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RENEWABLE AGRICULTURAL FIBERS AS REINFORCING FILLERS IN PLASTICS
Prediction of thermal properties

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Thermal properties such as melting and crystallization are important aspects in understanding the morphology and its contribution to the physical properties of semicrystalline polymers, such as polypropylene. The inclusion of fillers, which are small particles dispersed in the continuous polymer phase, often complicates the predictability of these properties by acting as nucleating agents or defect origins.

This paper discusses the creation and use of empirical models based on experimental data for predicting and optimizing the thermal properties of agricultural filler-polypropylene (AgFiller-PP) composites, including peak melting temperature (T_m), peak crystallization temperature (T_c) and percent of crystallinity (X_c). Experiments were performed using differential scanning calorimetry (DSC) to gather data necessary for building appropriate prediction models. Finally, additional experiments were carried out to test the prediction results generated by the models.

Keywords: *composite, particulate composite, predictive models, thermal conductivity, thermal properties*

Introduction

When two or more individual materials combine to form a new material with improved characteristics, a composite is created. In a simplistic model neglecting minor components like additives, a thermoplastic composite can be considered as a two-component system, that is consisted of the continuous phase of polymer, such as polypropylene (PP), and the dispersed phase of filler, like agricultural crop by-products including wheat straw, soy hull, soy stems and more. The use of agricultural fillers (AgFillers) in PP can lead to desirable cost reduction and improvements in selected properties, although other properties may be compromised. The changes in these properties can be controlled by manipulating aspects like filler or polymer type, as well as blend ratios. By systematic experimentation and the aid of models, optimization is made possible to achieve a delicate balance of maximizing desired property enhancements while minimizing any sacrifice in other properties. Artificial neural network (ANN) models are a novel tool that is capable of such tasks, and enables more efficient product design processes compared to conventional regression models.

The objective of this paper is to investigate the effects on the properties of composite materials, when their constituent AgFiller and PP types and usage levels are varied. Experimental data were collected and implemented into ANN designs to allow prediction and in turns for the optimization of these properties by manipulating formulation parameters.

AgFiller-PP composites

The use of fillers in polymer systems has been practiced for over a century [1]. Up until the mid-1990s, the research and use of lignocellulosic material as filler mostly focused on wood fibers [2]. In recent years, agricultural by-products have received increased attention as alternative fillers due to their low cost and abundance. AgFillers can be used in both thermoplastic [3, 4] and thermoset [5, 6] polymer matrices, and the choice of polymer for making composites greatly depends on the intended application of the material. Meanwhile, the selection of AgFiller varies mainly according to local crop availability. Some researchers, such as Jacob *et al.* [6] and Panthapulakkal and Sain [7], utilized AgFillers in the form of fibrous reinforcements. Although the presence of the fibers provided improved mechanical properties of the composite [6], the steps required to prepare the fibers can be complex and costly, often involving both mechanical and chemical treatment [7]. A more economical approach is to incorporate AgFillers into composites in the form of particulate fillers, similar to a flour, to replace the use of traditional mineral fillers such as

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calcium carbonate, mica and talc. The outcome of this practice is a composite with increased tensile and flexural moduli but little improvement on the strength of the composite [8].

PP is known as a commodity thermoplastic by its versatility in many applications. Its large annual production quantity contributes to its low cost, and discarded PP can be recycled and reused by melting and forming the material into new products. As a semi-crystalline material, the crystalline structures in PP give order on the molecular level and are a source of the polymer's strength, and therefore high percentage of crystallinity is desired [9]. Crystallinity can be manipulated by adding fillers that serve as nucleating agents, as shown in the study by Albano *et al.* [10], where it was demonstrated that composites containing inorganic particulate fillers showed increases in crystallization temperature as well as the percentage of crystallinity when compared to pure PP. The most commonly used method for studying melting and crystallization is by differential scanning calorimetry (DSC), where heat flow is measured over a range of temperatures and any phase change is recorded.

Artificial neural networks

Artificial neural networks (ANNs) are a more recent technique to model complex relationships. ANNs allow the interpretation of relationships among variables of high-dimensional space [11], thus demonstrating advantage over conventional modeling methods. The use of ANNs in areas of material science and pharmaceutical engineering has increased significantly in recent years, as exemplified in the study of reinforced aluminum matrix composites by Altinkok [12], and the research by Leane *et al.* [13] on the in vitro dissolution of sustained release minitablets. An ANN model consists of an input layer, an output layer, and a number of hidden layers. These layers are arranged in parallel, and in each layer processing elements called neurons are placed [14]. Figure 1 illustrates the basic construction of an ANN model with one hidden layer.

With the number of neurons in the input and output layers fixed by the number of variables, the number of hidden layers as well as the number of neurons in the hidden layer can be varied to construct the most appropriate model. The universal approximation theory suggests that a network with only one hidden layer but a large number of neurons can be used to relate any input to any output [15]. However, too many neurons could over interpret patterns and could result in memorization, prohibiting the network's ability to generalize [13]. On the other hand, too few neurons in the network could deter the model's ability to classify patterns in the data. To transform inputs into outputs through the hidden layers, various transfer functions can be employed. Examples of these functions include the hard limit, log sigmoid, liner, radial basis and hyperbolic tangent sigmoid transfer functions. Data weighting and normalization are regularly employed to avoid overflows, as outlined by Elkamel *et al.* [14] in their modeling of ozone levels as a function of the concentrations and types of chemicals present in the atmosphere. A number of computer software packages, such as Matlab and GraphPad Prism, are available to efficiently perform ANN construction, training and execution.

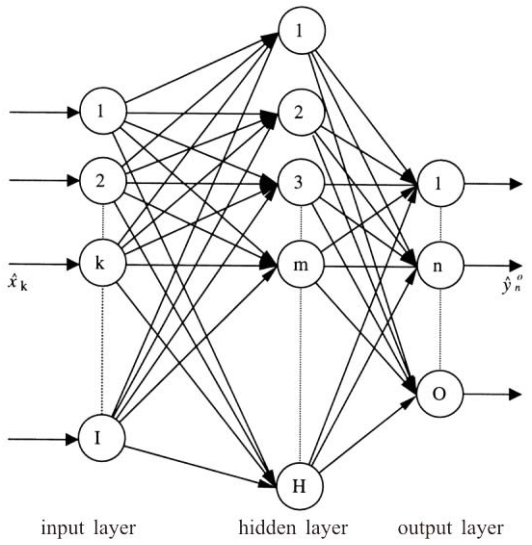

Fig. 1 Architecture of a one hidden layer feed-forward neural network [14]

Experimental

Materials

Wheat straw (WS), soybean hulls (SH), ground soybean hulls (gSH) and soy stems (SS), were used as AgFillers in this study. A high viscosity PP impact copolymer (SG 0.9; MFI 1.5, 230°C, 2.16 kg), and a random sample of post-consumer PP recyclate (rPP), containing mostly food containers, collected from the Region of Peel Material Sorting Facility, Ontario, were used as the polymer matrix.

Methods

AgFiller-PP composites of various blend recipes were compounded and pelletized using a Haake Minilab micro compounder. Examples of blend recipes include 100 mass% polymer, 80 mass% polymer with 20 mass% AgFiller and 60 mass% polymer with

40 mass% AgFiller. Furthermore, the composition of the polymer phase in each recipe was varied by changing the ratio of vPP and rPP. DSC was used to study melting and crystallization of selected samples, using a TA Instruments Q10 model apparatus. Approximately 10 mg of sample was cut from a larger pellet or strand at a random location. The sample was then placed in a hermetic aluminum pan, crimp-sealed and loaded into the DSC chamber purged with nitrogen. The test was programmed with three steps. First, a heating step from ambient (23°C) to 210°C at 10°C min^{-1} removed any thermal history of the composite. The sample was then held isothermally at 210°C for 5 min. The second step involved cooling the sample from 210 to 30°C at 10°C min^{-1}. After the second step the sample was again held isothermally at 30°C for 5 min. The final heating step from 30 to 210°C, at 10°C min^{-1}, would again melt the material. Crystallization and melting information are gathered from data produced in steps 2 and 3.

Crystallinity was calculated from melting peak areas. The percentage of crystallinity (X_c) in a composite material is determined by:

$$X_c = \frac{\Delta H}{\Delta H^0}\frac{100}{w} \quad (1)$$

where ΔH is the heat of fusion of the PP composite, ΔH_0 is the heat of fusion of 100% crystalline PP, and w is the polymer mass fraction in the composite [3]. According to references [16, 17], ΔH_0 of 209 J g^{-1} was used for calculation.

Results and discussion

Figures 2 and 3 illustrate the DSC endotherms of AgFiller-vPP composites during cooling step 2 and melting step 3, respectively. A shift in crystallization temperature was detected in Fig. 2 for all AgFiller-PP composites when compared to that of pure PP. Specifically, crystallization of the composites occurred at higher temperatures. The reason for the change in crystallization temperature could be that the AgFiller served as nucleating agents to promote formation of spherulite crystals, similar to the way mineral fillers increases T_c of talc-PP composites [10]. From Fig. 3, it could be seen that the melting point experienced little changes, regardless of AgFiller type used.

DSC endotherms of rPP (Fig. 4) showed distinct bimodal crystallization behaviour. In the study of die-drawn polypropylene by Taraiya *et al.* [18], it was suggested that the presence of a second crystallization peak was likely due to the presence of copolymers. Since copolymers are common in injection molding applications to provide additional impact resistance, this explanation is plausible, considering the source of the rPP tested was mainly injection molded food containers. The bimodal crystallization peaks were eliminated by the addition of AgFiller. Furthermore, as the ratio of rPP in the composite increased, the

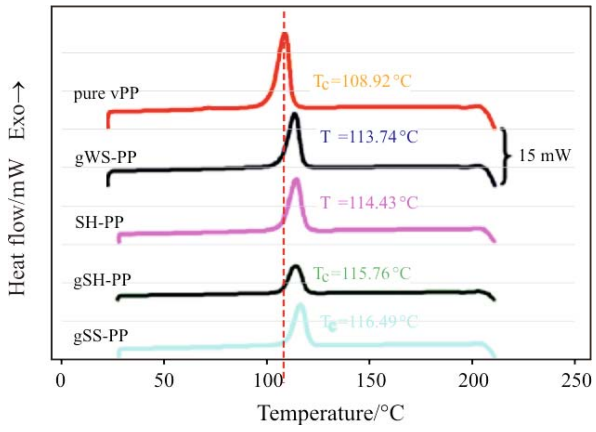

Fig. 2 DSC curves during cooling step for AgFiller-PP composites and pure vPP

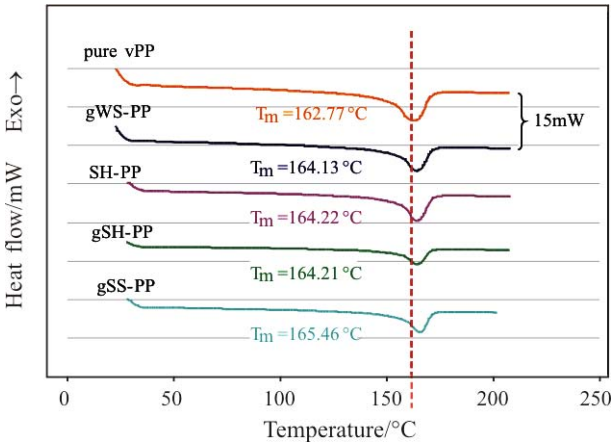

Fig. 3 DSC curves during second heating step for AgFiller-PP composites and pure vPP

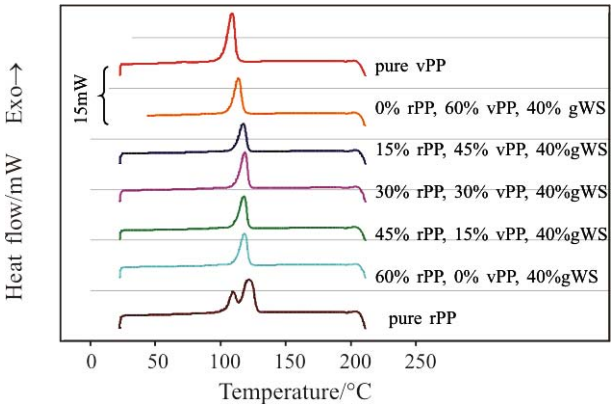

Fig. 4 DSC endotherms during cooling step of experiment, for gWS-PP composite with increasing rPP content

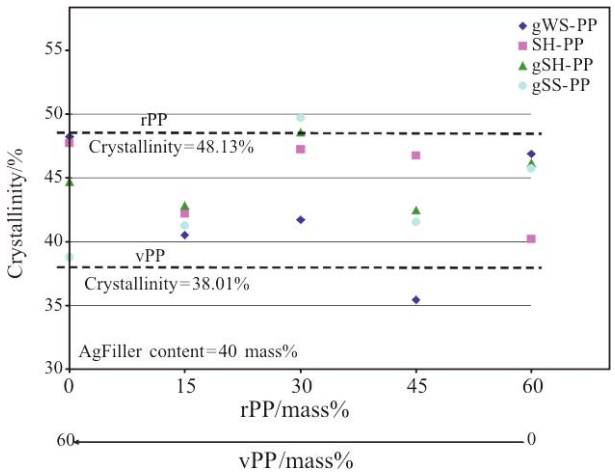

Fig. 5 Crystallinity of AgFiller-PP composites at various rPP levels

peak crystallization temperature of the composite also increased.

The levels of crystallinity of AgFiller-PP composites are shown in Fig. 5. It was determined that X_c of AgFiller-PP composites were not greatly affected by the amount of rPP in the composition. Instead, changes in X_c were mostly caused by changes in AgFiller type. All composites containing rPP, showed crystallinity similar to or lower than that of pure rPP, based on a typical range of ±3–5% of statistical significant difference among crystallinity values. Except in the case of two data points, the range for X_c of AgFiller-PP composites were bound by the X_c of vPP and rPP.

ANN modelling

An executable program was compiled using Matlab 7.0, consisting of three sections. The first section designs and trains the model, the second calculates results using the trained model, and the third tests the model with a separate data set. The training data set was consisted of 75% of the experimental data, randomly selected, while the remaining 25% composed the test data. The input neurons were made up of the four input variables: AgFiller type, AgFiller percentage, vPP percentage and rPP percentage. Two hidden layers of neurons were used, and training was performed using log sigmoid-linear (LS-PL) transfer functions. The number of neurons and the number of iterations for training were varied for each property studied. A separate model was constructed for each of the three thermal properties, namely T_m, T_c and % crystallinity.

On first attempts, 15 neurons were used in each hidden layer to construct the ANN models. However, the results showed overmapping of the training data, such that the model was too rigid to generalize for the test data. The number of input neurons were subsequently lowered, and it was determined that 4 to 6 neurons were sufficient to give accurate predictions. ANN model designs, as well as the prediction accuracy using the 'training' data set, for each thermal property are summarized in Table 1. A second data set was used to test the prepared models and the results proved to be satisfactory. The average error on crystalline temperature, and melting temperature was always less than 1.3 and 0.25, respectively. The average error on % crystallinity was always less than 9%. Although this is higher than that of the previous two variables but is nevertheless an acceptable upper bound on the error.

Cross plots of predicted and measured thermal properties were generated to check the accuracy of the ANNs developed. Figures 6 to 8 showed the comparison of the estimated and actual values of the training and test data sets, displayed on the same axes. The accuracy of the predictions was assessed using the R^2 of the predictions. An ideal model would produce a perfect positively diagonal relationship between the estimated and actual data, with an R^2 of 1. All training data showed good prediction (R^2>0.8). The predic-

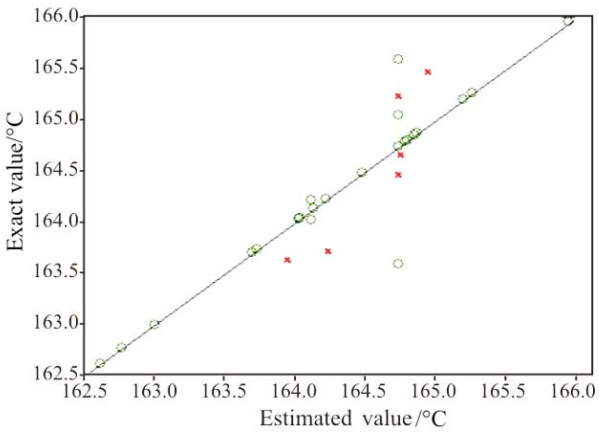

Fig. 6 ANN o – training and x – test results for the prediction of melting temperature of AgFiller-PP composites

Table 1 ANN training design and results

Property examined	# Neurons	# Iterations	Training R^2	Average error
Crystallization temperature/°C	5	113	0.99129	0.12270
Melting temperature/°C	6	75	0.86784	0.06852
Crystallinity/%	4	250	0.96548	0.86132

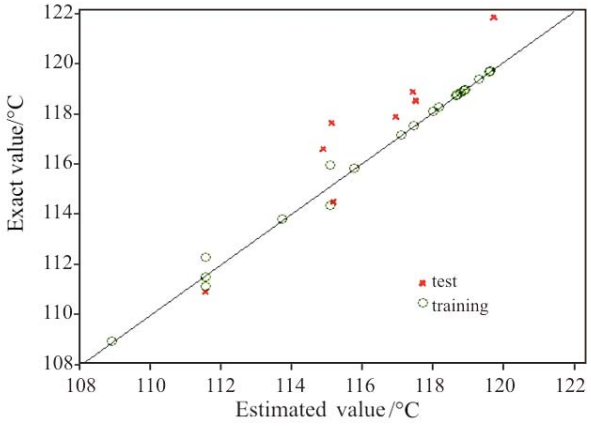

Fig. 7 ANN o – training and x – test results for the prediction of the crystallization temperature of AgFiller-PP composites

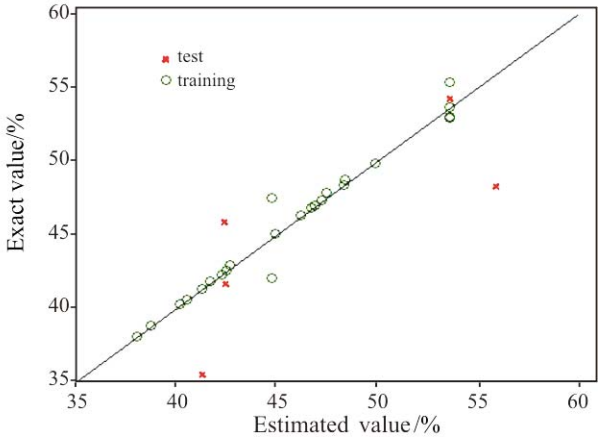

Fig. 8 ANN o – training and x – test results for the prediction of the percentage of crystallinity of AgFiller-PP composites

tions on test data showed acceptable to good accuracy. In addition, it is to be noted that the range of variations in properties such as melting temperature was very small (approximately 3°C). Therefore, the ANN model was in fact able to provide a good prediction (within 1°C).

In addition to thermal properties, other aspects such as processibility and mechanical strength are also important in the development of AgFiller-PP composites. For many applications, such as in the manufacture of automotive parts and consumer goods by injection molding, the composite material requires low viscosity for ease of processing, while desiring high physical strength and stiffness. Figure 9 shows a matrix of scatter plots which outlines the correlations between the four main input variables (AgFiller type, AgFiller level, vPP level and rPP level) and some important properties. This matrix allows relationships containing strong correlations be identified, such as in the case of vPP% and T_c. The importance of each property can then be ranked, and the outputs can be

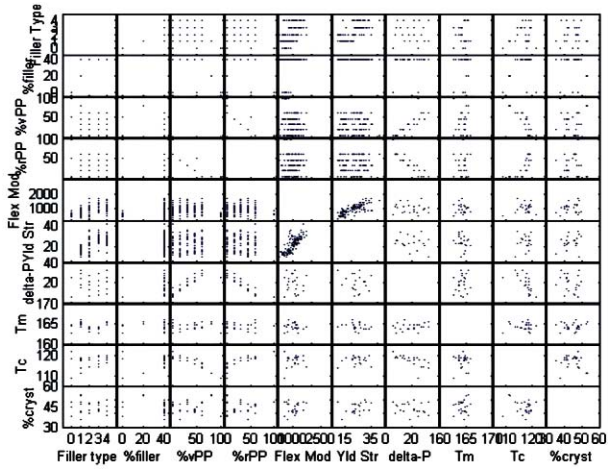

Fig. 9 Scatter plot of inputs (1–4) and outputs (5–10) to identify correlations

weighted according during the construction of ANN models. As future work, the optimization of these properties can be achieved by combining inverted ANN models for each property. Finally, to predict acceptance and feasibility of the designed composites in the marketplace, neural networks can be employed again when combined with other modeling methods, as demonstrated in the work of Lin *et al.* [19]. Other methods, such as the SWOT (strength, weakness, opportunities and threat) analysis are also useful for such work.

Conclusions

In this work, the thermal properties of AgFiller-PP composites were studied using DSC. Crystallization temperature (T_c), melting temperature (T_m) and crystallinity (X_c) were evaluated. It was shown that T_c and X_c increased when AgFillers were added to pure PP, while little change was observed in T_m. The presence of rPP also caused T_c of the composites to increase. The experimental results were randomly divided into a 'training' and a 'test' data set, consisting respectively of 75 and 25% of total data, and were used to prepare ANN models of each thermal property. Networks with 2 hidden layers and 4 to 6 neurons per layer were constructed. These networks were found to well represent both the training and test data, yielding satisfactory correlation coefficients.

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