Improvement in properties of nanocomposite materials by temperature control

Ruziye Çamkerten¹, Sebahat Erdoğan¹*, Ayla Altınten¹ & Mustafa Alpbaz²

¹Department of Chemical Engineering, Faculty of Engineering, Gazi University, 06570, Maltepe, Ankara, Turkey
²Department of Chemical Engineering, Faculty of Engineering, Ankara University, 06100, Tandogan, Ankara, Turkey

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Polystyrene/nano-SiO₂ composites with different silica contents have been prepared by using nano-silica particles of 10 nm and polystyrene obtained in batch jacketed reactor with self-tuning PID (STPID) temperature control. The relationship between final properties of nanocomposite material and polymer matrix properties with control has been studied and the composites thus prepared are characterized by means of differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), scanning electron microscope (SEM) and hardness tests. It is observed that higher mechanical and thermal properties of nanocomposites could be obtained using polystyrene produced with STPID temperature control under optimal conditions which are precalculated for average number of molecular weight of 52000 and monomer conversion of 50%. It is also found that hardness and thermal stability of nanocomposite materials increase with increasing nano-silica contents, as expected. The same thermal stability increase is observed in DSC thermograms.

Keywords: Batch reactor, Nanocomposite, Temperature control, Polystyrene/nano-silica composites

Polymers are widely used in electronics, cosmetics, automotive material and bio medicine sciences and other industries. Polymers encapsulating nano-sized inorganic particles such as SiO₂, TiO₂, clay show improved thermal, mechanical, optical and other properties due to the combined effect of properties of organic polymers and inorganic particles. The interaction between nanoparticles and polymer matrix controls the nanocomposite properties. So, nanoparticle geometry, nanoparticle orientation, type of functional groups, molecular weight of the polymer chain, and other properties are important. Only a slight change in nanoparticle type, polymer material properties and other processing conditions¹ can alter micro structure of nanocomposite with the changes in nanocomposite properties. For this reason, further research and development in this area is still needed although there are many studies and research in the processing and development of better models for polymer nanocomposites.

Ray and Okamoto² studied about the academic and industrial aspects of preparation, characterization, material properties, rheology and processing of polymer/layered silicate nanocomposites. A wide range of polymer matrices is covered in this review. Katsakis et al.³ investigated the thermal stability of polymethylmethacrylate (PMMA)/silicate nano and microcomposites by dynamic mechanical experiments. Bansal et al.⁴ showed that the thermal mechanical properties of polymer nanocomposites are critically affected by polymer particle wetting behaviour and for this behaviour molecular weight is important.

Rong et al.⁵ studied the preparation and characterization of titanium dioxide nano particle/ polystyrene composites via radical polymerization. They found that there is an increase in the molecular weight of free polystyrene as well as the amount of bonded polystyrene on the TiO₂ particles when the amount of styrene monomer increases in the initial monomer feed. Molecular weight distribution is broadened with increasing the feed of monomer. There are similar studies⁶-¹³ on the preparation of nanocomposites and the effect of filler on mechanical and thermal properties of the nanocomposite materials.

Xie et al.¹⁴ studied glass transition behaviour on nanocomposites processed from polystyrene of different molecular weights and silica nanoparticles of 10-15 nm diameter. They studied trends in the glass
transition behaviour by changing the matrix molecular weights and silica weight fractions. Mu et al.\textsuperscript{15} studied the effect of molecular weight of the polymer on load transfer in nanotube/polymer composites and observed the importance of molecular weight of the polymer matrix to the load transfer in nanocomposites. As it is known, molecular weight and molecular weight distribution are important for the quality of polymer product. To obtain a polymer with desired properties, the polymerization reactor conditions should be controlled precisely. Up to now, although much research work has been done on the preparation and properties of polymer nanocomposite materials, further work is necessary to understand the role of some factors like operating conditions, molecular weight, etc. Processing conditions can also affect the nature of the particle polymer interface. In the present study, polystyrene of desired properties predetermined has been obtained in a jacketed batch reactor with temperature control. Self tuning PID (STPID) control method was used for this aim. The controller parameters were obtained by using genetic algorithm. Then polystyrene and silica nano particles of 10 nm in diameter were used to prepare the nanocomposites over a range of weight fractions. The prepared nanocomposite materials were characterized by means of SEM, TGA, DSC techniques and by hardness test. The results were compared with the properties of nanocomposite materials prepared from polystyrene obtained without control.

**Experimental Procedure**

**Reactor model and optimization**

Free radical polymerization reactors can be modeled in terms of a set of differential equations. For the optimization of the operating conditions of the batch solution polymerization process of styrene, these model equations were used. To calculate the optimal temperature trajectory to reach desired properties in minimum time, the Hamiltonian maximum principle was applied. The model equations and optimization have already been described in detail\textsuperscript{16,17}. Temperature of the polymerization reactor influences the monomer conversion and the molecular weight.

**Self-tuning PID control with genetic algorithm**

In this study, STPID control method has been applied to the jacketed batch polymerization reactor to control the optimal temperature of polymerization. As controller an on-line digital computer was used to keep the reactor temperature at precalculated optimal set point path. STPID control was based on CARMA (ARMAX, autoregressive moving average with external input) model\textsuperscript{18} developed between the heat input and the reactor temperature, as shown below:

\[
y(t) = \frac{B}{A} u(t-1) + \frac{C}{A} e(t) \quad \text{or} \quad y(t) = \frac{B}{A} z^{-1} u(t) + \frac{C}{A} e(t)
\]

The control equation \( u(t) \) is given as follows

\[
u(t) = \frac{S}{R} [r(t) - y(t)]
\]

where \( r(t) \) is the set point; and \( S \) and \( R \), the polynomials in the backward shift operation \( z^{-1} \), as shown below:

\[
S = s_0 + s_1 z^{-1} + s_2 z^{-2} \\
R = 1 - z^{-1}
\]

The degrees of \( S \) and \( R \) were taken as two and one respectively for this system. The system transfer function from the solution of Eqs (1)-(4) becomes

\[
y(t) = \frac{b_0 z^{-1}}{1 + a_1 z^{-1} + a_2 z^{-2}} u(t) = \frac{B}{A} u(t-1) \quad \text{and} \quad \text{(5)}
\]

\[
y(t) = \frac{b_0 z^{-1} (s_0 + s_1 z^{-1} + s_2 z^{-2}) r(t)}{(1 - z^{-1}) (1 + a_1 z^{-1} + a_2 z^{-2}) + b_0 z^{-1} (s_0 + s_1 z^{-1} + s_2 z^{-2})}
\]

\[
y(t) = \frac{BS}{T} r(t-1)
\]

The closed-loop tailoring polynomial \( T \) can be given in the form of

\[
T = 1 + t_1 z^{-1} + t_2 z^{-2} + t_3 z^{-3}
\]

where \( t_1, t_2, t_3 \) and \( a_1, a_2, b_0 \) are the tuning parameters of STPID controller. To estimate these parameters, genetic algorithm (GA) which has been described elsewhere\textsuperscript{17,19} was used. GA with the optimum parameters predetermined was used to select optimum STPID control parameters \( K_c, \tau_d, \tau_l \) within the given ranges. STPID control algorithm with these parameters was implemented in the experimental system to obtain polystyrene.
Materials used

Styrene (Merck) and nanosilica particles with specific gravity of 2.2 and particle size of 10 nm were used as supplied. Benzoyl peroxide (Merck) and toluene (Merck) were used as the initiator and solvent respectively. Benzoyl peroxide was recrystallised using chloroform (Merck) and methanol (Merck).

Polystyrene production

Polymerization of styrene was carried out in a cylindrical glass jacketed reactor of 1000 mL with a dished bottom equipped with a heater, thermocouples, condenser and impeller. Nitrogen is bubbled from the bottom through the reaction mixture to keep oxygen out of the reactor. Temperature of the reactor was measured by a thermocouple and was transferred into a computer through A/D converters. A thyristor unit manipulated the power of the heater to maintain the temperature on the optimal path according to the signals coming from the computer. Temperature control of the reactor was carried out by using STPID controller implemented into the experimental system. The temperature and the heat manipulated were monitored on the computer VisiDAQ main screen. Figure 1 shows the experimental system. The reactor was first charged with 70-30 (v/v) styrene-toluene solution. This mixture was heated to the calculated optimum reactor temperature. Then the initiator was poured to start the polymerization. During the experiments, 5 mL of samples were taken from the reactor at intervals of 15 min. Monomer conversion and molecular weights of these samples were determined by use of precipitation method and Ubbelohde viscometer respectively. Polystyrene obtained in this reactor with STPID control and without control was used in the preparation of nanocomposites.

Composite preparation

Nano-silica particles were added into the polystyrene toluene solution obtained in the reactor. The added silica was adjusted as 0, 3, 5, 7% by weight relative to styrene. To obtain a homogeneous dispersion of the nanosilica particles, this mixture was stirred at 300 rpm for 10 min with a high speed stirrer and kept in ultrasonic bath. To remove the solvent toluene, this solution was poured in a petri dish and then dried first under ambient conditions followed by in an oven under vacuum at 120°C for 3 h. At the end, composite plates with a diameter of 25 mm and a thickness of 2 mm were obtained and used for thermal and mechanical testing. Before testing, these plates were dried in an oven for 12 h at 80°C. For comparison, similar composite materials were prepared from the polystyrene obtained in the same reactor without control. For reference, pure polystyrene (PS) was also treated in the same way.

Characterization and measurement

Thermogravimetric analyses were carried out at a heating rate of 10 °C/min under nitrogen atmosphere from 25°C to 600°C by using Setaram Setsys Evolution 1750 thermal analyzer. DSC measurements were carried out on Setaram Setsys Evolution 1750 DSC analyzer.

The surface morphologies of composite materials were examined with SEM JEOL6360 model scanning electron microscope after having been coated with gold.

Mechanical properties were determined by means of hardness tests. Shore D hardness test was carried out using a Durotech-M202 hardness tester.

Results and Discussion

To increase the quality of polymer product and ensure reproducibility, it is necessary to control precisely the polymerization reactor. Process optimization can also have a significant strategic impact on polymerization process economy. The molecular properties such as molecular weight are easily affected from the operating conditions. For this reason, the optimum conditions and optimum temperature path to reach desired polymer properties ($M_{nd}=52000$ and $X_{d}=50\%$) evaluated using
Hamiltonian optimization method\textsuperscript{20} were used in this work. These optimum conditions are given below:

- \( M_0 (\text{mol/L}) : 6.092 \)
- \( I_0 (\text{mol/L}) : 0.015 \)
- \( T_{R, \text{first}} (\degree C) : 92.7 \)
- \( t_f (s) : 10200 \)
- \( X_d (%) : 50 \)
- \( M_{\text{nd}} (\text{g/mol}) : 52000 \)
- \( T_{ci} (\degree C) : 21 \)
- \( T_{co} (\degree C) : 76 \)
- \( v_c (\text{mL/s}) : 0.5 \)
- \( Q (\text{kW}) : 75 \)

In order to accomplish temperature control of the polymerization reactor by STPID controller, the control parameters were found by GA\textsuperscript{17}. The best STPID Armax model parameters \((a_1, a_2, b_0, t_1)\) were determined by using optimum GA parameter values \((N=40, p_c=60\%, p_m=7\%\) and \(M=30)\) chosen among the generations after a number of executions with different values of parameters. These STPID model and tuning parameters are: \(a_1 (0.04037)\), \(a_2 (0.24730)\), \(b_0 (0.00073)\), and \(t_1 (-0.28824)\).

Later STPID control algorithm was implemented in the experimental system and polystyrene with desired properties was obtained under the optimal conditions. The same experiment without control was also repeated to compare the results. The temperature changes of reactor with control and without control were shown in Fig. 2. Figure shows that the agreement between theoretical and experimental results is very satisfactory and control shows a good performance. For the samples without control, there is a temperature increase of 26 \(\degree C\) at about 1000s (Fig. 2). The response produces larger overshoots and more oscillations. The experimental conversions and average molecular weight values measured by sampling successively during the experiments are given in Table 1. The polymer product has a molecular weight of 55000 under control and 47000 without control. These experimental findings show that the polymer product with desired properties are obtained in minimum time by operating the batch jacketed reactor at optimum conditions under STPID control with GA.

The composites were prepared by using two different polystyrene: polystyrene obtained with control and without control. Polystyrene/nano-silica composites with different silica contents are visualized in SEM images to show the distribution of the silica particles in the matrix (Fig. 3). There is a marked difference in surface topography between pure PS and PS nanocomposites.

Figures 4 and 5 present TGA and DSC results of pure polystyrene produced under control and polystyrene/nano-SiO\textsubscript{2} composite with 7 wt\% SiO\textsubscript{2} content obtained under the same conditions respectively. Final weight loss of pure PS and nanocomposite is 100\% and 90\% respectively. For pure PS, 100\% weight loss observed between 364 \(\degree C\) and 431 \(\degree C\) is attributed to the decomposition of

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conversion</th>
<th>Molecular weight</th>
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<tr>
<td>Desired</td>
<td>50</td>
<td>52000</td>
</tr>
<tr>
<td>STPID control</td>
<td>63</td>
<td>55000</td>
</tr>
<tr>
<td>Without control</td>
<td>75</td>
<td>47000</td>
</tr>
</tbody>
</table>

Table 1—Experimental conversions and number of average molecular weight values

Fig. 2—Temperature profile for the polymerization with control and without control

Fig. 3—SEM photographs of PS composites with 5\% nano-silica obtained (a) with control, (b) without control and (c) pure PS
polystyrene. The polystyrene/nano-silica composite shows an increase in the initial degradation temperature of 27 °C from 364 °C for pure polystyrene to 391 °C for nanocomposite with 7 wt% of nano-SiO₂. The thermal stability of the nanocomposites and PS obtained without control has also been studied by TGA. Nanocomposites obtained show higher thermal stability when compared to the pure polystyrene. Nanocomposites obtained with control also exhibit a remarkable increase in thermal stability when compared to the nanocomposites obtained from the polystyrene prepared without control. For uncontrolled samples degradation temperature changes from 360 °C for pure PS to 382 °C for nanocomposite with 7% silica. The degradation temperatures of the composite materials are summarized in Table 2.

The thermal stability of the nanocomposites with control and without control systematically increases with increasing silica content. Pure polystyrene samples obtained with control have 4-5 °C higher decomposition temperature than that of polystyrene obtained without control. This difference for nanocomposites obtained from the polystyrene prepared with control and without control is about 9-11 °C. This result shows the effect and importance of the precise control on the properties of polystyrene and therefore on the nanocomposite material. DSC analysis shows that the melting behaviour of the nanocomposites changes and glass temperature of materials increases. As it is observed from thermograms (Figs 4 and 5), the endothermic peak for pure PS is observed at 430 °C, and that for nanocomposite with 7 wt% silica content at 444 °C.

Mechanical properties were determined by means of hardness. The hardness increases linearly with increasing silica content. The curves obtained for the use of polystyrene with control and without control show similar trends. Hardness is higher for the nanocomposites obtained from the polystyrene with control.

All the PS-silica nanocomposites are transparent and there is no change in color. It may be due to the well-dispersibility of silica in polystyrene matrix and nano size of silica. SEM micrograph also confirms the good dispersion of silica particles in the polystyrene matrix and as a result of this dispersion there is a change in the surface morphology.

### Conclusion

Nanocomposites of polystyrene with different loading of silica fillers with 10 nm diameter have been prepared by using two different polystyrene materials. As expected, the hardness and thermal stability of these composite materials increase with silica content. It is also observed that higher hardness and thermal stability values are observed for the composites prepared by using PS obtained with control. So, accurate control of operating conditions...
and product, and automation of process can be of great benefit to industry in producing polymeric and nanocomposite materials.

**Nomenclature**

- $e(t)$ : Error signal
- $I_o$ : Initial initiator concentration, mol/L
- $K_c$ : Proportional gain
- $M$ : Maximum number of generation
- $M_o$ : Initial monomer concentration, mol/L
- $M_{nd}$ : Desired number-average molecular weight
- $N$ : Population size
- $Q$ : Heat given from the electrical heater, kW
- $p_c$ : Probability of crossover
- $p_m$ : Probability of mutation
- $r(t)$ : Set point
- $T_R$ : Reactor temperature, °C
- $T_{ci}, T_{co}$ : Inlet and outlet coolant temperature, °C
- $t_f$ : Polymerization time, s
- $\tau_d$ : Derivative time
- $\tau_I$ : Integral time
- $u(t)$ : Controller output
- $v_c$ : Coolant flow rate, mL/s
- $X_d$ : Desired monomer conversion
- $y(t)$ : Process output

**References**