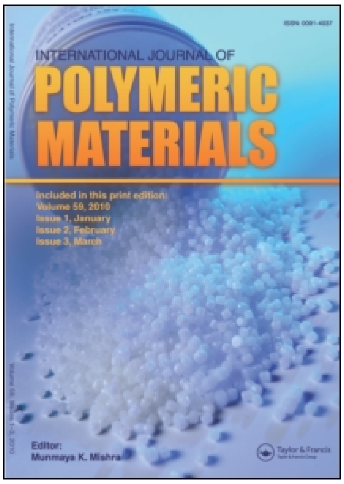

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PERCENTAGE AROMATIZATION AND CYCLIZATION MASS-LOSSES IN A PAN-PRECURSOR USED AS A HOLLOW-FIBER CARBON MEMBRANE-III

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Hollow-fiber carbon membranes were produced by the pyrolysis of acrylonitrile-based precursors that were spun using a wet phase-inversion technique. The fibers were used in the catalytic conversion of cyclohexane. Thermogravimetric (TGA) and variance analyses were carried out on the fibers produced. The TGA analyses involved the determination of the percentage aromatization and cyclization mass-losses as functions of process variables, such as polymerization temperature, monomer concentration, stirrer speed and initiator concentration. An empirical approach was adopted that employed statistical experimental designs that were used to recognize analytical and statistical methods that translated the process responses into comprehensible terms. A low methylcrylate (MA) concentration and a high azo-bis-isobutyronitrile (AIBN) concentration yielded a polymer that resulted in a precursor with low mass loss during carbonization. Both high AIBN concentration and low stirrer speed on the one hand and a high polymerization temperature at a low stirrer speed on the other hand yielded a low mass loss. The response plot function of the percentage mass loss indicated that a low MA concentration at a low polymerization temperature would give the lowest mass loss. Chemical shrinkage, corresponding to the cyclization process, started only at temperatures ≈200°C, while the aromatization process commenced above 350°C.

Keywords: acrylonitrile, methylacrylate, cyclization, aromatization, stirrer speed, polymerization temperature, thermogravimetry

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INTRODUCTION

The membrane industry has grown considerably during the past few decades and further significant growth in the fields of gas separation and pervaporation are envisaged in the near future. The main disadvantages of existing membranes are their poor mechanical and thermal properties. The search for membranes with good mechanical strength, and which are thermally and chemically stable at elevated temperatures, has resulted in the development of inorganic membranes. These inorganic membranes exhibit superior separation properties, but are limited by their low packing density and unit reaction volume. Attempts to produce a membrane that has all the advantages offered by inorganic membranes and also has a high packing density and unit reaction volume has led to the production of hollow-fiber carbon membranes [1].

Although the unique separation properties of hollow-fiber carbon membranes have been shown by Linkov [1], no attempt has yet been made to use hollow-fiber carbon membranes as supports in a catalytic membrane reactor. The use of catalytic membrane systems for the selective removal of components from gaseous waste streams is becoming a major industrial operation. The advantages afforded by catalytic membrane reactors in promoting a favorable shift of the reaction equilibrium of a chemical reaction by selective removal of one of the reaction products from the reaction zone has long been recognized [2–4]. Hollow-fiber carbon membranes combined with platinum group metals not only provide high packing density, but also a high unit reactor volume, making the development of this technology a worthwhile effort.

Linkov et al. [5–11] discussed the preparation and the uniformity of a microporous carbon layer coated on carbon membranes, using ethanol-nitrogen as a wetting-permeating agent. They concluded that the pyrolytic coating of carbon membranes with TiC and subsequent chlorine treatment resulted in the formation of a thin microporous carbon layer on the surface of the membranes. Mimicking cyclization reactions, the thermal chemistry of some hexene–, hexane– and hexa diene–containing products, were studied by Tjandra and Zaera [12] under ultra-high vacuum conditions at ≈ 160 K, at which temperature there was bond scission. Further heating of the systems induced the desorption of hexene, hexane, iodohexane, benzene and cyclohexane. Becue et al. [13] studied the influence of cesium in Pt-NaCsβ on the physico-chemical and catalytic properties of Pt clusters in the aromatization of n-hexane. They concluded that the increase in Cs content in the NaCsβ zeolite support resulted in a decrease in cyclohexane adsorption and Pt exchange capacity and that the selectivity to aromatization is much higher on the Pt-Csβ catalyst than on the Na-containing Pt-NaCsβ catalyst.

In this study, hollow-fiber carbon membranes were prepared and investigated for their behavior at high temperature. This involved the determination of the percentage mass losses during pyrolysis, as a function of polymerization conditions (MA and AIBN concentrations, stirrer speed and polymerization temperature).

EXPERIMENTAL

Hollow-fiber carbon membranes were synthesized and spun into fibers. They were then stabilized and carbonized. The percentage cyclization and mass loss though carbonization were determined. A single-sided "F-test" was statistically performed for each of the treatment combinations on each of the responses. The "F-ratio" was calculated from the relation: F-ratio = Mean sum of squares ÷ Mean estimate of error variance.

Synthesis of PAN–Based Copolymers, Preparation of Spinning Solution and Spinning of Hollow-Fiber Precursors

The synthesis, preparation of spinning solution and spinning of the precursors have been described previously [14].

Stabilization and Carbonization of the PAN Precursors

During the drying period, the carbon membranes tended to adhere to each other. They had, therefore, to be carefully separated and inspected. Any PAN precursors or parts of the precursors that had visible defects were removed. A silica powder (Aerosil 200) was subsequently used during the stabilization and carbonization processes to keep the precursors from sticking to each other.

The precursors were stabilized and carbonized in a single operation, inside a ceramic tube oven, under nitrogen atmosphere. It was imperative to maintain a nitrogen flow so as to remove all the by-products formed. Furthermore, air was excluded during the stabilization and carbonization processes, since it would result in oxidation of the carbon structure. The precursors were first stabilized by heating to a temperature of 350°C, at a rate of $\approx 2°\mathrm{C\ min}^{-1}$, followed by carbonization by heating at the same rate, up to a temperature of 750°C. Following carbonization, the membranes were washed with water, then with acetone, and dried in air.

Factorial Design for PAN Copolymers

The factorial design for PAN copolymers has been described earlier [14]. The complete experimental design with treatment combinations is shown in Table 1, while the amounts of monomers, solvents and the polymerization conditions are summarized in Table 2.

Thermogravimetric Analysis, TGA

The eight AN-based copolymers synthesized for the fractional factorial designed experiments were analyzed thermogravimetrically. These

TABLE 1 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 2 Actual Amount of Monomers and Solvents and the Polymerization Conditions

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
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
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
6	7	54.00	36.01	0.99	0.336	60	1
4	8	54.00	36.00	0.98	0.33	70	3.5

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

analyses were done to determine the mass losses for each of the PAN-based copolymers under specific thermal treatment conditions. The samples were heated from ambient temperature to 270°C at a rate of 5°C min^{-1}. All analyses were done in an atmosphere of nitrogen, with a flow rate of 90 ml min^{-1}. An average mass of 10 mg copolymer was used. In this study, using the TGA, the percentage mass losses during aromatization and cyclization of PAN-precursor suitable for use as catalytic hollow-fiber carbon membrane were obtained.

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 (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. The total sum of squares for each set of responses was used as an arithmetic check, e.g. for the % total mass loss during carbonization, as shown in Table 3. The calculated estimate

TABLE 3 Calculation of Sum of Squares for % Total Mass Loss During Carbonization

Run #	Response (% total mass loss)
1	41.38
2	40.52
3	53.36
4	45.56
5	39.32
6	41.91
7	41.31
8	44.18
$\sum(\text{Response})^2$	15238.10
$(\sum \text{Responses})^2 \div 8$	1904.76
Total SS = (15238.1 − 1904.76) =	1333.34

SS = Sum of Squares.

TABLE 4 Estimate of Error Variance for the Responses

Response	Estimate of error variance
% Total mass loss	16.94
% Cyclisation mass loss	9.09
% Aromatization mass loss	6.95

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 4 above.

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

of error variance is shown in Table 4. This error of variance was used to determine the F-ratio for each treatment combination. A single-sided "F-test" was performed on each of the treatment combinations to determine the probability of level of significance. The detailed procedure followed in performing the "F-test" is given in the Table 5.

Each of the treatment combinations has only one degree of freedom; therefore, the mean sum of squares is equal to the sum of squares. The calculated mean estimates of error variance are shown in Tables 6, 7 and 8 for the percentage mass loss, percentage cyclization and percentage aromatization.

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

TABLE 5 Procedure for Performing 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 6 Response (% Total Mass Loss) from the Treatment Combination

Treatment combination	Degrees of freedom	Sum of squares	F-ratio	% level of significance
A	1	24.85	1.47	>10
B	1	56.60	3.34	>10
C	1	1.28	0.08	>10
D	1	6.52	0.38	>10
AB ≡ CD	1	20.25	1.20	>10
AC ≡ BD	1	24.95	1.47	>10
AD ≡ BC	1	5.54	0.35	>10
Total	7	140.06		

TABLE 7 Response (% Cyclization) from the Treatment Combination

Treatment combination	Degrees of freedom	Sum of squares	F-ratio	% level of significance
A	1	1.60	0.18	>10
B	1	22.31	2.45	>10
C	1	0.25	0.028	>10
D	1	7.605	0.84	>10
AB ≡ CD	1	4.03	0.44	>10
AC ≡ BD	1	19.16	2.11	>10
AD ≡ BC	1	4.09	0.45	>10
Total	7	59.045		

TABLE 8 Response (% Aromatization) from the Treatment Combination

Treatment combination	Degrees of freedom	Sum of squares	F-ratio	% level of significance
A	1	16.70	2.40	>10
B	1	30.70	4.45	>10
C	1	0.058	0.008	>10
D	1	10.63	1.53	>10
AB ≡ CD	1	13.73	1.98	>10
AC ≡ BD	1	4.53	0.65	>10
AD ≡ BC	1	2.58	0.37	>10
Total	7	78.93		

variance. If the sum of squares value of a treatment combination is higher than that of the estimate of error 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

TABLE 9 Factors that Have Influence on the Responses

Response	A	B	C	D	AB ≡ CD	AC ≡ BD	AD ≡ BC
% Total mass loss	√	√				√	
% Cyclisation mass loss		√				√	
% Aromatization mass loss	√	√					

this assumption. Table 9 shows the factors that have influence in the case of each response.

A typical TGA trace for one of the 8 copolymer samples is shown in Figure 1. All other samples showed similar trends. Each shows two characteristic inflexion points. The TGA results are shown in Table 10. The percentage mass losses obtained from the TGA analyses were used to interpret the significance of each of the factors of the fractional factorial design on the polymerization process. Different combinations of factors were plotted against mass losses. These plots are shown in Figures 2–4. The percentages of the total mass-loss, aromatization mass-loss and cyclisation mass-loss were plotted as functions of MA and AIBN concentrations, polymerization temperature and stirrer speed.

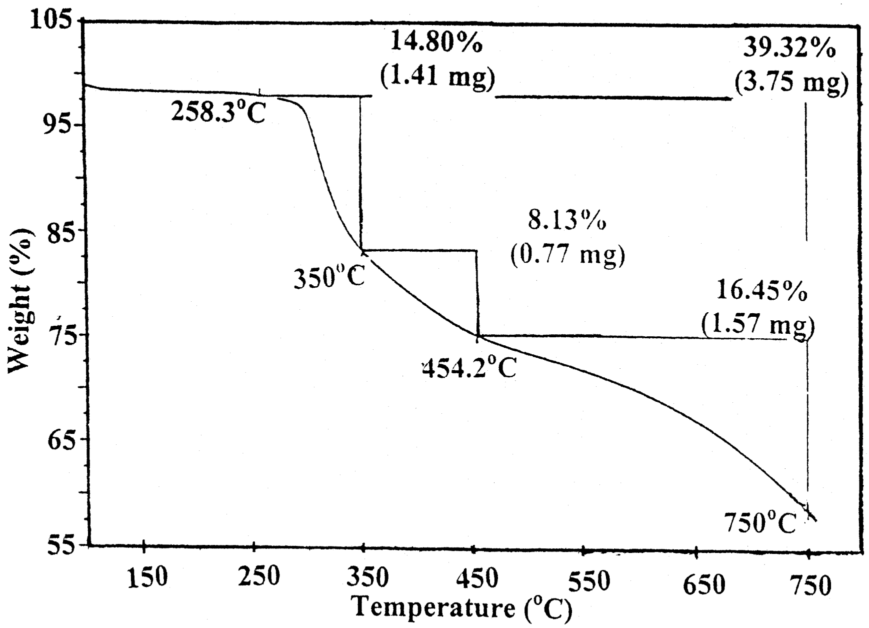

FIGURE 1 Typical TGA curve for one of the eight AN/MA copolymer samples.

TABLE 10 TGA Analyzed Data for PAN/MA Copolymers

Sample #	Sample mass, g	Initiator temp., °C	1st inflex. temp., °C	2nd inflex. temp., °C	Mass loss at 1st inflex., %	Mass loss at 2nd inflex., %	Total mass loss, g	% Total mass loss
1	9.44	276.4	343.1	469.4	16.06	9.70	3.83	40.52
2	10.52	284.7	336.1	456.9	16.20	12.87	4.35	41.31
3	10.72	270.8	343.1	470.8	23.56	17.58	5.72	53.36
4	10.31	269.4	344.4	458.3	20.17	11.10	4.56	44.18
5	12.19	280.5	350.0	463.9	15.42	12.21	5.05	41.38
6	9.52	258.3	350.0	454.2	14.80	8.13	3.75	39.32
7	19.37	266.7	338.9	462.5	17.73	13.24	4.34	41.91
8	10.45	254.2	345.5	471.9	17.44	17.41	4.76	45.56

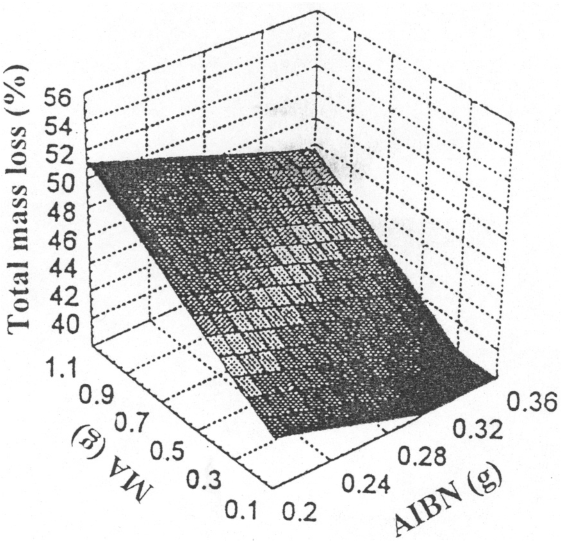

FIGURE 2a % total mass loss of PAN-based hollow-fiber membrane as a function of AIBN and MA concentrations.

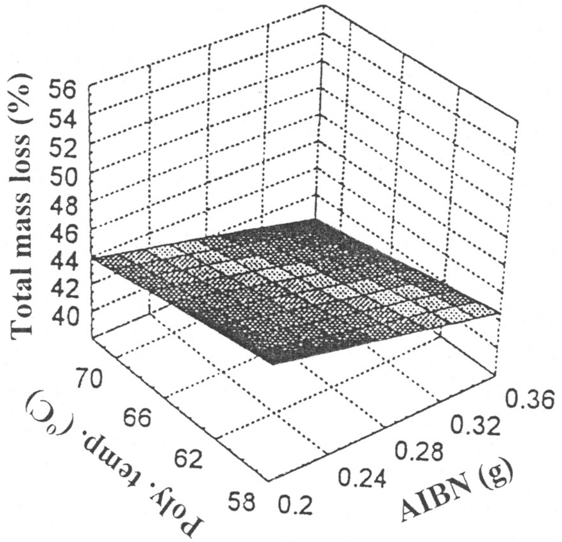

FIGURE 2b % total mass loss of PAN-based hollow-fiber membrane as a function of AIBN concentration and polymerization temperature.

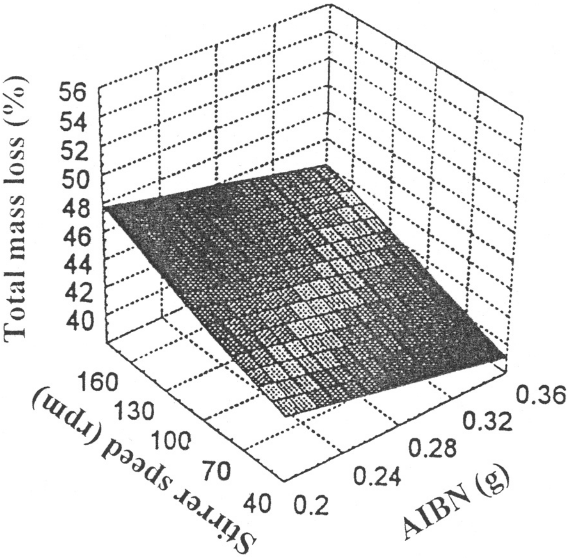

FIGURE 2c % total mass loss of PAN-based hollow-fiber membrane as a function of AIBN concentration and the stirrer speed.

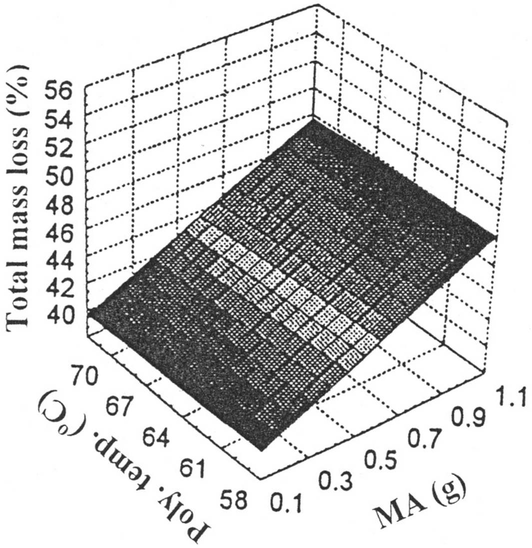

FIGURE 2d % total mass loss of PAN-based hollow-fiber membrane as a function of MA concentration and the polymerization temperature.

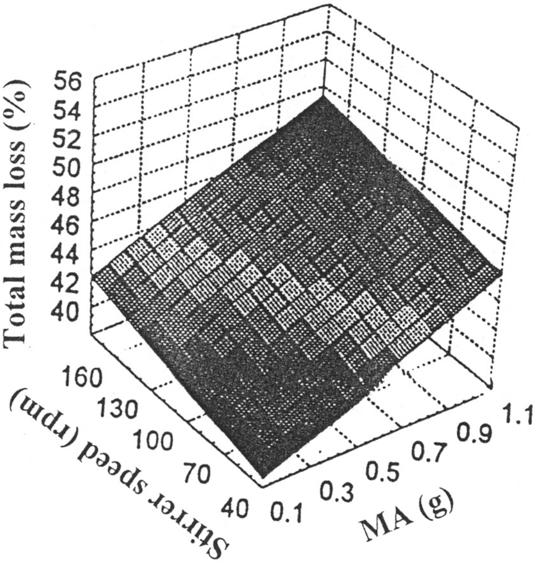

FIGURE 2e % total mass loss of PAN-based hollow-fiber membrane as a function of MA concentration and the stirrer speed.

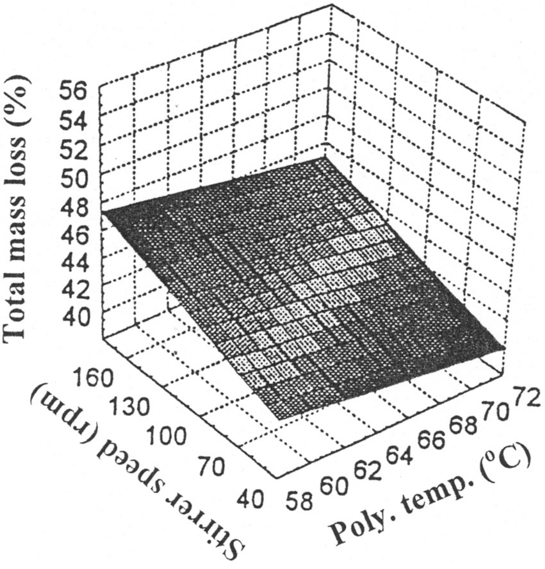

FIGURE 2f % total mass loss of PAN-based hollow-fiber membrane as a function of the polymerization temperature and the stirrer speed.

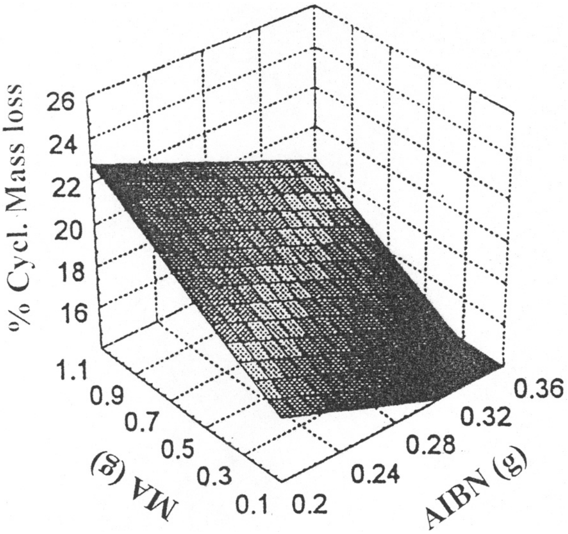

FIGURE 3a % cyclization mass loss of PAN-based hollow-fiber membrane as a function of AIBN and MA concentrations.

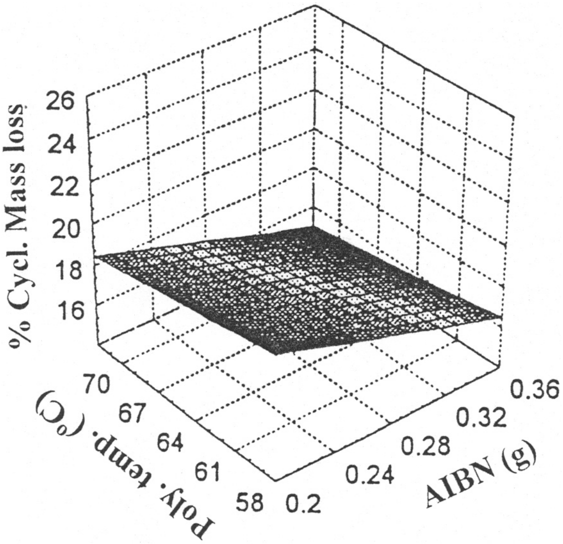

FIGURE 3b % cyclization mass loss of PAN-based hollow-fiber membrane as a function of AIBN concentration and polymerization temperature.

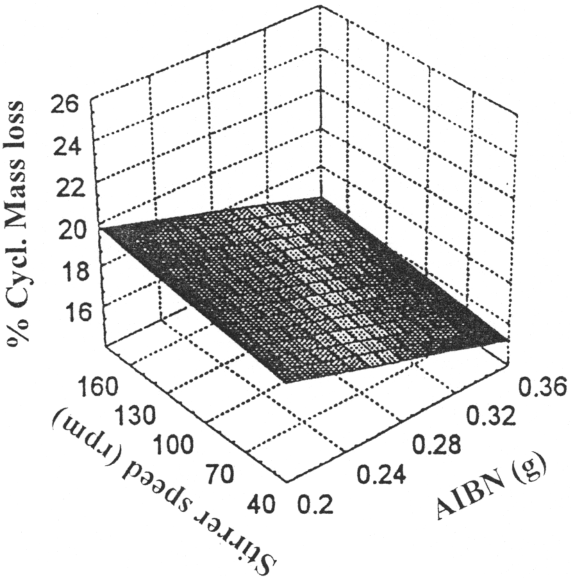

FIGURE 3c % cyclization mass loss of PAN-based hollow-fiber membrane as a function of AIBN concentration and the stirrer speed.

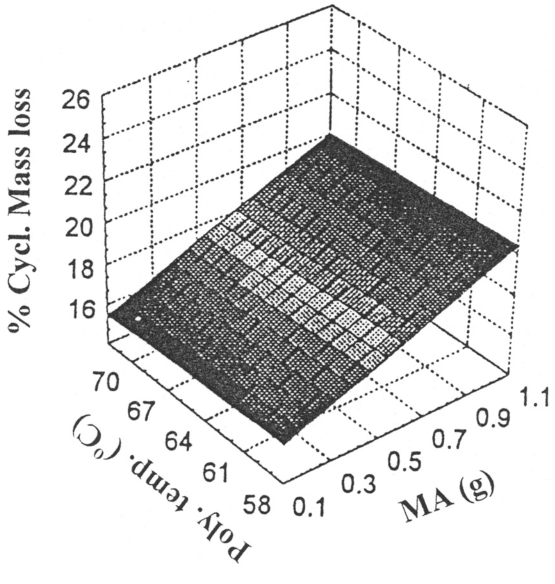

FIGURE 3d % cyclization mass loss of PAN-based hollow-fiber membrane as a function of MA concentration and the polymerization temperature.

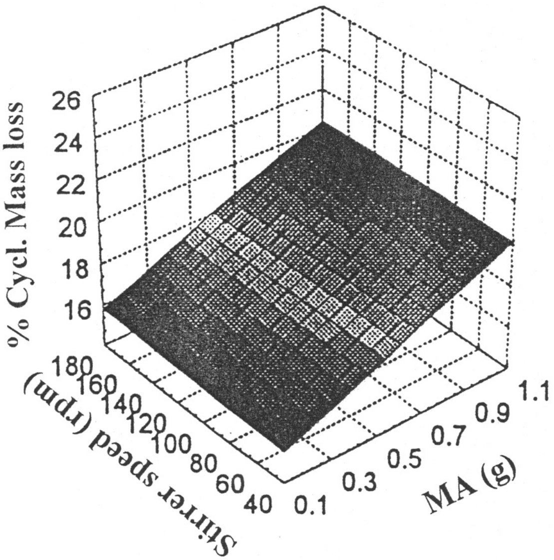

FIGURE 3e % cyclization mass loss of PAN-based hollow-fiber membrane as a function of MA concentration and the stirrer speed.

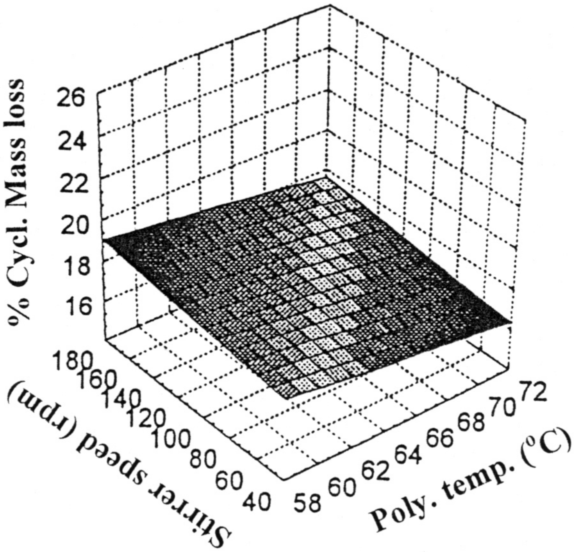

FIGURE 3f % cyclization mass loss of PAN-based hollow-fiber membrane as a function of the polymerization temperature and the stirrer speed.

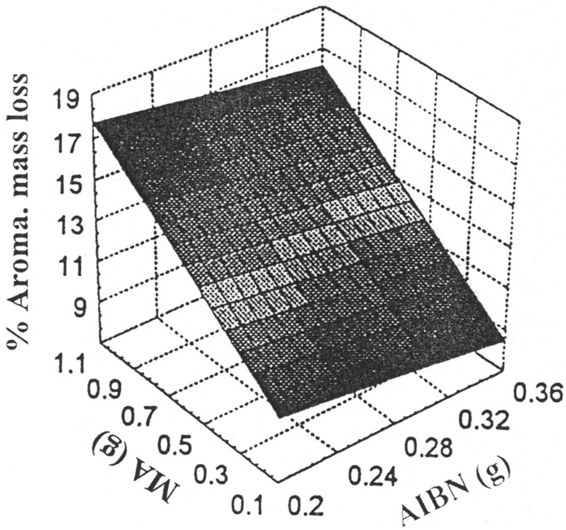

FIGURE 4a % aromatization mass loss of PAN-based hollow-fiber membrane as a function of AIBN and MA concentrations.

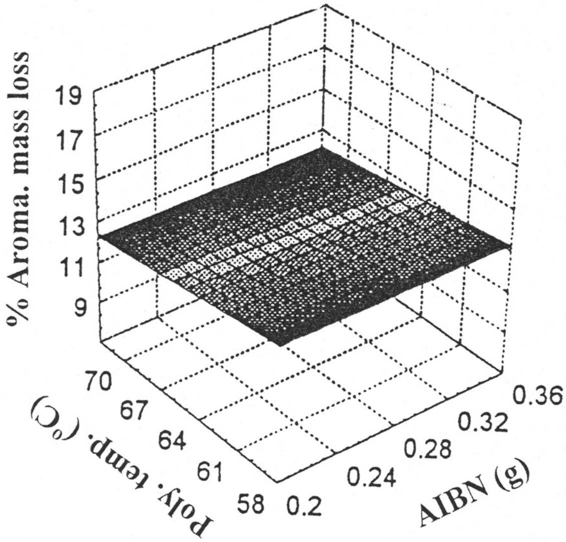

FIGURE 4b % aromatization mass loss of PAN-based hollow-fiber membrane as a function of AIBN concentration and polymerization temperature.

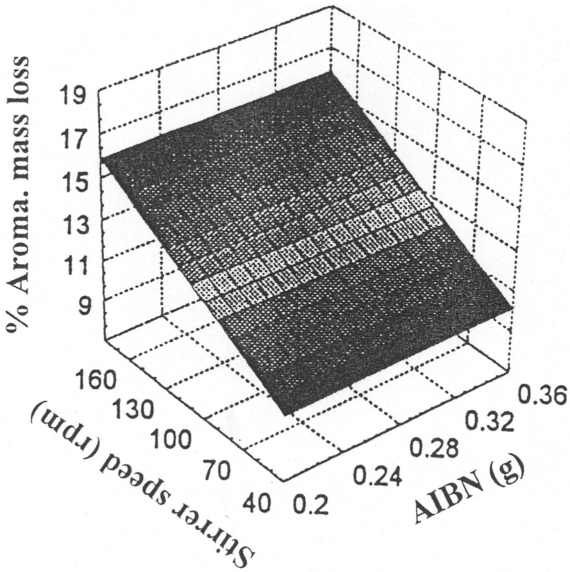

FIGURE 4c % aromatization mass loss of PAN-based hollow-fiber membrane as a function of AIBN concentration and the stirrer speed.

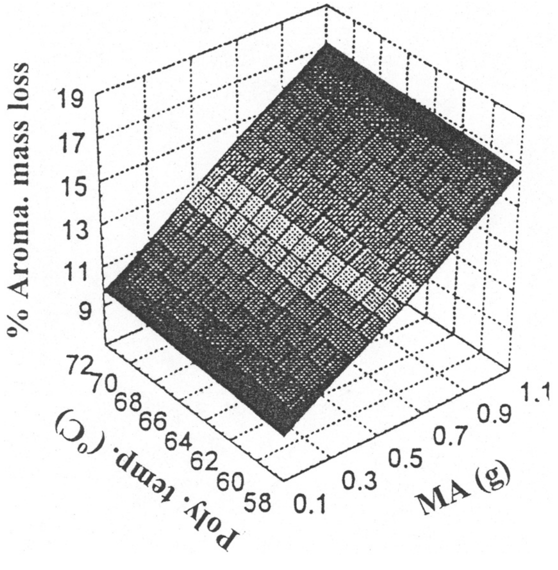

FIGURE 4d % aromatization mass loss of PAN-based hollow-fiber membrane as a function of MA concentration and the polymerization temperature.

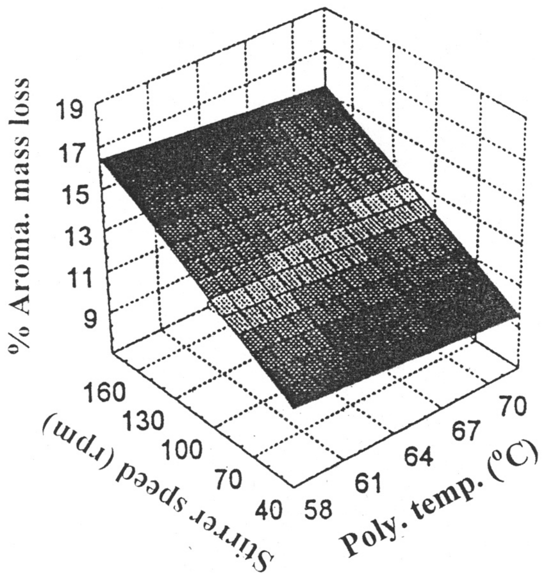

FIGURE 4e % aromatization mass loss of PAN-based hollow-fiber membrane as a function of the polymerization temperature and the stirrer speed.

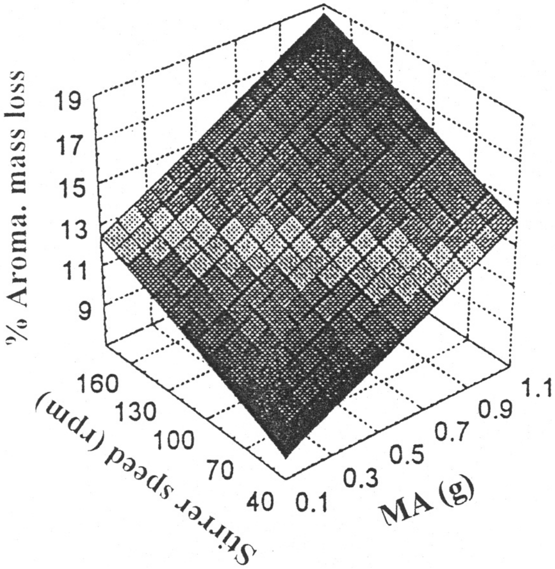

FIGURE 4f % aromatization mass loss of PAN-based hollow-fiber membrane as a function of MA concentration and the stirrer speed.

From Figure 2a it can be seen that a low MA concentration and a high AIBN concentration yielded a polymer that resulted in a precursor with low mass loss during carbonization. In Figure 2b, a high concentration of AIBN at low polymerization temperature yielded the lowest mass loss during carbonization ($\approx 41.5\%$). A high concentration of AIBN and a low stirrer speed yielded a low mass loss, as shown in Figure 2c. An estimated response function plot of MA concentration, polymerization temperature and percentage mass loss during carbonization indicated that a low MA concentration at a low polymerization temperature would give rise to the lowest mass loss, as shown in Figure 2d. It was noted, however, that both high and low temperature values with low MA concentrations yielded a relatively low mass loss. Figure 2e shows that a low MA concentration results in a low mass loss at a low stirrer speed. A high polymerization temperature at a low stirrer speed results in the lowest mass loss, as can be seen in Figure 2f. These results correlate well with the results obtained from variance analysis. Temperature did not have a great effect on the response and, therefore, it could be concluded that the two-factor interaction that has an influence on the response was the interaction of the MA concentration and the stirrer speed.

A close observation of the MA concentration and the polymerization temperature showed that the concentration of MA had a significant influence on the percentage mass loss and that if a low percentage mass loss is required, then a low MA concentration is desirable. This is in accordance with the results of the analysis of variance, as illustrated in Table 4. Furthermore, polymerization temperature did not have a large influence on the mass loss during carbonization in the temperature range investigated.

The first inflexion point on the TGA curves of the 8 PAN-based copolymers is assumed to represent the exothermic cyclization reaction that occurs during thermal stabilization at temperatures up to 350°C. During this period, there was an increase in thermal stability of the polymers [15]. The formation of the chain ring structures retards the degradation reactions that would have resulted in considerable mass loss during thermal treatment. An estimated response surface plot for the mass loss due to cyclization was plotted against two variables simultaneously, as shown in Figures 3(a–f). The plots are very similar to those for the total mass loss against the process variables discussed in Figures 2(a–f), and do in fact show similar trends. Although polymerization temperature did not have a large effect on the mass loss during thermal treatment, it must be remembered that the polymerization temperature was investigated only in a very narrow range and that if a wider range was chosen for investigation it could, very well, play a leading role. The influence of low MA and high AIBN concentrations indicates that chain length plays an important role in the mass loss during thermal treatment. To understand this phenomenon better, a closer look at the roles that AIBN and MA play in the polymerization process is necessary. AIBN plays a leading role in the initiation of the free radicals that start and maintain the polymerization reaction. Theoretically, the more AIBN present, the more polymerization sites will be available and slightly shorter polymer chains will be formed, noting that in precipitation polymerization, the radical chain end is basically immobile.

MA is incorporated into the PAN structure to produce carbon fibers that are more flexible and mechanically stronger. The incorporation of MA in the chain structure, however, disrupts the cyclization process. Since the cyclization process involves the formation of chain structures that stabilize the macromolecules, disruption of the cyclization process also means less stable macromolecules. This, in turn, means that the degradation reaction is probably not retarded effectively; therefore, a higher mass loss will be obtained. As evident in Figures 2(a–f), the stirrer speed plays a significant role in the mass loss during stabilization and carbonization. When a high stirrer speed is used, smaller particles are formed in the emulsion. The higher stirring speed will enhance the termination process between growing radicals. This will result in shorter polymer chain lengths and a polymer with low average molecular mass [15]. One could reason, therefore, that at low stirrer speeds the chances of two free-radical ends meeting become less than at high stirrer speeds.

The second inflexion point on the TGA curves shown in Figure 1 represents the aromatization process that takes place at temperatures above 350°C. The aromatization mass loss as a function of the process variables for the polymer samples is shown in Figures 4(a–f). Although the results for the 8 polymer samples show similar characteristics to those of the total mass loss, the influence of the MA concentration is more prominent. During the carbonization process, the dynamics of gas evolution strongly influences the mechanical properties of the final product. Gases that evolve at temperatures above 350°C are hydrogen cyanide, hydrogen, ammonia, water and nitrogen. The initiation temperature for this study is defined as the temperature at which mass loss commences. Up to the initiation temperature, no significant mass loss was observed. Ermolenko et al. [16] reported that up to the initiation temperature, a low temperature shrinkage mechanism is at work. This mechanism is of a physical nature and its dependence on heating rate is weak. Chemical shrinkage, corresponding to the cyclization process, starts only at temperatures above 200°C, as evident from the TGA curve, shown in Figure 1.

CONCLUSION

Hollow-fiber carbon membranes can be reproduced if very strict control is exercised over the polymerization conditions when manufacturing the acrylonitrile and methylacrylate copolymers. Process variables such as stirrer speed, polymerization temperature, MA and AIBN concentrations influence the properties of the copolymer produced and hence influence the properties of the carbon membranes produced from the precursor manufactured from the copolymer. At about 200°C, chemical shrinkage, which corresponds to the cyclization process, while the aromatization process commences at temperatures above 350°C. Both high AIBN concentration and low stirrer speed, on the one hand, and a high polymerization temperature and a low stirrer speed, on the other hand, yielded a low mass loss.

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