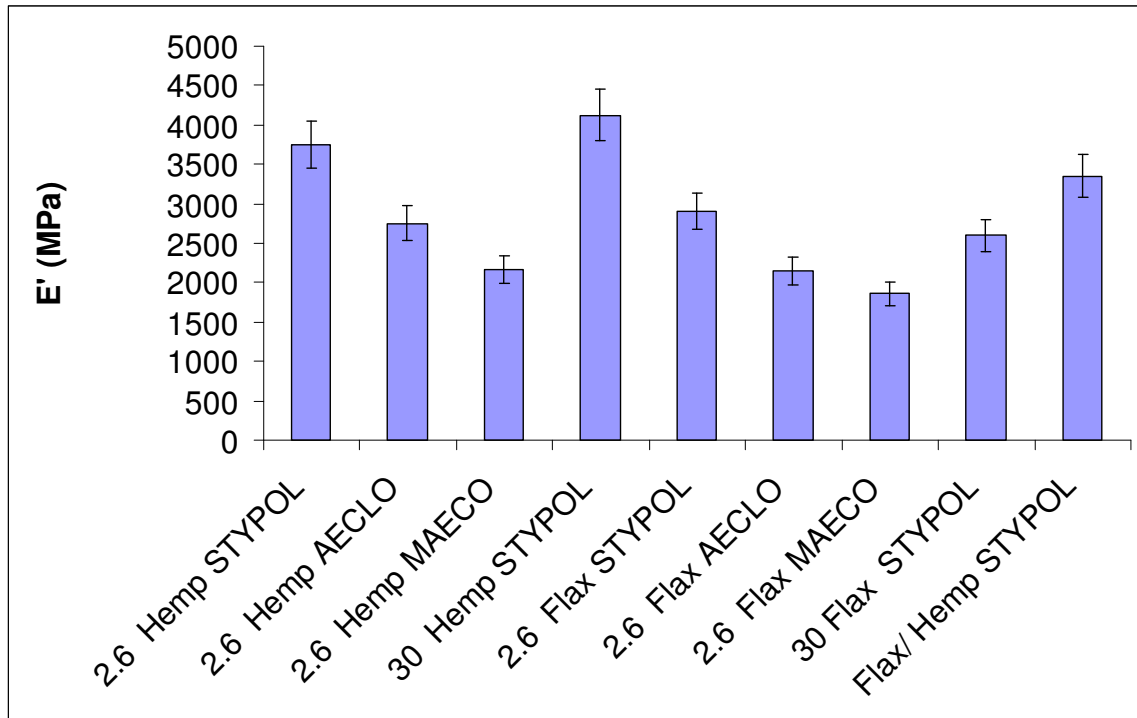


Figure 6-Storage modulus of biocomposites at 25 °C

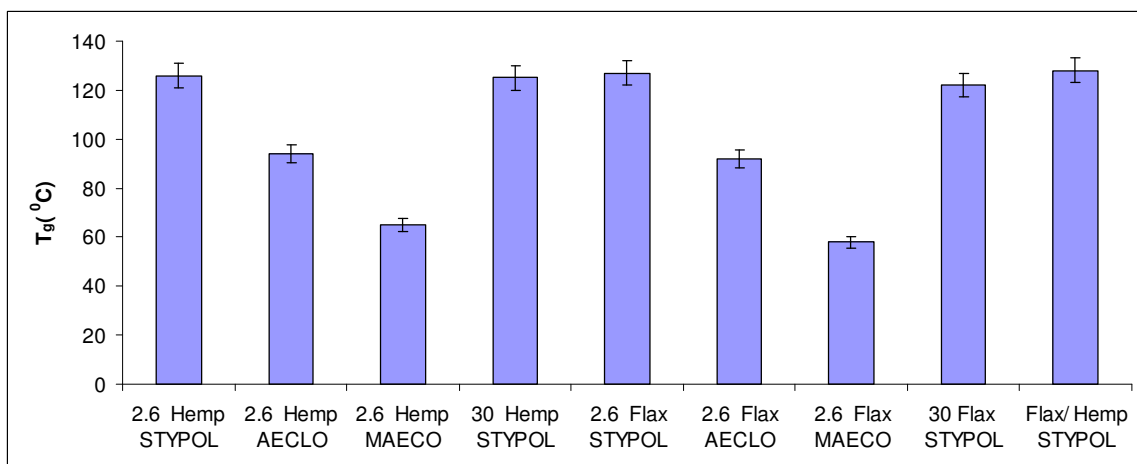


Figure 7-Glass transition temperature of Biocomposites

4. CONCLUSIONS

Two canola oil based resins – MAECO and AECO/AECLO – were synthesized and evaluated as neat resins. Hemp and flax fiber mats were manufactured. Biocomposites using these resins and mats were successfully manufactured using VARTM. While the modulus and T_g of MAECO was better than that of AECO and AECLO, the latter resulted in better composites in addition to a mat impregnation rate comparable to that for unsaturated polyester. Permeability of mats manufactured in this study did not vary with fiber type and needle punch density.

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