On the Mathematical Modeling of Mechanochemical Degradation of Acrylonitrile–α-Methyl Styrene–Vinyl Acetate Terpolymer in Conditions Simulating the Wet-Spinning

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Synopsis

This article aims to carry out mathematical modeling of the mechanochemical degradation process of acrylonitrile–α-methyl styrene–vinyl acetate ternary copolymer in conditions that simulate its wet-spinning from dimethyl formamide solution. The influence of some factors on the mechanochemical degradation process is studied. Based on a great number of experiments a regression equation is determined, which correlates the intrinsic viscosity of the copolymer solution with the mechanical process variables (the length and length/diameter ratio, solution concentration, and pressure).

INTRODUCTION

Mechanochemical degradation of the polymers in solution in different conditions of mechanical stress has been treated in a great number of articles. So, the fact has been revealed that by ultrasonic treatment,[1-3] cryolysis,[4,5] high speed stirring,[6-9] laminar,[10] or turbulent flow[11,12] in capillaries of the polymer solution, the molecular weight decreases, the efficiency of the mechanochemical degradation process depending on the parameters of mechanical regime and solution concentration.

Few articles, however, deal with the mechanochemical degradation induced by the capillary shearing of the polymer solutions, in spite of the practical implications of this process, mainly in the case of wet-spinning.[13-15]

This article is based on the observation that the molecular weight of the polymer from a product obtained by wet-spinning is less than that of the polymer from spinning dope. Starting from this premise, we approach the study of mechanochemical degradation of acrylonitrile–α-methyl styrene–vinyl acetate terpolymer by capillary shearing of its solutions in dimethyl formamide (DMF) in conditions which simulate the industrial wet-spinning. The aim of this article is mathematical modeling of this process taking as an evaluation criterion of the molecular phenomena the intrinsic viscosity, which correlates with the parameters of the mechanical regime (geometrical characteristics of the capillary, spinning pressure, and solution concentration).

TABLE I
Parameters of Mechanodegradation Process and Their Limits of Variation

Variable	Limits of variation	
	x_{min}	x_{max}
Length of the capillary (L), x_1 (mm)	20	45
Length to diameter ratio (L/D), x_2(mm/mm)	51.4	100
Solution concentration (C %) x_3 (%)	10	22
Pressure (P), x_4 (atm)	5	15

EXPERIMENTAL

The studied ternary copolymer (92.2% acrylonitrile, 4.5% vinyl acetate, and 3.3% α-methyl styrene) was obtained by solution-suspension method, being used for the obtaining of MELANA fibers. The intrinsic viscosity in DMF solution (25°C) is 2.04.

Solutions which were put to shearing tests in capillaries were obtained by solving the copolymer in DMF at 60 ± 5°C. The experiments were carried out on a laboratory equipment presented in a previous article.[16] The coagulation of the polymer was realized in a water bath at 20 ± 2°C.

The intrinsic viscosity, determined at 25°C in DMF, by the single point method,[17] was chosen as a criterion for the evaluation of mechanochemical degradation process.

Processing Data

The equipment allowed us to study the influence of some basic parameters on the mechanodegradation process, each one taken at five levels. These parameters (independent variables) and their limits of variation are given in Table I. Ninety-six experiments were carried out at different shearing conditions realized by different combinations of the independent variables.

The experimental results were processed on a FELIX-C-256 computer, by the regression method in order to obtain the regression equation of the form:

$$Y = a_0 + a^T x + x^T A x \tag{1}$$

where a_0 = the intercept, a = the vector of linear regression coefficients, x = the vector of the independent variables, and A = the matrix of the second order regression coefficients.

The simplified flow diagram of the program is given in Figure 1. Eight subroutines are used in this program,[18] the main program and TRANS, COMPAR, and PLOTRS subroutines being written by the authors of this article.

Subroutine CORRE computes the correlation coefficients between all the variables. The ORDER subroutine select the correlation matrix between a
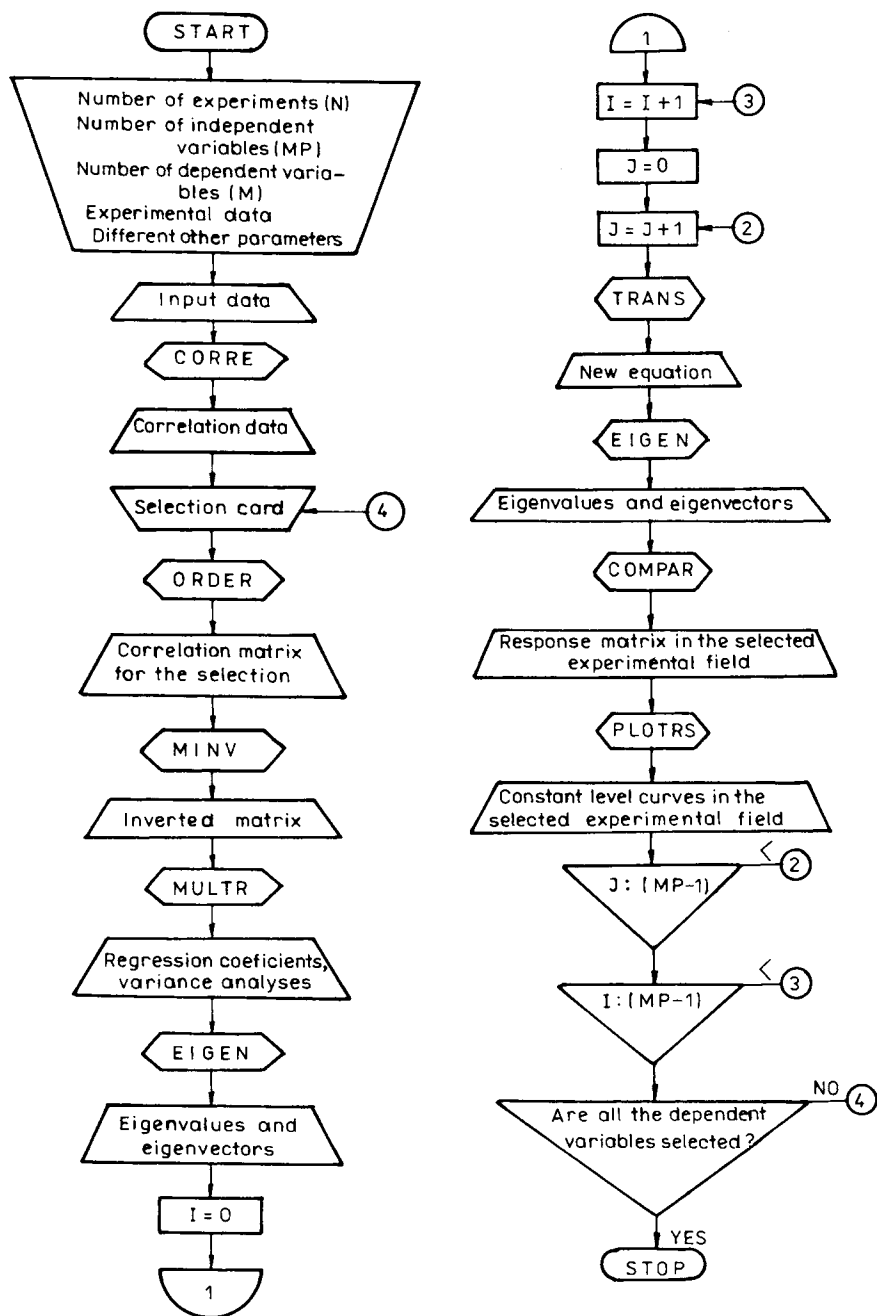
Fig. 1. Simplified flow diagram of the program.

dependent and the independent variables. Then the MINV subroutine inverts the correlation matrix and, in MULTR subroutine the regression equation is obtained, or the response surface. This response surface was tested against the "F" test.

In order to study the response, the eigenvalues and eigenvectors of this surface defined by

$$\det(A - \lambda I) = 0 \qquad (2)$$

are computed in EIGEN subroutine.

For the response surface of the intrinsic viscosity, two of the eigenvalues were positive and two were negative, so that this surface presents a saddle point in the four-dimensional experimental field.

By using the TRANS, COMPAR, and PLOTRS subroutines, particular response surfaces in two-dimensional fields are obtained. To obtain such a particular equation in two variables, the other two ones are taken at the middle of the experimental field. The COMPAR subroutine computs and prints the matrix of the viscosity in the selected experimental field, and the PLOTRS subroutine plots the constant level curves of the response surface. If the particular response surface presents a stationary point in the selected experimental field, the program computes and prints the value of the viscosity in this point and its coordinates.

RESULTS AND DISCUSSION

The obtained experimental results show that in all cases a mechanodegradation process undergoes, which can be evaluated by the decrease of the intrinsic viscosity of the polymer solution. The extent of the mechanodegradation depends on the process variables. The following regression equation correlates the intrinsic viscosity with the independent variables:

$$[\eta] = 1.4273 + 0.0069x_1 + 0.0021x_2 + 0.0206x_3$$

$$- 0.0047x_4 + 0.00007x_1^2 - 0.00006x_1x_2$$

$$+ 0.00002x_1x_3 - 0.00018x_1x_4 - 0.00008x_2^2$$

$$- 0.0002x_2x_3 - 0.0007x_2x_4 - 0.0005x_3^2$$

$$+ 0.0007x_3x_4 + 0.0026x_4^2$$

The multiple correlation coefficients (0.8862) and "F" value (21.2) show a good significance of this equation.

By taking three variables at values corresponding to the middle of the experimental field, a new equation is obtained, which shows the influence of the fourth variable. So, the variation of intrinsic viscosity with each variable of the mechanodegradation process is presented in Figure 2.

The increase of the capillary length determines a longer action of wall shearing stress which is responsible for the mechanodegradation. As a consequence, the extent of the mechanochemical degradation increases as this variable increases (curve 1).
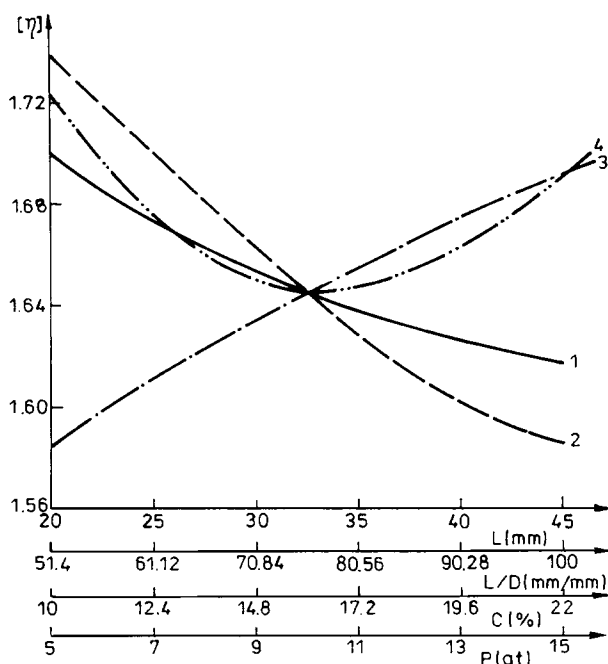
Fig. 2. The influence of the mechanodegradation process variables on the intrinsic viscosity: (1) capillary length; (2) length to diameter ratio; (3) solution concentration; (4) pressure (the middle of the experimental field).

The length to diameter ratio constitutes an important geometrical characteristic of the capillary, acting as a variable of the mechanodegradation process. The increase of this ratio is due both to the increase of the length or the decrease of the diameter of the capillary. As the diameter decreases wall shearing, stress increases due to the increase of shear rate. As a result intrinsic viscosity undergoes a more intensive decrease, as compared with the previous case (curve 2).

Another variable of the mechanodegradation process in similar conditions to wet-spinning is the solution concentration. The influence of this variable on the efficiency of mechanodegradation is not yet elucidated. Some researchers found out more intensive mechanodestructive effects in concentrated solutions[19,20] and others at low concentrations.[21,22] In our studies one can see that the most intensive mechanodestructive process takes place at lower concentrations (curve 3). This effect has the following explanation. At the concentrations used in this article (greater than 10%), as the value of this variable increases, the primary effects of the mechanodegradation are stronger. The great number of the macroradicals formed in conditions of a higher viscosity, due to the increase of the concentration, favors the termination reaction by chain transfer. As a consequence, some crosslinkings appear to a small extent which account for the increase in viscosity, masking the effects of mechanodegradation. So, it was found out that the process of dissolution of the filaments obtained by spinning the most concentrated solutions is much slower (about three times longer), an indirect evidence for a polymer structure with a low crosslinking degree.
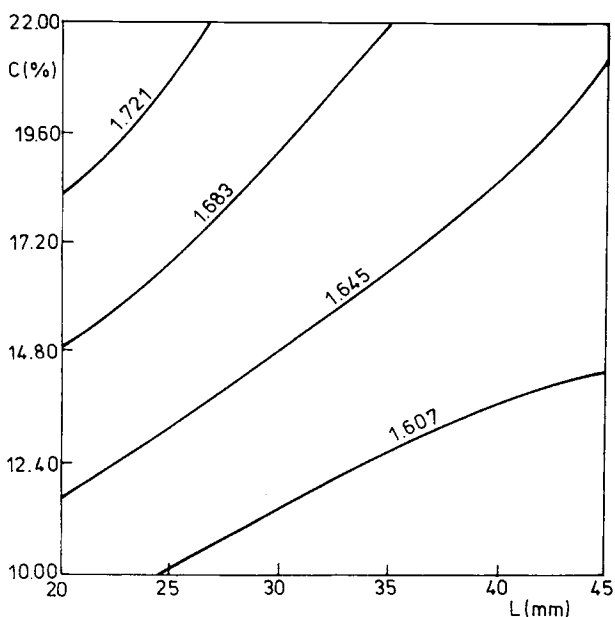
Fig. 3. Constant level curves of intrinsic viscosity in the experimental field of capillary length and solution concentration (the rest of variables are taken in the middle of their variation domain).

An important variable of the mechanodegradation process is the pressure which forces the polymer solution through capillaries. The curve giving the influence of this parameter (curve 4) shows a minimum of intrinsic viscosity value at a pressure of 10 atm. The decrease of the intrinsic viscosity with the increase of the pressure in the field from 5 to 10 atm is due, evidently, to the enhancement of the wall shearing stress. At pressures higher than 10 atm, the number of primary molecular splittings increases, so increasing the number of macroradicals. Together with their stabilization by recombination or disproportionation, chain transfer reactions take place, facilitated by the decrease of polymer "free volume" due to the pressure increase.[23,24] By the recombination of the secondary macroradicals thus formed, a crosslinking effect appears, which is much more enhanced at higher values of the pressure. These findings are in agreement with the fact that the dissolution rate of the mechanodegradated polymer is lower, as compared with the initial polymer.

By carrying out capillary shearings at pressures higher than 10 atm and using polymer solutions in the presence of a radical acceptor (DPPH), we noticed a continuous decrease of the intrinsic viscosity. It is clear that in these conditions the primary macroradicals formed by the mechanodegradation process were inactivated by the reaction with radicalic acceptor and so chain transfer reaction responsible for the crosslinkings is suppressed.

Information on the simultaneous influence of the process variables are obtained from the analysis of the response surfaces presented in Figures 3–6. The constant level curves from Figure 3 reveal the fact that the most intensive effects of mechanodegradation are obtained by solutions of lowest concentrations in the longest capillaries. Also, intensive mechanodestructive
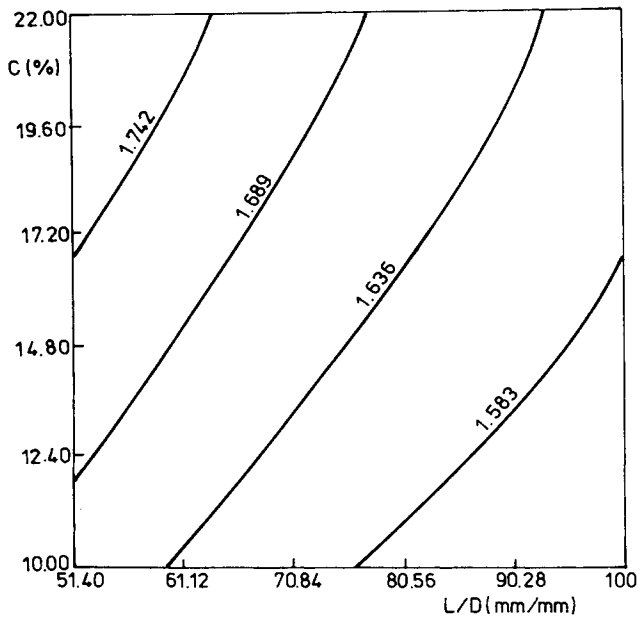
Fig. 4. Constant level curves of intrinsic viscosity in the experimental field of length to diameter ratio and solution concentration (the rest of variables are taken in the middle of their variation domain).
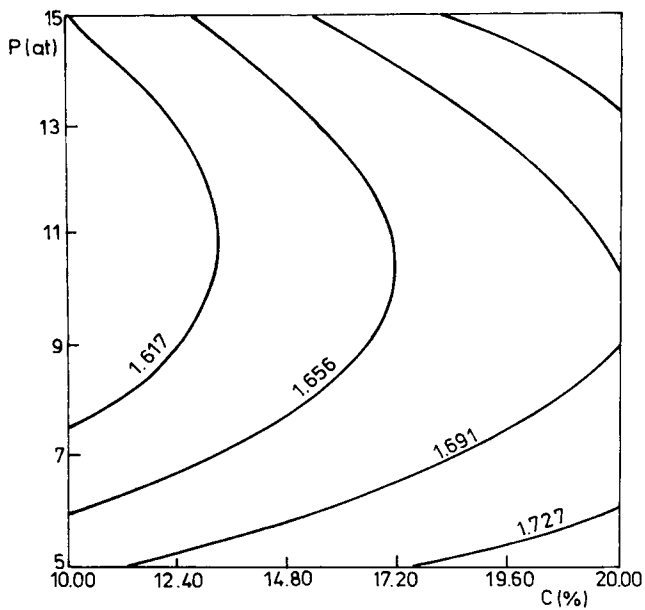

Fig. 5. Constant level curves of intrinsic viscosity in the experimental field of solution concentration and pressure (the rest of variables are taken in the middle of their variation domain).
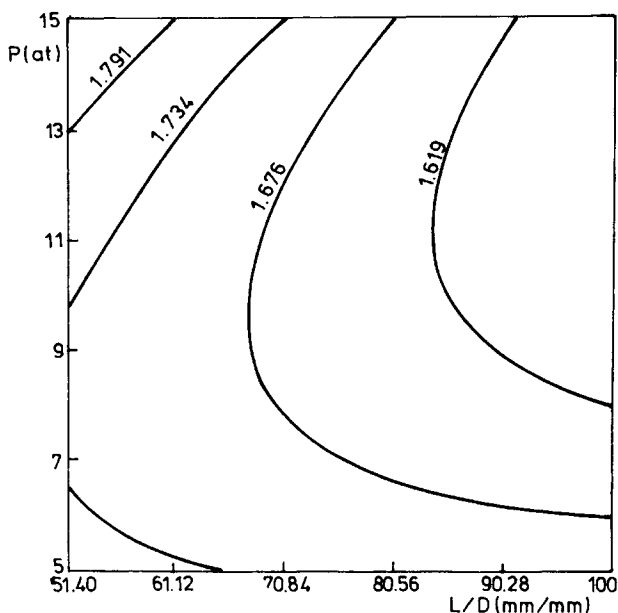
Fig. 6. Constant level curves of intrinsic viscosity in the experimental field of length to diameter ratio and pressure (the rest of variables are taken in the middle of their variation domain).

effects results at maximum length and minimum solution concentration, or maximum length to diameter ratio and minimum solution concentration (Fig. 4).

The behavior of the tested copolymer at both the simultaneous influence of the solution concentration and pressure, and capillary geometry and pressure, respectively, is of much interest. At a certain value of solution concentration, the mechanodegradation is about the same at low or high pressure (Fig. 5). But irrespective of the solution concentration a maximum degradation effect is recorded at a pressure of 10 atm. Similarly, the same extent of mechanodegradation is attained for a given length to diameter ratio, if it is working at low or high pressure, the intrinsic viscosity being minimum at maximum value of this parameter (Fig. 6).

One has to remark, in this last case, that, for each value of the L/D ratio, there is a certain pressure which leads to a maximum intrinsic viscosity of the copolymer. As a consequence, in order to avoid the mechanodegradation by capillaries shearing of the polymer solutions, in conditions simulating the wet-spinning, one has to use capillary of low length and length-to-diameter ratio, solutions of high concentration, and pressures corresponding to lower limit of the used experimental field (5 atm).

CONCLUSIONS

1. In conditions that simulate the wet-spinning the ternary copolymer based on acrylonitrile, α-methyl styrene, and vinyl acetate undergoes intensive mechanodestructive processes.

2. The mechanodegradation process is methematically represented by a nonlinear regression equation.

3. The intensity of the mechanodegradation process depends on the geometrical characteristics of the capillaries, solution concentration, and pressure.

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