Preparation of polystyrene/montmorillonite nanocomposites: optimization by response surface methodology (RSM)

S. Erdem YALÇINKAYA[1], **Nuray YILDIZ**[1,*], **Mehmet SAÇAK**[2], **Ayla ÇALIMLI**[1]

[1]*Ankara University, Faculty of Engineering, Department of Chemical*
Engineering, 06100 Tandoğan, Ankara-TURKEY
e-mail: nyildiz@eng.ankara.edu.tr
[2]*Ankara University, Faculty of Science, Department of Chemistry,*
06100 Tandoğan, Ankara-TURKEY

Preparation of polystyrene (PS)-montmorillonite nanocomposites was carried out in 3 steps: purification and determination of the cation exchange capacity (CEC) of clay, synthesis of organoclay, and preparation of nanocomposites. In organoclay synthesis, 3 types of surfactants, long-chained (cetyltrimethylammonium bromide (CTAB)), short-chained (tetraethylammonium bromide (TEAB)), and ringed (benzyltriethylammonium bromide (BTEAB)), were used. Gallery distances of pure clay and organoclays (CTAB-O, TEAB-O, and BTEAB-O) were determined by X-ray diffraction (XRD) analysis as 1.25, 2.09, 1.52, and 1.63 nm, respectively. Preparation of nanocomposites was carried out by in situ polymerization. Composites, containing 2%, 4%, and 6% organoclay by mass, were characterized by XRD, thermogravimetric analysis (TGA), gel permeation chromatography (GPC), and transmission electron microscope (TEM). The synthesized nanocomposites showed an exfoliated structure and a higher decomposition temperature in comparison with pure PS. A new approach was tried in nanocomposite preparation using response surface methodology (RSM).

Key Words: Montmorillonite, organoclays, polymer, polystyrene, nanocomposites, RSM.

---

*Corresponding author

Introduction

Polymer-clay nanocomposites are one of the newest composite types. Their importance has mainly been understood after the year 2000. Polymers are used as a matrix in these types of composites, and clay minerals act as reinforcement material. By combining these 2 different structures, new materials can be synthesized that have better physical and chemical properties according to their components. This inspiring idea first came from Toyota scientists in their pioneering work. [1,2] By combining a polymer matrix with relatively low clay loadings, they achieved composites that had higher thermal stability and improved mechanical properties.

Different types of clay are present in nature that can be used in polymer-clay nanocomposite preparation. In general, a montmorillonite (MMT)-type mineral found in bentonite clay is used in nanocomposite preparation. MMT is a smectite-type clay and has a layered structure, in which reside exchangeable Na^+ and Ca^{++} cations. Layers are made of an octahedral (O) sheet and 2 tetrahedral (T) sheets. These sheets form a TOT structure and are called a clay layer; its thickness ranges between 0.96 and 1.50 nm. The width and length of an MMT layer can be a few hundred nanometers. [3] The most crucial property in the synthesis of polymer-MMT nanocomposites is the dispersion of clay layers in the polymer matrix. Since the monomer is organic and MMT is inorganic, good dispersion seems impossible without further modification of MMT. In order to achieve this goal, the interlayer distance of the MMT layers must be enlarged by other means, thus increasing the hydrophobicity of clay. This process is done by exchanging inorganic cations with larger organic cations in the MMT layers. [4] Through an ion exchange reaction of ammonium salts between the inorganic cations that reside between the MMT layers, organophilization is carried out. At the end of this reaction, organophilic MMT, which has a higher hydrophobicity degree and a higher interlayer distance, is obtained.

The type of composite is determined by the distribution of MMT layers in the polymer matrix. There are 3 types of composites that can be formed. The first is a traditional microcomposite that can be formed if the interlayer distance of clay remains unchanged. The others types are both nanocomposites. If the interlayer distance increases but the layer morphology remains unchanged, an intercalated nanocomposite structure is obtained. The other type of nanocomposite is the exfoliated structure, which can only be obtained if the clay layers totally disperse in the polymer matrix. The nanocomposite preparation can be carried out in various ways: exfoliation-adsorption, bulk polymerization, melt intercalation, and template synthesis. [5] Each method has its advantages and disadvantages.

Scientists have attempted much research in order to prepare intercalated or exfoliated PS-clay nanocomposite structures. This type of nanocomposite preparation was primarily performed by bulk polymerization, solution polymerization, and melt intercalation. Chigwada et al. [6] used both the melt intercalation and bulk polymerization methods. Intercalated composites were obtained with bulk polymerization, but they reported no change in the intergallery distance of composite prepared with melt blending. Jang et al. [7] used montmorillonite- and hectorite-type clays to synthesize nanocomposites. They synthesized intercalated nanocomposites with both types of the clays by using bulk polymerization. Xie et al. [8] prepared PS-clay nanocomposites with solution polymerization; exfoliated nanocomposite structure is obtained with this method. Different from the works above, Zhong et al. [9] and Fu et al. [10] used reactive surfactants in order to prepare organoclay. They stated that using reactive surfactants made exfoliation easier. Usage of an organoclay with an intergallery distance of 1.64 nm, which is a relatively low value for an organoclay, and successful preparation of exfoliated nanocomposites showed that reactive surfactants make preparation of exfoliated nanocomposites easier. [9] All the works above

prepared either exfoliated or intercalated nanocomposites and all had better thermal and physical properties than pure PS.

In this study, preparation of polystyrene-MMT nanocomposites was attempted by using 3 types of modified organoclays in order to study the effects of surfactant type. Long-chained (cetyltrimethylammonium bromide (CTAB)), short-chained (tetraethylammonium bromide (TEAB)), and ringed (benzyltriethylammonium bromide (BTEAB)) surfactants were chosen for organoclay synthesis. The bulk polymerization method was used for nanocomposite preparation. Characterization was done by X-ray diffraction (XRD), transmission electron microscopy (TEM), gel permeation chromatography (GPC), and thermogravimetric analysis (TGA). After the characterization of prepared nanocomposites, a new approach was tried using response surface methodology (RSM). RSM is a statistical method for various processes using specially designed experimental programs in order to achieve the desired response. The prepared composites were thermally characterized by TGA. By using experimental results from TGA, a mathematical model of the nanocomposite preparation process was obtained.

Materials and methods

Natural clay (Reşadiye, Tokat, Turkey) was provided by Karakaya Bentonit A.Ş. Methylene blue was purchased from Sigma-Aldrich Chemical Co. Cetyltrimethylammonium bromide (CTAB), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (BTEAB), and styrene were purchased from Fluka. Methanol and toluene were purchased from Riedel-de Haën. Benzoyl peroxide and chloroform were purchased from Merck. Benzoyl peroxide was recrystallized in chloroform and methanol mixture before use. All other chemicals were used as received.

Experiments were carried out in 3 steps: purification and determination of the cation exchange capacity (CEC) of the natural clay, organoclay synthesis, and PS-MMT nanocomposite preparation. Response surface methodology (RSM) was used to investigate the effects of clay percent and polymerization time on mass loss temperature of the nanocomposite.

Purification and CEC determination

For precipitation of impurities, 10 g of natural clay was dispersed in 1 L water. After 24 h of decantation process, impurities were separated from the clay-water mixture by filtration. The suspension was centrifuged at 5000 rpm for 15 min and then filtrated in order to separate the precipitated clay minerals. Pure montmorillonite mineral was obtained by removing the liquid part of the suspension in a vacuum oven for 24 h. The CEC of the MMT was determined by the methylene blue test (ANSI/ASTM C837-76).

Organoclay synthesis

For synthesis, 10 g of pure MMT was dispersed in 800 mL of water under continuous stirring. The surfactant solution was prepared in 200 mL of water in a separate container. The amount of surfactant added was calculated with the CEC value (110 meq/100 g clay) of MMT, and it was 2% higher than the exact amount by mass. The calculated amount was added to 200 mL of water in the separate container and was dissolved by continuous stirring. After this, homogeneous surfactant solution was added to the dispersed MMT solution.

After continuous stirring for 4 h, the resulting product was separated by centrifugation and washed with deionized water 3 times. Synthesized organoclay was dried in a vacuum oven for 48 h and ground into a powder. For nanocomposite preparation, particles smaller than 75 μm were collected and stored in a desiccator.

The mentioned steps were carried out for CTAB, BTEAB, and TEAB surfactants. In Figure 1, molecular structures of each surfactant are shown. Synthesized organophilic products (organoclays) were marked as CTAB-O, BTEAB-O, and TEAB-O.
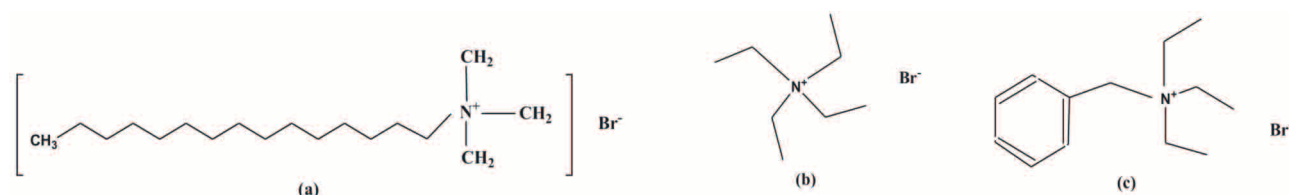

Figure 1. a) Long-chained CTAB surfactant, b) short-chained TEAB surfactant, c) ringed BTEAB surfactant.

Nanocomposite preparation

Nanocomposite preparation was carried out in a polymerization tube of 50 mL. The desired amount of organophilic MMT was weighed and dispersed in 2 mL of styrene monomer. The mixture was stirred for 1 h. After obtaining a homogeneous organophilic MMT-styrene mixture, benzoyl peroxide (1.5% by weight of styrene) was added to the tube and the mixture was stirred for 15 min. After mixing, the polymerization tube was kept in a water bath at 80 °C for 4 h without stirring. At the end of polymerization, the composite was removed from the tube and crushed. After the polymerization and crushing, the samples were put in a vacuum oven for 24 h at 80 °C. For comparison, pure PS was also obtained as described above without adding the organophilic MMT.

Experimental design with RSM

Response surface methodology (RSM) consists of a group of empirical techniques devoted to the evaluation of relations existing between a cluster of controlled experimental factors and the measured responses according to one or more criteria.[11,12]

The effects of 2 variables, organoclay content and polymerization time, on the preparation of the nanocomposite were studied using RSM. The most common experimental design used in RSM is the central composite design (CCD), which has equal predictability in all directions from the center.[13] According to the CCD, the total number of combinations is $2^k + 2k + n_0$, where k is the number of independent variables and n_0 is the number of repetitions of the experiments at the center point.[14] The range and the levels of the variables investigated in this study are shown in Table 1. On the basis of preliminary experiments, the ranges of organoclay content and time were chosen as 2%-6% and 3-5 h, respectively.

The response of the system was expressed by the following second degree polynomial equation:[13]

$$Y = B_0 + \sum_{i=1}^{n} B_i x_i + \sum_{ij} B_{ij} x_i x_j + \sum_{j=1}^{n} B_{jj} x_j^2, \tag{1}$$

where Y is the predicted response and 2 variables are involved; hence, n takes 2 in this study. Thus, by substituting the value 2 for n, Eq. (1) becomes:

$$Y = B_0 + B_1 x_1 + B_2 x_2 + + B_{12} x_1 x_2 + + B_{11} x_1^2 + B_{22} x_2^2 + \varepsilon, \tag{2}$$

where x_1 and x_2 are input variables, B_0 is a constant, B_1 and B_2 are linear coefficients, B_{12} is the interaction coefficient, B_{11} and B_{22} are quadratic coefficients, and ε is the experimental error.

Table 1. Coded value of independent variables and experimental ranges.

Factor	Name	Coded lower limit	Coded higher limit	Real lower limit	Real higher limit
X_1	Clay percent, %	-1	1	2	6
X_2	Time, h	-1	1	3	5

In this study, a 2^2 full factorial central composite design for 2 independent variables each at 5 levels with 5 axial points (with an axial distance of ± 1.40) and 5 replicates at the center points was employed to fit a second-order polynomial model, which indicated that 13 experiments were required for this procedure (Table 2). To study the thermal improvement via response surface methodology, 50% of the mass loss temperature of the nanocomposites was chosen as the response variable. Design Expert software (version 6.0.6, Stat-Ease, Inc., Minneapolis, USA) was used for regression and graphical analysis of the data obtained. The fit of the regression model was checked by the adjusted coefficient of determination (R_{Adj}^2). The statistical significance of the model was determined by the application of Fisher's F test.

Table 2. Experimental design and real values.

Experiment no.	X_1	X_2	Clay percent, %	Time, h	Temperature, °C
1	-1.41	0	2	3	409
2	-1	-1	6	3	427
3	1	-1	2	5	421
4	0	0	6	5	424
5	1	1	1.17	4	413
6	1.41	0	6.83	4	428
7	0	0	4	2.59	415
8	-1	1	4	5.41	420
9	0	0	4	4	425
10	0	1.41	4	4	426
11	0	0	4	4	427
12	0	-1.41	4	4	425
13	0	0	4	4	431

Characterization

Pure clay, organoclays, and nanocomposites were analyzed by XRD, TGA, GPC, and TEM.

X-ray diffraction (XRD)

Pure clay, organoclay, and nanocomposites were analyzed with a Rigaku D/Max 2200 X-ray diffractometer. The device was operated with a Cu X-ray source ($\lambda = 1.54$ Å).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed with a Shimadzu DTG-60. Temperatures increased from 20 to 600 °C with a 15 °C/min heating rate under inert N_2 atmosphere.

Gel permeation chromatography (GPC)

The molecular weight measurements were performed with an Agilent 1100 GPC-RID. PSM60-S and PSM1000-S analytical columns were used. Before GPC analysis, nanocomposites were dissolved in toluene in order to remove clay platelets. The device was calibrated with various PS standards. The mobile phase was tetrahydrofuran.

Transmission electron microscopy (TEM)

TEM images were obtained with a LEO 906 E TEM device. The operating voltage was 100 kV. Nanocomposites were cut to 70 nm with a Leica Ultracut model ultratome. After cutting, samples were placed on copper grids for examination.

Results and discussion

The CEC of natural clay was found to be 110 meq/100 g clay. This is a relatively high value for montmorillonite-type minerals. In previous studies, similar CEC results were found with the same type of clay.[15]

Characterization of organoclay

Various organoclays were synthesized with CTAB, BTEAB, and TEAB surfactants. One of the most important properties of layered silicates is the intergallery distance (d_{001}) between the clay layers. This distance can be calculated with data gathered from X-ray diffraction.

The X-ray diffractogram of natural MMT is shown in Figure 2a. The peak point was at 6.898° and the intergallery distance of clay was determined to be 1.25 nm.

X-ray diffractograms of 3 organoclays are shown in Figure 2b. The interlayer spacings of the organoclays changed with the quaternary ammonium cations used in synthesizing. The interlayer spacings of CTAB-O, BTEAB-O, and TEAB-O organoclays were determined as 2.09, 1.63, and 1.52 nm, respectively. The largest interlayer spacing was obtained for CTAB-O organoclay. These results showed similarities with those organoclays in the literature that were synthesized with the same surfactants.[16,17]
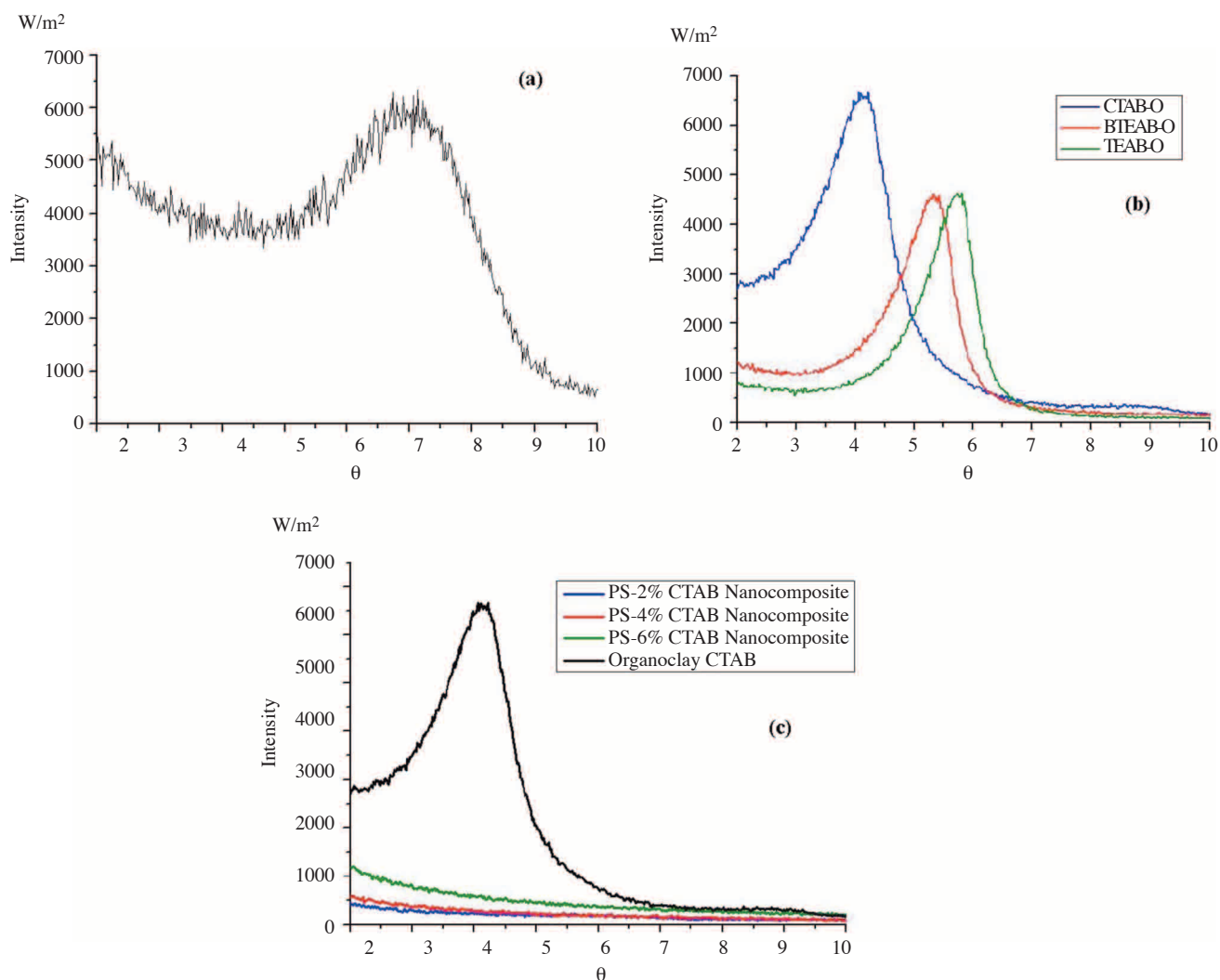
Figure 2. XRD spectra of a) natural clay, b) synthesized organoclays, c) CTAB-O organoclay and nanocomposites containing 2%, 4%, and 6% CTAB-O organoclay.

Characterization of nanocomposite

The type of nanocomposite was determined by XRD analysis. In Figure 2c, XRD spectra of CTAB-O organoclay and nanocomposites containing 2%, 4%, and 6% CTAB-O organoclay by mass are shown. There were no visible peaks in any of the nanocomposites. Absence of a diffraction peak means that the former layered crystal structure was changed into an exfoliated structure. Clay layers were exfoliated perfectly in the PS matrix. For nanocomposites prepared with BTEAB-O and TEAB-O surfactants, a good level of dispersion was not achieved in styrene medium. It is thought that the degrees of hydrophobicity of both organoclays were not high enough for them to perfectly disperse in highly hydrophobic styrene. In Figure 3, each organoclay can be seen in styrene medium. As seen in the figures, CTAB-O was perfectly dispersed in the medium while others were not.
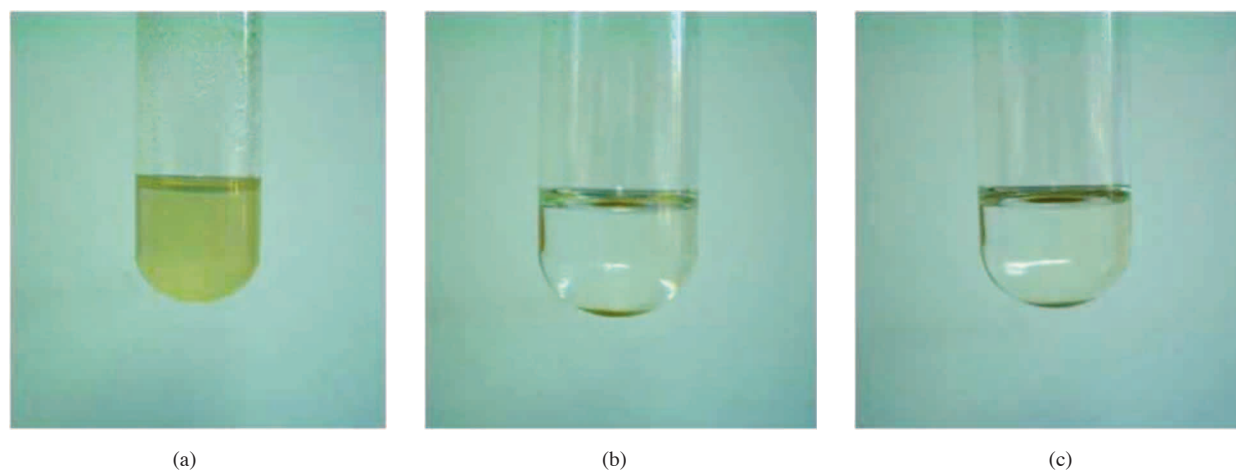
587

(a) (b) (c)

Figure 3. a) CTAB-O styrene mixture, b) BTEAB-O styrene mixture, c) TEAB-O styrene mixture.
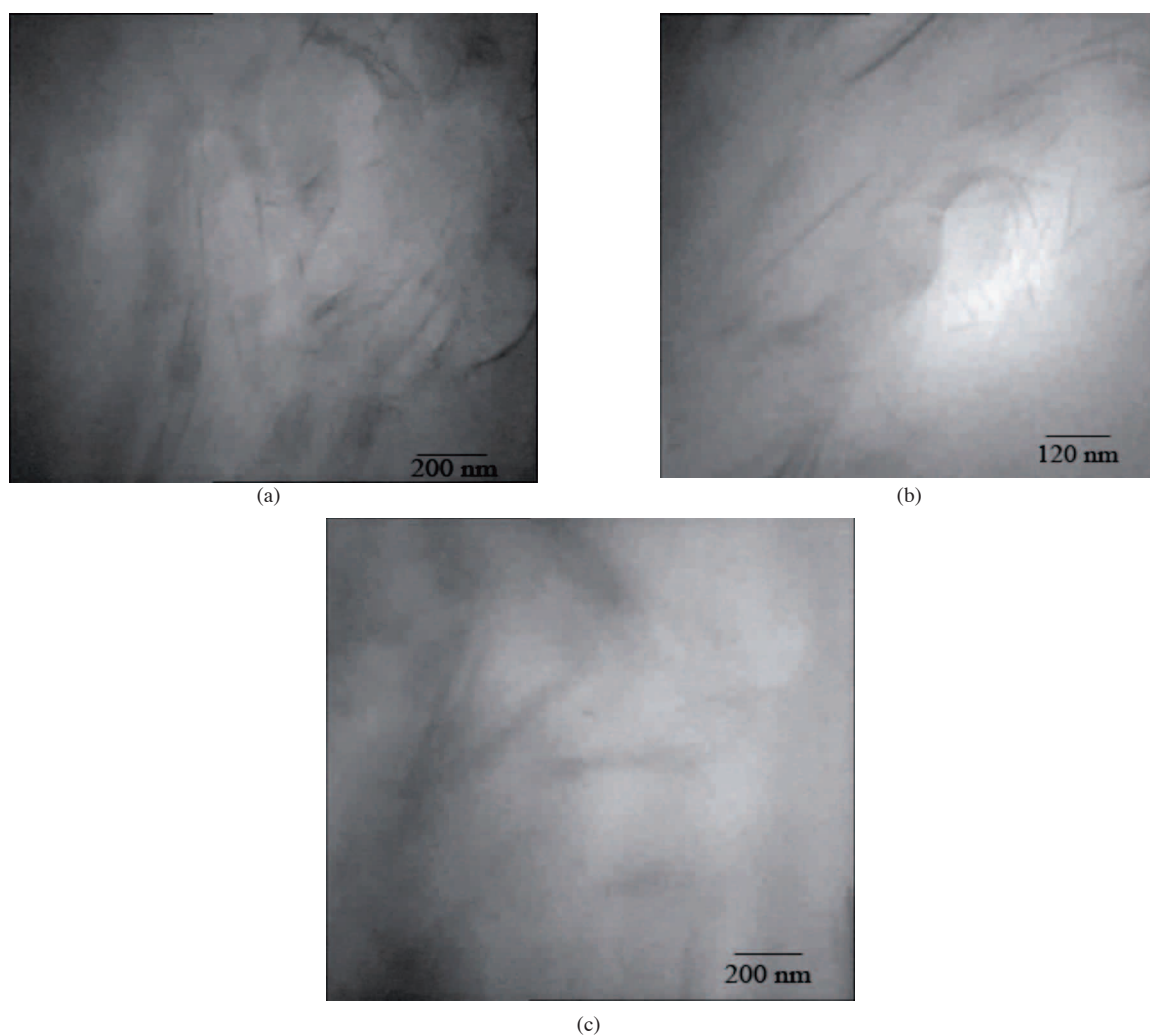

(a) (b)

(c)

Figure 4. TEM images of a) PS-2% CTAB-O, b) PS-4% CTAB-O, c) PS-6% CTAB-O.

Figure 4 shows TEM images of nanocomposites containing 2%, 4%, and 6% CTAB-O organoclay by mass. Dark lines are MMT layers dispersed in the polymer matrix. All of the images show that exfoliated MMT structure was obtained. TGA curves of pure PS and prepared nanocomposites can be seen in Figure 5. It is clearly seen that the decomposition temperature of the composite increases with increasing MMT content. Nanosized MMT layers prohibit the decomposed chemicals from moving away from the system, thus increasing the decomposition temperature.[18]
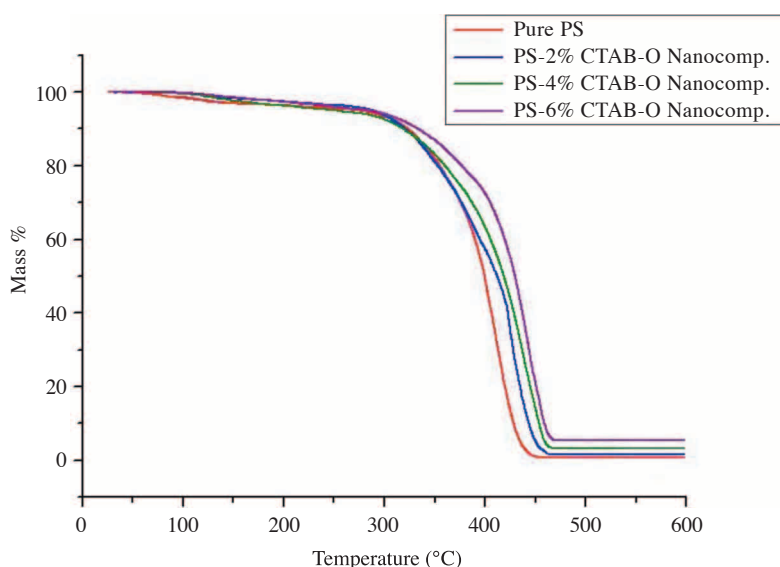

Figure 5. TGA curves of pure PS and nanocomposites.

Table 3 shows the 50% mass loss temperatures of the nanocomposites and pure PS. With increasing clay content of composites, 50% mass loss temperature improved by about 30 $^\circ$C, comparing pure PS to 6% PS-clay nanocomposite. These results are in agreement with previous studies.[10,17] Another crucial set of data can be seen from the graph by looking at the mass that remained at a constant temperature. The mass of the products that remained at 400 $^\circ$C is shown in Table 3. Comparing the pure PS with 6% PS-clay nanocomposite, it is seen that increasing the clay content slows down the thermal degradation of the nanocomposites. GPC results are shown in Table 3. M_n is the number average molecular weight and M_w is the weight average molecular weight value. HI is the polydispersity index of polymers. The results showed that there was no significant molecular weight difference between pure PS and PS in the nanocomposites. Zhong et al.[9] have found that the molecular weight of a polymer decreases with increasing clay content due to the high viscosity environment. There are also reports in which the molecular weight of a polymer in composite decreases[19] or stays constant.[20] This difference can be caused by the viscoelastic properties of clay from different origins.

Response surface method (RSM)

Experimental design was done with Design Expert software, version 6.0.6. After evaluating the data gathered from the design, a quadratic model was suggested. Acceptability of the suggested model was confirmed with variance analysis (ANOVA).

Table 3. Thermal properties and molecular weight data of pure PS and PS in the nanocomposites.

Sample	50% mass loss temperature (°C)	Remained mass percent (%)	M_n (g/mole)	M_w (g/mole)	HI
Pure PS	403	49	32000	82000	2.5
PS-2% CTAB-O nanocomposite	417	57	26,000	87,000	3.3
PS-4% CTAB-O nanocomposite	424	62	35,000	88,000	2.5
PS-6% CTAB-O nanocomposite	432	72	29,000	84,000	2.8

Variance analysis results are shown in Table 4. A P > F value lower than 0.05 shows conformity of model parameters. According to the ANOVA results, clay percent, time, square of clay percent, and square of time are the determining parameters. Since 2 parameters were investigated, there is only 1 internal coefficient, which is the clay percent-time interaction. Its P > F value is lower than 0.05, so this coefficient is also a determining parameter for the suggested model. The standard deviation of the model is 2.01.

Table 4. ANOVA results of the suggested model and coefficients calculated by the least squares method.

Parameter	F-value	P > F	Calculated coefficient	Degree of freedom	Standard deviation
Constant	23.60	-	426.80	1	0.90
X_1	54.91	0.0001	5.28	1	0.71
X_2	7.96	0.0257	2.01	1	0.71
X_1^2	13.81	0.0075	-2.84	1	0.76
X_2^2	32.26	0.0008	-4.34	1	0.76
$X_1 X_2$	13.87	0.0074	-3.75	1	1.01
Model	23.60	0.0003	-	-	-
Lack of fit	0.19	0.8959	-	-	-
Standard deviation	-	2.01	-	-	-
R^2	-	0.9440	-	-	-
Adj. R^2	-	0.9040	-	-	-

R^2, the regression coefficient, shows the interaction between the chosen independent variables and suggested model. In this model, the R^2 value was found to be 0.9440, and this indicates that only 5.6% of the nanocomposite preparation process was not explained by the model. The accuracy of the suggested regression model can be inspected with the F-value. The model's F-value was found to be 23.60. This value shows the acceptability of the model and also shows that there could be an error as large as the F-value with a probability of only 0.03%.

By comparing the P > F values shown in Table 4, it can be said that the clay percent (X_1) had the most crucial effect on temperature response. Effectiveness of the model parameters can be listed as clay percent

(X_1), square of time (X_2^2), square of clay percent (X_1^2), and time (X_2) in decreasing order according to the P > F value.

Model coefficients were calculated by the least squares method. The F-values, standard deviations, and degrees of freedom of coefficients are shown in Table 4.

The model of nanocomposite preparation is shown in Equation 6 in terms of coded variables:

$$Y = 426.80 + 5.28^* X_1 + 2.01^* X_2 - 2.84^* X_1^2 - 4.34^* X_2^2 - 3.75^* X_1^* X_2 \quad (3)$$

The results of analysis showed that the experimental values were significantly in agreement with the predicted values and also suggested that the model of Eq. (3) was satisfactory and accurate (Figure 6a). The plot of the quadratic model with the experimental ranges is shown in Figure 6b. The shape indicates that there was a significant interaction between the parameters of polymerization time and clay content. The 50% mass loss temperature increased with increasing the clay content from 2% to 6% PS-clay nanocomposite.
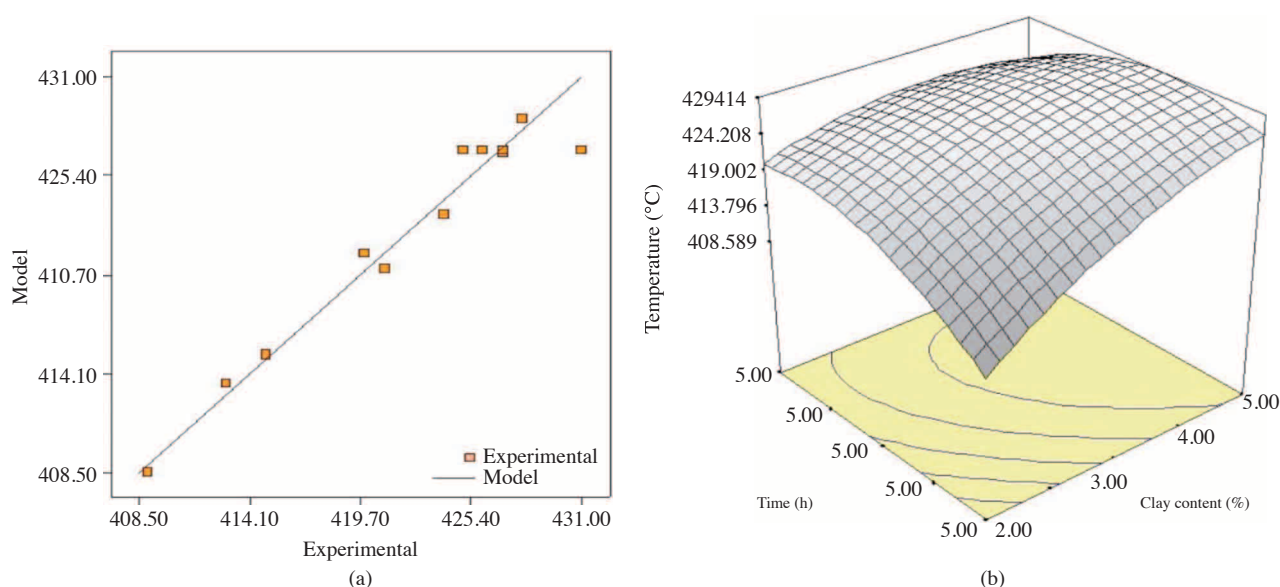

Figure 6. a) Model (predicted) versus experimental values in the preparation of nanocomposites, b) effect of polymerization time and clay content on decomposition temperature.

The optimum values of the variables were obtained by solving Eq. (6) using Design Expert software: 3.8 h and 6% clay percent, with 429 °C as the decomposition temperature. In order to verify this result, preparation of nanocomposite was carried out at optimum conditions. The experimental decomposition temperature was found to be 428 °C. This result showed us that the model prediction was performed successfully.

Conclusions

In this study, Reşadiye (Tokat, Turkey) bentonite was used to prepare PS-clay nanocomposites via bulk polymerization. Three types of organophilic MMT were used to prepare the composites. Nanocomposite preparation was attempted with each of the organoclays, but nanocomposites were obtained only with CTAB modified

organoclay because of the other 2 organoclays' inability to disperse in the styrene matrix. Nanocomposites were characterized with XRD, GPC, TEM, and TGA analysis. Exfoliated nanocomposite structure was achieved at 2%, 4%, and 6% clay loadings. Thermal properties were improved by increasing the clay content. Response surface methodology was used to model the polymerization system. For this, clay percent and polymerization time variables were chosen as independent variables. The 50% weight loss temperature was chosen as the response variable. With a series of specially designed experiments, a model was suggested and controlled by another experiment. The optimum conditions were 3.8 h and 6% clay, and the highest 50% weight loss temperature was 429 °C. The results showed that the modeling of the system was done successfully.

Acknowledgements

References

1. Usuki, A.; Kojima. Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. of Mater. Res.* **1993**, 8:1179-1184.

2. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T. *J. of Mater. Res.* **1993**, *8,* 1185.

3. Chamley H. *Clay Sedimentology*, Springer-Verlag, Berlin, 1986.

4. Okada, A.; Usuki, A.; Kurauchi, T.; Kamigaito, O. In *Hybrid Organic-Inorganic Composites*; Marck, J. E.; Lee, C. Y. C.; Bianconi, P. A., Eds.; ACS Symp. Series 585, 1995.

5. Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *28*, 1-63.

6. Chigwada, G.; Wang, D.; Jiang, D. D.; Wilkie, C. A. *Polym. Degrad. Stab.* **2006**, *91*, 755-762.

7. Jang, B.; Wilkie, C. *Polymer* **2005**, *46*, 2933-2942.

8. Xie, W.; Hwu, J. M.; Jiang, G. J.; Buthelezi, T. M.; Pan, W. P. *Polym. Eng. Sci.*, **2003**, *43*, 214-222.

9. Zhong, Y; Zhu, Z.; Wang, S. *Polymer* **2005**, *46*, 3006-3013.

10. Fu, X.; Qutubuddin, S. *Polymer* **2001**, *42*, 807-813.

11. Box, G. E. P; Wilson, K. B. *J. R. Stat. Soc.* **1951**, *B13*, 1-38.

12. Gao, Y.; Ju, X.; Qiu, W.; Jiang, H.; *Food Control* **2007,** *18*, 1250-1257.

13. Montgomery, G. C. *Design and Analysis of Experiments.* John Wiley and Sons, New York, 1997.

14. Muralidhar, R. V.; Chirumamila, R. R.; Marchant, R.; Nigam, P. *Biochem. Eng. J.* **2001**, *9*, 17-23.

15. Önal, M.; Sarıkaya, Y.; Alemdaroğlu, T. *Turk. J. Chem.* **2001**, *25*, 241-249.

16. Gönülşen, R.; Yıldız, N.; Çalımlı, A. *Adsorp. Sci. Technol.* **2003**, *21*, 135-147.

17. Essawy, H. A.; Bardan, A. S.; Youssef, A. M.; Abd El-Hakim, A. E. A. *Chem. Phys.* **2004**, *205*, 2366-2370.

18. Chen, G.; Liu, S.; Chen, S.; Qi, Z. *Macromol. Chem. Phys.* **2001**, *202*, 1189-1193.

19. Qi, R.; Jin, X.; Nie, J.; Yu, W.; Zhou, C. *J. Appl .Polym. Sci.* **2004**, *97*, 201-207.

20. Zhao, Q.; Samulski, E. T. *Polymer* **2006**, *47*, 663-671.