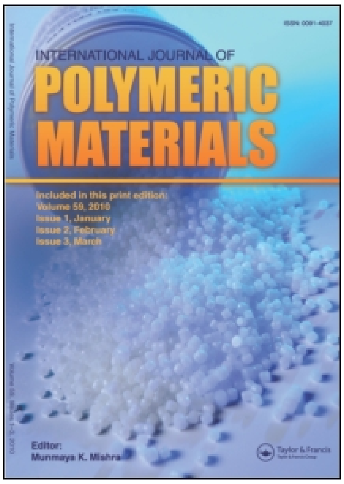

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EFFECT OF PROCESS VARIABLES ON THE INITIATION TEMPERATURE AND EXOTHERMIC HEAT FOR THE COPOLYMERIZATION OF ACRYLONITRILE AND METHYLACRYLATE-I

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EFFECT OF PROCESS VARIABLES ON THE INITIATION TEMPERATURE AND EXOTHERMIC HEAT FOR THE COPOLYMERIZATION OF ACRYLONITRILE AND METHYLACRYLATE-I

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Differential scanning calorimetry (DSC) experiments were carried out on a set of laboratory-synthesized copolymers of acrylonitrile/methylacrylate precursors meant for the manufacture of hollow-fiber carbon membranes. This was done to determine the effect of the polymerization process variables on the exothermic heat and exothermic initiation temperature. Factors such as methylacrylate monomer and azo-bis-isobutyronitrile (AIBN) initiator concentrations, stirrer speed and polymerization temperature were investigated as functions of the exothermic heat and the exothermic initiation temperature. An empirical approach was adopted that employed statistical experimental designs that were used to recognize analytical and statistical methods that translate the process responses into comprehensible terms. It was established that hollow-fiber carbon membranes can be reproducibly made by exercising very strict control over the polymerization conditions when using co-monomers of acrylonitrile (AN) and methylacrylate (MA). Process variables such as stirrer speed, polymerization temperature methylacrylate and azo-bis-isobutylonitrile concentrations influence the properties of the copolymer produced and hence the properties of any carbon membranes produced from a precursor manufactured from the copolymer. The effectes of the factors investigated, or the interactions of these factors on the variations observed in the initiation temperature, was rather inconclusive. This was ascribed to the unavoidable variation in the mass of the material used for the calorimetry experiments.

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Keywords: acrylonitrile, methylacrylate, exothermic heat, initiation temperature, stirrer speed, DSC

INTRODUCTION

Early literature on microporous activated carbon appeared in the 1940s. Activated carbon was initially prepared by carbonization and activation of organic materials, e.g. coconut shells, wood, peat and coal. In the 1950s, carbon molecular sieves were produced by the pyrolysis of various organic residues. In more recent times, microporous activated carbon has been widely and successfully used in the metallurgical field for the leaching of cyanides from gold [1]. Polymeric-based membranes (especially PAN-precursors) for separation processes and molecular transport phenomena have been extensively discussed in recent times [2–10]. It was recently discovered that an extensive microporous system could be developed in a solid carbon matrix by the selective oxidation of an inter-crystalline material of a suitable precursor [3,11]. Properties such as strong adsorption at low temperatures, activated diffusion defects, and molecular size and shape have selectively led to the development of molecular-sieve carbon for gas separations [4,5–9,12]. To produce carbon membranes by pyrolysis, the precursors must be of a type that yields no pores larger than those of sieving molecular dimensions [13]. Molecular sieve carbons have been obtained by pyrolysis of many thermosetting polymers, such as poly(furfuryl alcohol) [14], cellulose [15], cellulose triacetate [16], saran copolymers [17], polyacrylonitrile [3–5,11,18] and phenol formaldehyde [19]. Recently, a composite membrane exhibiting high stability and durability was reported by Kawai and Nogi [20]. This membrane has a low-porosity layer with enhanced separation properties, and a more porous layer which increases permeation rates through the composite membrane. Bauer and Marie [21] prepared carbon supports from a C-C composite material and adjusted the porous structure by impregnation with carbonized material. Schnidler and Maier [22] prepared carbon membranes from polyacrylonitrile treated with aqueous hydrazine solutions and from cellulose treated with a phosphoric acid solution. After treatment, the polymers were pre-oxidized at temperatures of 180°C to 350°C and carbonized at temperatures of 600°C to 3000°C. The resulting membranes had a narrow pore-size distribution. Alimova et al. [23] employed a method that involved the application of an active coating of carbon by vacuum thermal evaporation to the surface of poly(vinyltrimethylsilane) and obtained a layer thickness of between 500–700 Å. Ishiyama et al. [24] prepared Co and Ni catalysts in a carbon membrane by dispersing Co or Ni hydroxides in a cellulose acetate membrane in hydrogen at 450°C. The membrane pore structure is formed during the carbonization process by the emergence of organic gases within the carbon matrix, leading to a highly distorted carbon material. Various workers showed that the pore system consisted of pores with relatively wide openings and narrow constrictions [21,23]. Most of these constrictions were located near the outer surface of the carbon matrix and were created by surface oxides [25].

Various activation and carbonization techniques were used in attempts to demonstrate that gases permeate through the carbon membranes via a pore system of molecular dimensions. The pore system can be activated by either stationary or dynamic methods. In the stationary method, gas pressures are kept equal on both sides of the membrane. This method leads to the relatively slow creation of comparatively homogeneous pores. With the latter method, pressures on the two sides of the membrane are different. Although this method leads to a faster opening of the pores, it can be detrimental to the formation of a particular membrane configuration, since it also causes a breakdown in the molecular-sieve permselectivity. As soon as the pore dimensions become greater than those of the diffusing molecules, selectivity values correspond to the square root of the molecular masses, according to Knudsen diffusion [25]. A third method of activation involves the degassing of surface CO groups at high temperatures, which results in the formation of pores of intermediate size. This is done by evacuation at high temperatures (up to 400°C), which is effective for the opening of pores. At higher temperatures, pore closure by sintering takes place simultaneously with removal of surface oxygen groups: CO_2 and CO. Exposure to air must therefore be avoided [25].

In this paper, we examine the effect of polymerization variables (stirrer speed, polymerization temperature, methylacrylate and azobis-isobutyronitrile (AIBN) concentrations) on the exothermic heat and initiation temperature of polyacrylonitrile, PAN. This is to enable a clearer understanding of the prevailing factors (and their interplay) that influence the thermal properties of the PAN-precursor.

EXPERIMENTAL

Hollow-fiber carbon membranes were synthesized and spun into fibers, which were later stabilized and carbonized. The process variables that influence the exothermic heat and initiation temperature of the spun fibers were studied by DSC analysis. The responses to the process variables were statistically (using the "F-test" method) analyzed for the different treatment combinations.

SYNTHESIS OF AN/MA COPOLYMERS

The experimental set-up used for the copolymerization reaction of AN and MA is shown in Figure 1. The nitrogen inlet, condenser and overhead stirrer are connected to three of the outlets. The fourth outlet is used to introduce the reactants to the reactor. 270 g of dimethylformamide, DMF, 180 g of acrylonitrile, AN (which, before washing, contained the monomethyl ether of hydroquinone as a stabilizer, to prevent the monomer from polymerizing spontaneously at room temperature), and 2.46 g of methylacrylate, MA, were placed in the reactor together with 270 ml of distilled water. The stabilizer in the AN had to be removed before the monomer could be used in the polymerization reaction. This was done by washing the monomer with several equal volumes of dilute NaOH at 0°C. However, at this temperature 7.2 wt-% AN dissolves in the aqueous phase, while 2.1 wt-% of the water dissolves in the AN. Therefore, the required amount of AN

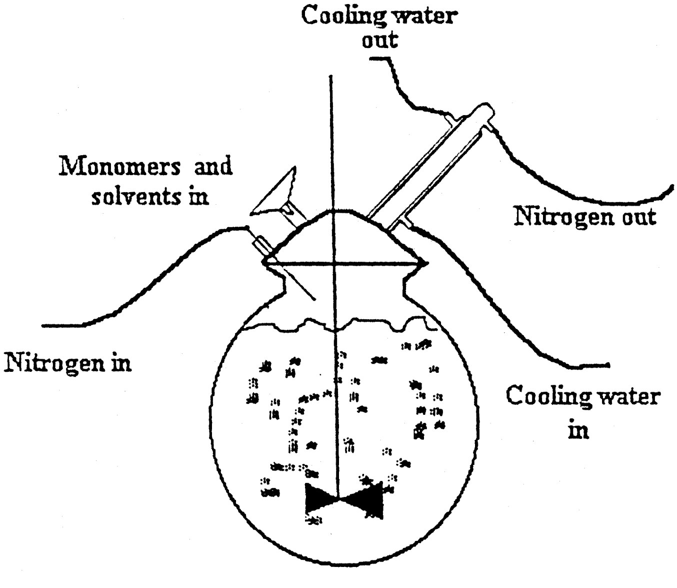

FIGURE 1 Polymerization reactor used for the reactions to prepare the AN/MA copolymers.

had to be calculated carefully, taking into account the amount lost in the washing process. The washed AN was dried overnight over calcium chloride pellets and filtered before being introduced to the polymerization mixture. The system was allowed to stabilize at 55°C before 1.35 g of the initiator, azo-bis-isobutyronitrile (AIBN), was added. After 20 minutes, polymer particles began to precipitate, causing the solution to become milky. As soon as precipitation started, a further 500–600 ml of distilled water was added to the polymerization mixture. The system was then left overnight, to ensure complete reaction. After cooling to room temperature, the copolymer was removed from the reactor and thoroughly washed with acetone (Saarchem Holpro, AR-grade). Following filtration, all the unreacted monomers, DMF and water were removed. The remaining DMF and water were removed after drying at 60°C in a vacuum oven.

FACTORIAL DESIGN FOR AN/MA COPOLYMERS

Factorial design is a very useful technique for the determination of the effects of several variables with very few experiments. The technique differs from the conventional methods used for the determination of the factors that influence a given process. In conventional methods, the variables are changed one at a time while the others are kept fixed. In a factorial design, all the factors are varied simultaneously in a planned fashion and their significance is determined statistically. Although the copolymerization of AN with MA has been investigated by others [25,26], no information is given on the factors that influence the copolymerization process and the properties of the copolymer. A screening design was therefore carried out for the copolymerization of AN and MA in a mixed solvent of water and DMF. To reduce the experimenting time, a fractional factorial design was employed. The process variables, each at two levels, were chosen and their significance on the copolymerization process studied. The process variables, with their coded letters, descriptions and levels are presented in Table 1. A half-factorial treatment of 4 factors at two levels is a 2^{4-1} factorial and requires 8 combinations of levels. There are four three-factor interactions (ABC, ABD, ACD and BCD), six two-factor interactions (AB, AC, AD, BC, BD and CD) and one four-factor interaction (ABCD). The two-factor interactions are divided into three pairs of aliases, e.g. AB = CD. To obtain valid estimates of the main effects, the three-factor interactions and the four-factor interactions can be neglected. Effects can, however, not be discarded out of hand, but they should rather be decided on in a rational manner. The interaction effects that will be neglected, in the sense that their effects will be

TABLE 1 Process Variables Used in the Factorial Design at Two Levels

Factor	Variable	Unit	Description	Level (*llf*)	Level (*hlf*)
A	Initiator	g	Amount of initiator	0.2625	0.4125
B	MA	g	Amount of MA or AN	0.6830	2.73
C	Temperature	°C	Polymerization temp.	60.00	70.00
D	Stirrer speed	rpm	Speed at which suspension is stirred	50.00	159.00

llf = low level factor, *hlf* = high level factor.

TABLE 2 The Complete Experimental Design, with Treatment Combinations Having a Half Replicate for a 2^4 Factorial

Standard run Order	Factor A	Factor B	Factor C	Factor D	Treatment Combination
1	*llf*	*llf*	*llf*	*llf*	–
2	*llf*	*llf*	*hlf*	*hlf*	CD
3	*llf*	*hlf*	*llh*	*hlf*	BD
4	*llf*	*hlf*	*hlf*	*llf*	BC
5	*hlf*	*llf*	*llf*	*hlf*	AD
6	*hlf*	*llf*	*hlf*	*llf*	AC
7	*hlf*	*hlf*	*llf*	*llf*	AB
8	*hlf*	*hlf*	*hlf*	*hlf*	ABCD

llf = low level factor, *hlf* = high level factor.

TABLE 3 Actual Amounts of Monomers and Solvents and the Polymerization Conditions Used for Polymerization Reaction

Run #, (Random order)	Run #, (Standard order)	DMF, g	AN g	MA, g	AIBN, g	Temp., °C	Stirrer Speed, rpm
2	1	54.04	36.02	0.27	0.21	60	1.0
7	2	54.02	36.02	0.27	0.21	70	3.5
3	3	54.01	36.04	1.02	0.21	60	3.5
8	4	54.00	36.00	0.34	0.21	70	1.0
1	5	54.12	36.00	0.24	0.33	60	3.5
5	6	54.02	36.00	0.25	0.331	70	1.0
6	7	54.00	36.01	0.99	0.336	60	1.0
4	8	54.00	36.00	0.98	0.33	70	3.5

DMF = Dimethylformamide, AN = Acrylonitrile, MA = Methylacrylate, AIBN = Azo-bis-isobutyronitrile.

confounded with the block effects, will be used to generate the different blocks of the factorial design. To enable an estimate of the main effects and the interaction effects independently, without entanglement, orthogonality in the design is important when grouping the treatment combinations together in the respective blocks. For this study, ABCD was used as generator for the experimental blocks, leading to the following sets of aliases: A ≡ BCD, AB ≡ CD, B ≡ ACD, AC ≡ BD, C ≡ ABD, AD ≡ BC and D ≡ ABC.

The complete experimental design, with treatment combinations, is shown in Table 2, while the amounts of monomers, solvents and the polymerization conditions are summarized in Table 3.

DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS

The copolymer samples were heated in a DSC from ambient temperature to 350°C at a heating rate of 20°C.min^{-1}, in a nitrogen stream flowing at a rate of 54.6 ml.min^{-1}. An average copolymer sample mass of 6.5 mg was used. In this study, analyses of the DSC data were done so as to determine the extent of exothermic reaction taking place during carbonization of the PAN precursors.

RESULTS AND DISCUSSION

Analysis of Variance

The totals of each of the main factors and the two factor interactions were obtained by subtracting the sums of the responses at the high levels from the sums of the responses at the low levels. The effect of each factor was then calculated by dividing each total by four

TABLE 4 Procedure for Perfoming the "F-test"

Treatment Combination	Total	Effect	Degrees of Freedom	Sum of Squares
A	104059.20	26014.8	1	13.50×10^8
B	52861.77	13215.4	1	3.49×10^8
C	− 107025.12	− 26756.3	1	14.30×10^8
D	63251.73	15812.9	1	5.00×10^8
AB ≡ CD	118493.57	29623.4	1	17.60×10^8
AC ≡ BD	111829.71	27957.4	1	15.60×10^8
AD ≡ BC	65637.30	16409.3	1	5.40×10^8
Total			7	75.00×10^8

TABLE 5 Response (Exothermic Heat) from the Treatment Combination

Treatment Combination	Degrees of Freedom	Sum of Squares	F-ratio	% Level of Significance
A	1	41.41	0.029	>10
B	1	3184.02	2.25	>10
C	1	2060.82	1.46	>10
D	1	1770.13	1.25	>10
AB ≡ CD	1	64.98	0.046	>10
AC ≡ BD	1	1200.50	0.85	>10
AD ≡ BC	1	2972.21	2.10	>10
Total	7	11294.07		

(the number of values for each sum). The sum of squares was calculated thus:

$$\text{Sum of Squares, SS} = (\text{Total of main factors})^2 \div 8. \tag{1}$$

The numerator in the equation correlated to the total number of experiments carried out. A single-sided "F-test" was performed on each of the treatment combinations to determine the probability of percentage level of significance. Each of the treatment combinations has only one degree of freedom and, therefore, the mean sum of squares is equal to the sum of squares. Table 4 gives a detailed procedure followed in performing the "F-test", while Tables 5–7 show the responses (exothermic heat, exothermic peak temperature and exothermic reaction initiation temperature) and the F-ratios resulting from the different treatment combinations. The calculated estimate of

TABLE 6 Response (Exothermic Peak Temperature) from the Treatment Combination

Treatment Combination	Degrees of Freedom	Sum of Squares	F-ratio	% Level of Significance
A	1	7.20	0.38	>10
B	1	10.19	0.54	>10
C	1	14.50	0.77	>10
D	1	0.78	0.04	>10
AB ≡ CD	1	0.96	0.05	>10
AC ≡ BD	1	32.68	1.73	>10
AD ≡ BC	1	23.09	1.22	>10
Total	7	89.40		

TABLE 7 Response (Exothermic Reaction Temperature) from the Treatment Combination

Treatment Combination	Degrees of Freedom	Sum of Squares	F-ratio	% Level of Significance
A	1	5.58	0.71	>10
B	1	2.60	0.33	>10
C	1	7.70	0.97	>10
D	1	0.03	0.004	>10
AB ≡ CD	1	3.95	0.50	>10
AC ≡ BD	1	13.94	1.76	>10
AD ≡ BC	1	5.85	0.74	>10
Total	7	39.65		

error variance is shown in Table 8. This error of variance was used to determine the F-ratio for each of the treatment combinations.

From the results of the "F-test", it became clear that none of the factors had a significant influence on any of the responses. The chance of being wrong when postulating that any one of the factors had a significant influence is greater than 10% in the case of each treatment combination for each of the responses. In statistical terms, this is very large. It must be remembered, however, that this is true only for the range in which each factor was varied. It can be concluded therefore, that although a factor does not have a significant effect, it can still have an influence on the various responses. The influence of the different process variables on the various responses was determined by comparing the sum of squares value of each treatment combination with that of the estimate of error variance. If the sum of squares value of a treatment combination is higher than that of the estimate of error

TABLE 8 Estimate of Error Variance for the Responses

Response	Estimate of error variance
Exothermic heat	1412.60
Exothermic peak temp.	18.91
Initiation temp.	7.90

Due to confounding, a true error variance can not be calculated. However, an estimate of the error of the variance can be assumed. This was done using the sum of squares of the two-factor interaction. This can be done because the two factor interactions are confounded with each other. The equation below shows how the estimate of error variance was calculated. The values of the SS used, are those in Table 7 above.

Estimate of error of variance = $SS(AB \equiv CD + AD \equiv BD + AD \equiv BC)/3$.

TABLE 9 Factors that Have Influence on the Responses

Response	A	B	C	D	AB ≡ CD	AC ≡ BD	AD ≡ BC
Exothermic heat		✓	✓	✓			✓
Exother. heat temp.		✓	✓			✓	✓

variance, then the factor is said to have an influence on the response. The discussion on the influence of each of the factors on the process responses was based on this assumption. Table 9 shows the factors that have influence in the case of each response.

A typical DSC trace of one of the 8 copolymer samples is shown in Figure 2. All other samples showed similar trends. The DSC results are shown in Table 10. The exothermic heat and initiation temperature obtained from the DSC analyses were used to interpret the significance of each of the factors of the fractional factorial design on the polymerization process. The DSC analyses were done in order to determine the extent of the exothermic reaction taking place during

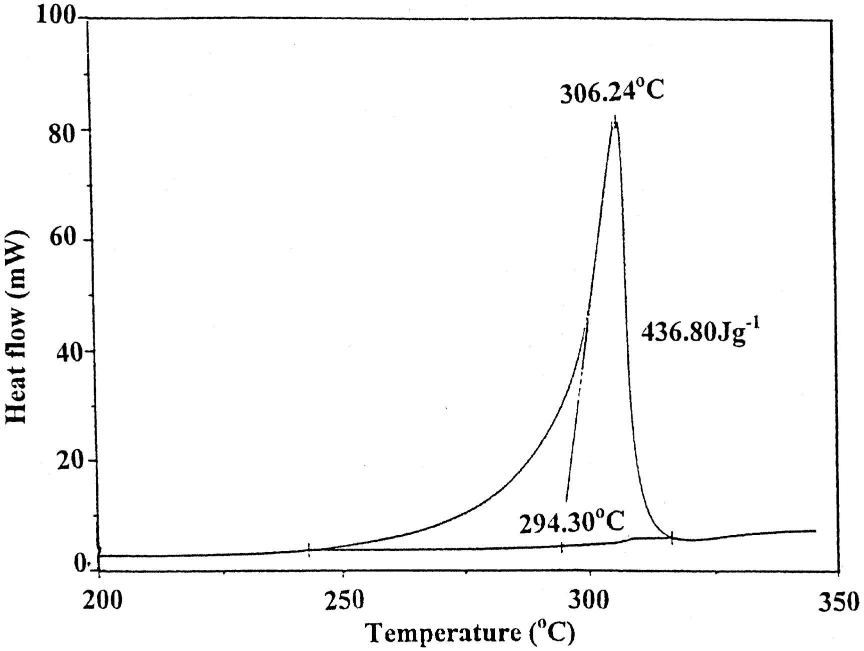

FIGURE 2 Typical DSC curve for one of the eight PAN/MA copolymer samples.

TABLE 10 DSC Analysis of AN/MA Copolymers

Sample	Sample mass, g	Initiation temp., °C	Peak temp., °C	Exothermic Heat, Jg^{-1}
1	6.8	293.41	303.57	360.9
2	6.6	292.42	302.73	387.4
3	6.8	290.17	299.27	334.3
4	6.1	289.66	298.77	339.6
5	6.9	294.30	306.24	436.8
6	6.7	293.99	307.07	441.8
7	6.6	287.56	297.56	376.4
8	6.9	292.44	304.64	395.0

carbonization as functions of MA and AIBN concentrations, polymerization temperature and stirrer speed. The exothermic heat recorded in the DSC analyses was used to interpret the significance of each of the factors of the fractional factorial design on the polymerization process. Different combinations were plotted against exothermic and initiation temperatures, as shown in Figures 3 and 4. The exothermic heat and initiation temperatures were plotted as functions of MA and AIBN concentrations, polymerization temperature and stirrer speed. Figure 3a shows that a high AIBN concentration and a low MA concentration leads to a polymer that yields a high

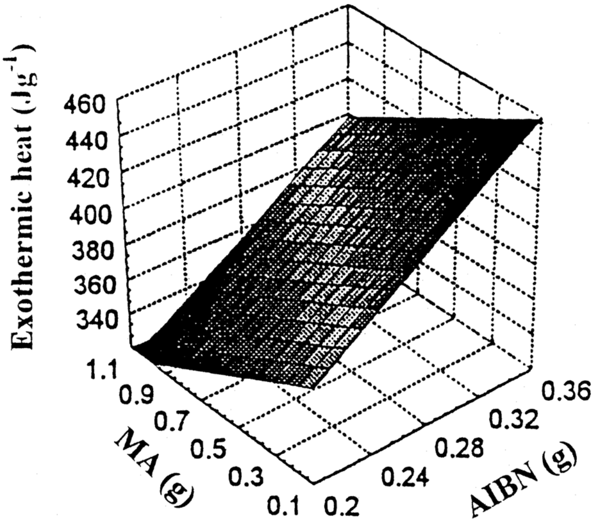

FIGURE 3a Exothermic heat as a function of AIBN and MA concentrations.

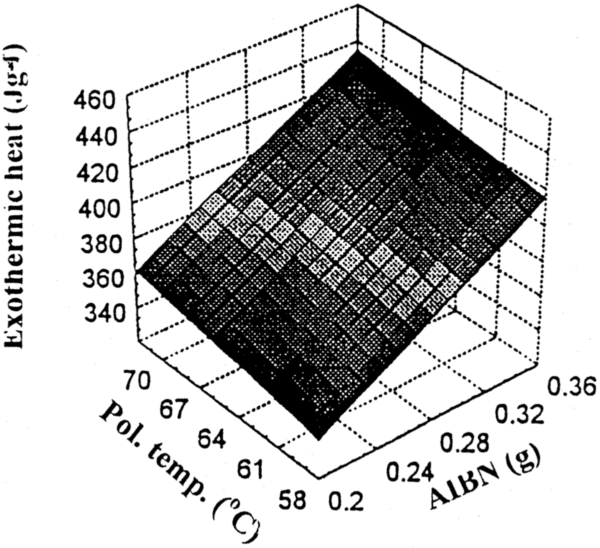

FIGURE 3b Exothermic heat as a function of AIBN concentration and polymerization temperature.

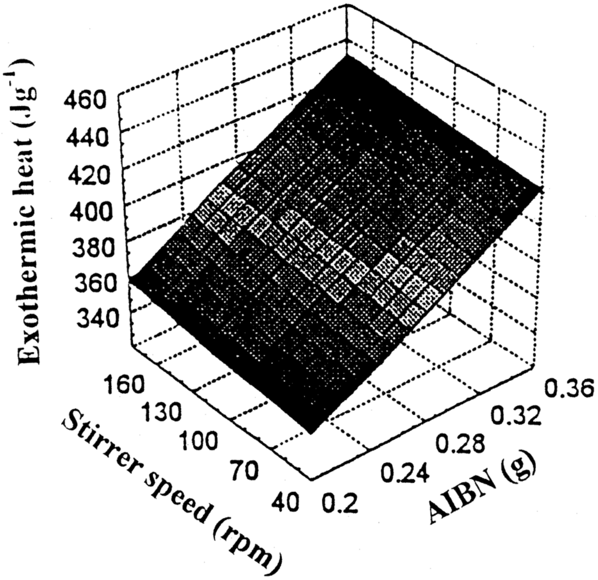

FIGURE 3c Exothermic heat as a function of AIBN concentration and the stirrer speed.

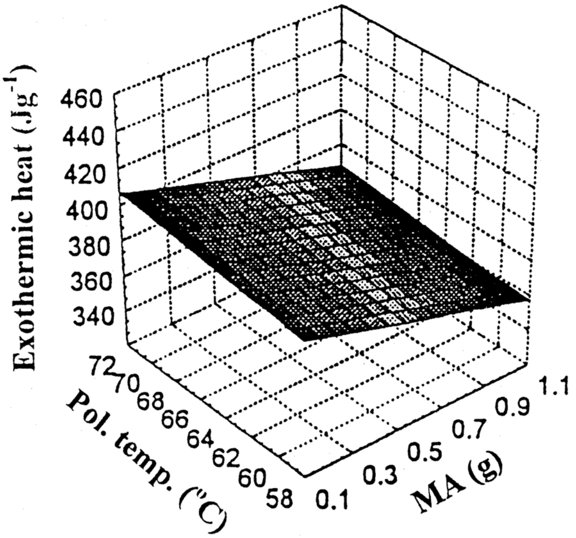

FIGURE 3d Exothermic heat as a function of MA concentration and the polymerization temperature.

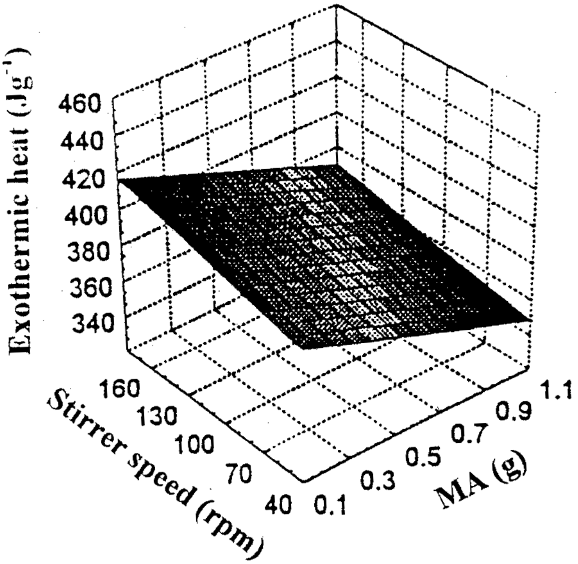

FIGURE 3e Exothermic heat as a function of MA concentration and the stirrer speed.

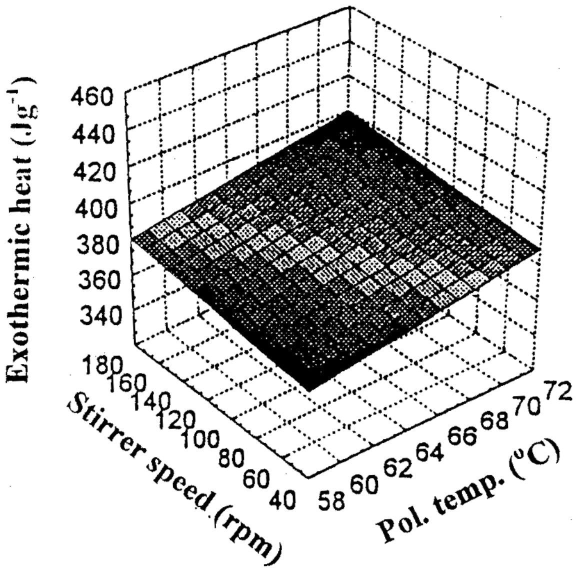

FIGURE 3f Exothermic heat as a function of the polymerization temperature and the stirrer speed.

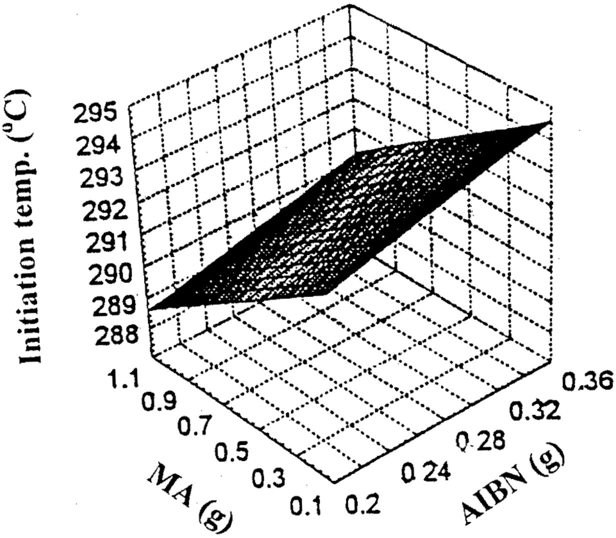

FIGURE 4a Initiation temperature as a function of AIBN and MA concentrations.

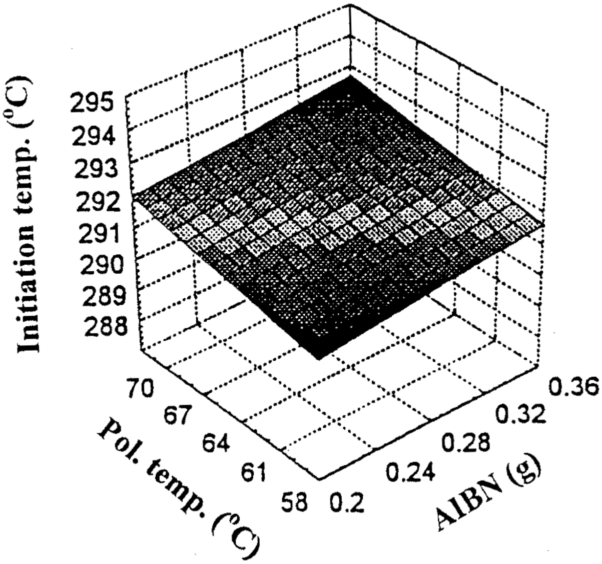

FIGURE 4b Initiation temperature as a function of AIBN concentration and polymerization temperature.

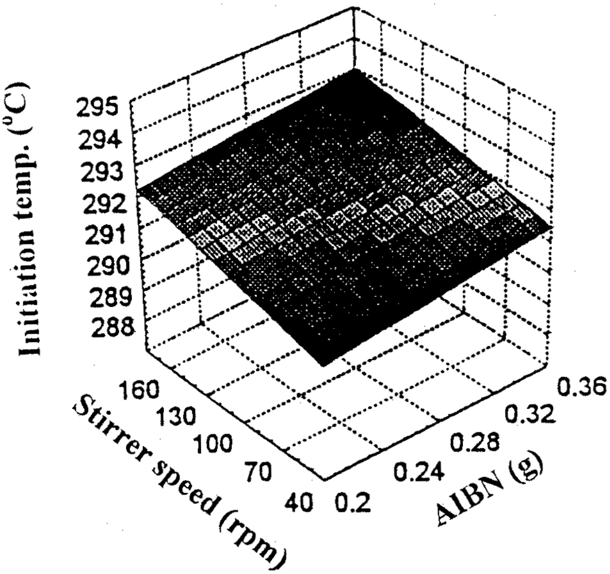

FIGURE 4c Initiation temperature as a function of AIBN concentration and the stirrer speed.

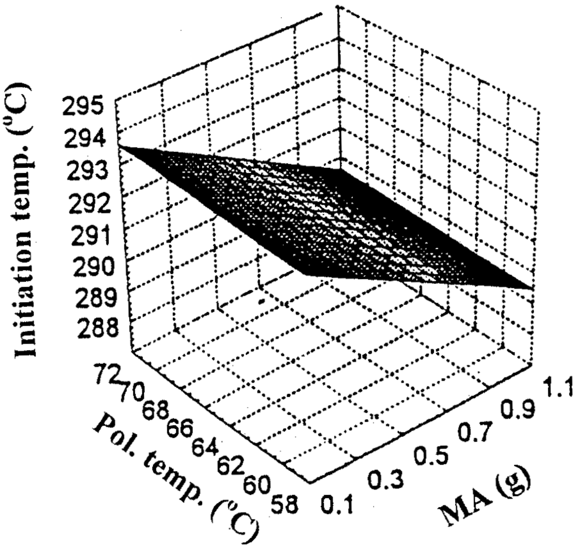

FIGURE 4d Initiation temperature as a function of MA concentration and the polymerization temperature.

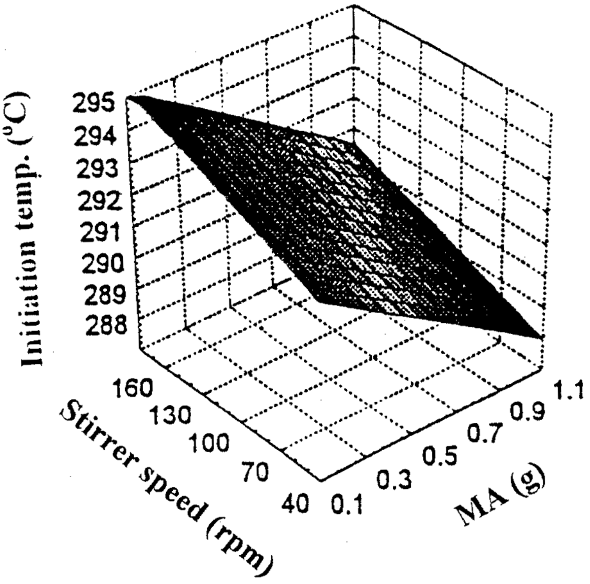

FIGURE 4e Initiation temperature as a function of MA concentration and the stirrer speed.

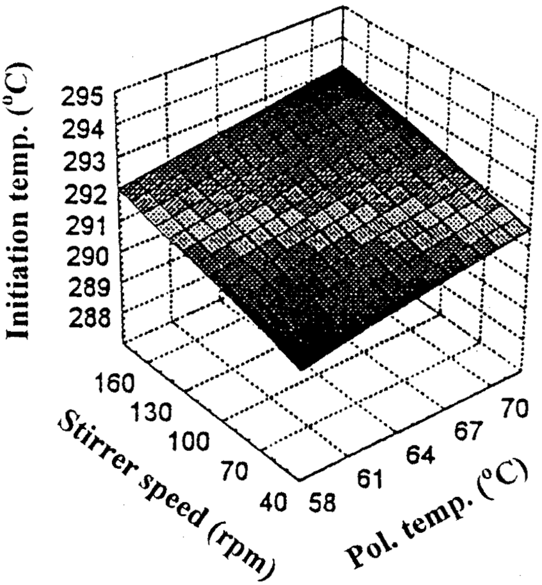

FIGURE 4f Initiation temperature as a function of the polymerization temperature and the stirrer speed.

exothermic heat upon thermal treatment. The analysis of variance showed that polymerization temperature did not have a large influence on the mass loss during thermal treatment [27], but results of our work indicated a very significant effect on the exothermic reaction taking place during thermal treatment, as indicated in Figure 3b. This was so since a high polymerization temperature with high AIBN concentration results in a low exothermic heat, while low polymerization temperature with a high AIBN concentration yields a high exothermic heat. The same tendency was observed for the stirrer speed and AIBN concentration, as presented in Figure 3c. The estimated response function plot of polymerization temperature, MA concentration and recorded exothermic heat, shown in Figure 3d, indicated that a low MA concentration with a low polymerization temperature value yielded a high exothermic heat. Again, the same tendency was observed for the stirrer speed and MA concentration, therefore low MA concentration and low stirrer speed resulted in high exothermic heat, as shown in Figure 3e. Figure 3f shows that both high and low stirrer speeds at low temperature resulted in a high exothermic heat. The highest exothermic heat was obtained with high AIBN and low MA concentrations and low polymerization temperature. The relative speed of the stirrer was irrelevant to the level of exothermic heat of reaction obtained. Variance analysis showed that the stirrer speed had a significant effect, as shown in Table 8. The sum of squares, calculated for the main effect and the interactions, showed that the sum of squares for stirrer speed is very close to the estimated error of variance and, judging from the above inference, the significance of the influence of the stirrer speed should be questioned. These levels for the process variables correspond well with those observed [27] from TGA analyses. It is therefore noted that both the AIBN and MA concentrations and the polymerization temperature have a clear and visible effect on the exothermic heat produced during thermal treatment of PAN-based precursors. On the contrary, the stirrer speed had no discernable effect on the exothermic heat produced. The exothermic peak observed on the DSC corresponded to the exothermic cyclization reaction observed on the TGA, that occurred during the stabilization process [27]. The heat flow observed in the DSC analyses would therefore be the exothermic cyclization heat on the TGA. The temperature indicated on the DSC curves was, therefore, the temperature at which the exothermic reaction started. From the results of the analysis of variance it was clear that this temperature did not vary significantly. The relationships between the variation in the initiation temperature and the process variables were plotted in Figures 4(a–f). Factors, or the interactions of the factors investigated, revealed an inconclusive effect on the initiation temperature; only the estimate of error variance for the responses indicated significant effect on the initiation temperature, as seen in Table 5.

CONCLUSIONS

The highest exothermic heat of reaction is obtained with high AIBN and low MA concentrations, and low polymerization temperature. The relative speed of the stirrer has little effect on the level of exothermic heat of reaction obtained. Factors, or the interactions of the factors investigated, revealed an inconclusive effect on the initiation temperature. Low MA concentration with a low polymerization temperature value yielded a high exothermic heat. A high AIBN concentration and a low MA concentration resulted in a high exothermic heat.

REFERENCES

[1] McEnaney, B. (1988). *Carbon*, **26**(3), 267.

[2] Chikawaga, J., Jacobs, E.D., Hundall, M.J. & Sanderson, R.D. (1996). *SA Journal of Chemical Eng.*, **8**, 31.

[3] Smith, S.P.J., Linkov, V.M., Sanderson, R.D., Petrik, L.F., O'Connor, C.T. & Keiser, K. (1995). *Miroporous Materials*, **4**, 385.

[4] Linkov, V.M., Sanderson, R.D., Lapidus, A.L. & Krylova, A.J. (1994). *Catalysis Letters*, **27**, 97.

[5] Fan, J., Ohya, H., Ohashi, H., Aihara, M., Takeuchi, T., Negishi, Y. & Semenova, S.I. (1999). *J. Membr. Sci.*, **162**(1–2), 125.

[6] Liang, C., Sha, G. & Guo, S. (1999) *Carbon*, **37**(9), 1391.

[7] Aminabhavi, T.M., Naik, H.G., Toti, U.S., Balundgi, R.H., Dave, A.M. & Mehta, M.H. (1999). *Polymer News*, **24**(9), 294.

[8] Qui, J. & Guo, S. (Nov. 1996). CN Pat. No: 1136476, A 27.

[9] Kim, K.W., Jung, S.H., Lim, Y.S. & Chung, Y.J. (1999). *Yoop Hakhoechi*, **36**(6), 577 (in Korean).

[10] Choi, S.-H. & Nho, Y.C. (1999). *Korea Polym., J.* **7**(1), 38.

[11] Linkov, V.M., Sanderson, R.D. & Ivakhnyuk, G.K. (1994). *Carbon*, **32**, 361.

[12] IUPAC Manual of Symbols and Terminology: Colloid and Surface, (1972), Appendix 2, Pt. 1.

[13] Mikhail, R.S. & Braunauer, J. (1975). *J. Colloid Interface Sci.*, **52**, 626.

[14] Marsh, H. & Wynne-Jones, W.F.K. (1964). *Carbon*, **1**, 269.

[15] Kipling, J.J. & Wilson, R.B. (1960). *Trans. Faraday Soc.*, **56**, 557.

[16] McEnaney, B. (1975). *Carbon*, **13**, 515.

[17] Adams, L.B., Baucher, E.A. & Everett, D.H. (1970). *Carbon*, **8**, 762.

[18] Spencer, D.H.T., Hooker, M.A., Thomas, A.C. & Napier, B.A. (1971). *Proc. 3rd Conf. Industrial Carbon and Graphite Society for Chemical Industry*, 467.

[19] Walker, P.L., Lamond, T.G. & Metcalfe III, J.E. (1970). *Proc. 2rd Conf. Industrial Carbon and Graphite Society for Chemical Industry*, London, 380.

[20] Kawai, T. & Nogi, T. (1986). *Japan Koho JP 60*, **202**, 703, Chem Abstr. 104:5251.

[21] Bauer, J.-M. & Marie, J. (1988). *Fr. Demande FR 2*, **582**, 956, Chem. Abstr., 107: 219559.

[22] Schindler, E. & Maier, F. (1988). *Ger. Offen. DE 3*, **621**, 257, Chem Abstr. 108:207039.

[23] Ya Alimova, L., Dzamaletdinova, I.E., Radzhabov, T.D. & Serebryakov, V.N. (1982). *Pat. USSR*, **924**, 063; *Chem Abstr.*, **97**:93664 (1983).

[24] Ishiyama, J. & Kurokava, Y. (1987). *Kagaku Kogyo*, *38*(7); *Chem Abstr.*, **108**:58303 (1988).

[25] Koresh, J.E. & Soffer, A. (1983). *Sep. Sci. Technol.*, **18**(8), 723.

[26] Koresh, J.E. & Soffer, A. (1987). *Sep. Sci. Technol.*, **22**(2), 973.

[27] Sanderson, R.D. & Sadiku, E.R. (2001). *Polymer* submitted.