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Prediction of thermal stability, crystallinity and thermomechanical properties of poly(ethylene oxide)/clay nanocomposites with artificial neural networks

Engin Burgaz[a,*], Mehmet Yazici[a], Murat Kapusuz[b], Sevim Hamamci Alisir[a], Hakan Ozcan[b]

[a] Department of Materials Science and Engineering, Ondokuz Mayis University, Kurupelit, 55139 Samsun, Turkey
[b] Department of Mechanical Engineering, Ondokuz Mayis University, Kurupelit, 55139 Samsun, Turkey

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ABSTRACT

The artificial neural network (ANN) technique with a feed-forward back propagation algorithm was used to examine the effect of clay composition and temperature on thermal stability, crystallinity and thermomechanical properties of poly(ethylene oxide)/clay nanocomposites. Based on dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) experiments, values of decomposition temperature, char yield, enthalpy of melting, storage modulus (E') and tan δ were successfully calculated by well-trained ANNs. The simulated data is in very good agreement with the experimental data. ANN results confirm that thermal stability of PEO nanocomposites increases with the decrease of enthalpy of melting and relative crystallinity, and there is a directly proportional relationship between the modulus (stiffness) and thermal stability. The ANN technique is confirmed to be a useful mathematical tool in the thermal analysis of polymer/clay nanocomposites.

1. Introduction

During the past two decades, polymer/clay nanocomposites have received great attention from both academia and industry since the properties of these materials can be greatly improved compared with the pure polymer or conventional polymer composites. These enhanced properties can be summarized as increased strength and modulus [1–3], increased thermal stability [4], improved barrier properties [5] and decreased flammability [6]. Different types of polymers have been used as matrix materials in order to fabricate polymer/clay nanocomposites with improved properties. Among these polymers, poly(ethylene oxide) (PEO) has been a promising material since it has been used in so many different areas such as denture adhesives, packaging films, thickening of water-based paints, friction reduction, purification of biological materials, and pharmaceutical drugs. In addition to these applications, poly(ethylene oxide) has been recognized as a potential solid polymer electrolyte (SPE) which can be used in rechargeable solid-state lithium-ion polymer batteries [7,8].

Poly(ethylene oxide) has a suitable structure that can provide fast ion transport [9,10], and also it has the capability of dissolving so many different salts [11]. On the other hand, the most important disadvantage of PEO is its low ionic conductivity at room temperature due to the high concentration of its crystalline phase. For this reason, many different methods have been used in order to minimize the concentration of PEO crystalline phase while maintaining its flexibility and mechanical stability which extends over a wide temperature range [12,13]. One of the most effective methods has been the addition of inorganic filler materials such as clay or silica nanoparticles to PEO [14–17].

In polymer composites, finding the optimum filler composition for the best mechanical and physical properties is a very time-consuming process. For this reason, intelligent computational systems have been used to reduce the routine experimental characterization in the development of new polymer composites [18–20]. Among these well-established computational techniques, artificial neural network (ANN), multiple linear regression (MLR) and support vector regression (SVR) can be given as the profound examples [21–24].

The ANN approach was recently introduced into the field of wear of polymers and it was shown that ANN is a helpful mathematical tool in the structure–property analysis of polymers based on a limited number of measurement results [19,25,26]. Besides wear properties of polymers, ANN technique was utilized to predict the stress relaxation of a polymer composite, and it was found out that the ANN model is more accurate over a wider range of stress and

* Corresponding author. Tel.: +90 362 312 1919x1562.
E-mail address: eburgaz@omu.edu.tr (E. Burgaz).

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temperature than those of the explicit nonlinear viscoelastic constitutive model [27]. Recently, the thermal degradation behavior of nylon6/feather keratin blends was successfully predicted by implementation of artificial intelligence techniques on experimental TGA data [28].

The mechanical and wear properties of short fiber reinforced polyamide composites were examined by ANN, and the results of the study showed that prediction quality of ANN has the potential to be improved if the database for the ANN training process could be enlarged or the configuration of network could be further optimized [29]. Other researchers also found the same results about the number of data, and showed that a larger training dataset should be required if the nonlinear relationship between the input and output is more complex [19,30,31]. In polymer/clay nanocomposites, ANN, MLR and support vector regression (SVR) methods were applied in order to correlate dynamical mechanical properties with temperature and clay composition. The study showed that SVR and ANN exhibit better performance when compared to MLR [32]. It was previously shown that the relationships between the conditions and the mechanical properties for compatibilized styrene/rubber blend are too complex to be explained by central composite design (CCD) polynomials, but are well described by the ANN models [33].

In this paper, the artificial neural network technique with a feed-forward back propagation algorithm was used to predict the effect of clay composition and temperature on the crystallinity, thermal stability and thermomechanical properties of PEO/clay nanocomposites. The purpose of this work is to emphasize the benefits of using the ANN method in the prediction of crystallinity, thermal stability and thermomechanical properties of untested PEO/clay nanocomposites without performing lengthy and time-consuming experiments. In polymer/clay nanocomposites, the general relations of thermal stability, crystallinity and thermomechanical properties with respect to temperature and clay composition are usually known. However, still extensive experimental measurements should be performed in order to know the exact value of each nanocomposite's property. This large scale of laboratory measurements could be effectively reduced by applying the ANN prediction technique to polymer/clay nanocomposites.

2. Experimental

2.1. Materials

PEO with average M_v = 200,000 g/mol was purchased from Aldrich. Na^+MMT (Cloisite Na^+) with an average cation exchange capacity of 1.0 meq./g was kindly supplied by Southern Clay Products. PEO and clay were dried at 50 and 60 °C, respectively for 24 h in a vacuum oven. The samples were prepared in a deionized water/methanol (3:1) solvent mixture. The mixtures were first stirred at 70 °C for 24 h. Then, homogenous solutions were ultrasonicated in an ultrasonic bath at room temperature for 1 h. The solid films were produced by casting a sample onto a glass mold by slowly evaporating the solvent in air for 3 days. The films with a thickness of ~150 μm were put in a vacuum oven at 50 °C for 24 h in order to get rid of the extra solvent. The dried films were stored in a dessicator prior to any characterization. PEO/clay nanocomposite samples that were prepared in this study consist of 0, 5, 10, 15 and 20 wt.% clay compositions.

2.2. Physical/chemical characterization

Determination of the thermal stability of materials was performed on a Perkin Elmer Thermogravimetric Analyzer Pyris 1 TGA. The measurements were conducted from 20 to 630 °C at a heating rate of 10 °C/min under N_2 flow. The thermal behavior of samples was studied with DSC (Perkin Elmer Diamond). About 7 mg of sample was placed in an aluminum pan and heated from 25 to 125 °C at 10 °C/min, then cooled back to −65 °C at 10 °C/min and heated again from −65 to 125 °C at 10 °C/min. The data of the third cycle was used. The reference was an empty aluminum pan. High purity nitrogen supplied at 50 mL/min was used as the purge gas. DMA of the nanocomposites was carried out using a Perkin Elmer Pyris Diamond DMA, at a fixed frequency of 1 Hz from −90 to 50 °C with a heating rate of 4 °C/min in tension mode. The sample size was 35 mm × 5 mm × 0.14 mm. Scanning electron microscopy (SEM) experiments were performed using a Zeiss ULTRA Plus FE-SEM. The SE detector and 1.00 kV accelerating voltage were used during the experiments. Attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy was performed using a Perkin Elmer Spectrum Two IR spectrophotometer (US). The sample surface was scanned in the 600–4000 cm^{-1} frequency range. The ATR-FT-IR spectra were recorded at room temperature. The background subtraction and baseline correction were done.

3. Proposed methodology

For the ANN prediction model, we used the MATLAB platform. The proposed ANN model is based on experimental results. All input data are normalized between 0 and 1 by using the normalization equation (Eq. (1)). The minimum and maximum values of experimental data are defined as x_{min} and x_{max}, respectively. High and low limits are defined as 1 and 0, respectively for the normalization between 0 and 1.

$$x_n = \frac{x - x_{min}}{x_{\max} - x_{\min}}(high\ limit – low\ limit) + low\ limit \quad (1)$$

The basic elements of the proposed ANN architecture are shown in Fig. 1. The structure of an ANN is organized in multiple layers such as the input layer, hidden layer(s), and output layer which are composed of units called neurons. The weight coefficient ($w_{i,j}$) that is directed from the ith neuron in the input layer to the jth neuron in the hidden layer is determined by the network. The data in the input layer is used according to the following rule (unless otherwise noted): 70%, 15% and 15% of the data are used for the training, validation and testing, respectively (here, the testing is done by ANN, itself). Each of the input data, x_i that is coming from the ith neuron in the input layer is multiplied by $w_{i,j}$ and added with b_j which is the bias of the jth neuron in the hidden layer. This operation is done for each neuron in the hidden layer. The result, u_j is operated by the transfer function to find y_j (The equation in the hidden layer of Fig. 1).

In the present work, for the networks containing one hidden layer, a tan-sigmoidal non-linear transfer function $\{f(x) = (1 - e^{-2x})/(1 + e^{-2x})\}$ was used between the input and hidden layer. For the networks containing two hidden layers, a tan-sigmoidal and log-sigmoidal $\{f(x) = (1/(1 + e^{-x})\}$ non-linear transfer functions were used as the first and second transfer functions, respectively. During the transition to the output layer, y_j is multiplied with $w_{j,k}$ which is the weight coefficient directed from the jth neuron in the hidden layer to the kth neuron in the output layer, and then added with b_k which is the bias of the kth neuron in the output layer. This result is operated by the purelin linear transfer function $\{f(x) = x\}$ to obtain the output value. In summary, a result is obtained from the values coming from two input neurons. This result is compared with the experimental data *via* the mean square error (MSE) performance function, and then the error value is calculated.

In this ANN prediction technique, feed-forward back propagation algorithm which has been widely used in polymer applications [18,34,35] was selected. This algorithm compares the experimental data with predicted data which was obtained by using feed-forward calculations. The weight coefficients and bias values were updated