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Gheorghe Hubca[a]; Iulia Pocsan[a]; Victor Kucinschi[a]; Mircea Teodorescu[a]; Mihai Dimonie[a]
[a] Faculty of Industrial Chemistry, Polytechnic University of Bucharest, Bucharest, Romania

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NEW ASPECTS REGARDING THE SYNTHESIS OF POLYVINYL ALCOHOL

GHEORGHE HUBCA,* IULIA POCSAN,
VICTOR KUCINSCHI, MIRCEA TEODORESCU,
and MIHAI DIMONIE

Faculty of Industrial Chemistry
Polytechnic University of Bucharest
1 Gh. Polizu Street, R-78126 Bucharest, Romania

ABSTRACT

Quantitative investigations on the evolution of the base-catalyzed alcoholysis of polyvinyl acetate have been carried out by performing the reaction in the mixing chamber of a Brabender-type micromixer or in an all-in-glass reactor fitted with a mechanical stirrer having arms from the bottom to the top of the reactor. The recorded Brabender diagrams displayed two peaks. The first one was ascribed to the gel phase while the second one was ascribed to the aggregation of polyvinyl alcohol particles. The increase of the hydrophobic character of the reaction medium by the addition of an alcohol with a longer hydrocarbon moiety (*n*-butanol) or of an aromatic hydrocarbon (benzene, toluene, *o*-xylene) determined the disappearance of the effect of agglomeration of the PVA particles.

INTRODUCTION

The most important procedure for the synthesis of polyvinyl alcohol is the base-catalyzed solution alcoholysis of polyvinyl acetate (PVAc). The main drawback of this is the large power consumption required by the "breaking down" of the gel which forms at a certain stage of the process [1–3]. In order to avoid the gel stage, a suspension procedure was developed using paraffin oil as a dispersing medium for the methanol solution of PVAc [4–6]. However, in this case the manufacture costs are increased due to the additional extraction step required for the removal of the paraffin oil absorbed onto PVA beads. Another drawback which affects the manufacturing capacity is that suspension processes cannot be managed in a continuous way.

The present paper describes a method for the improvement of the procedure of base-catalyzed solution alcoholysis of PVAc through a drastic decrease of the gel stage. The influence of the main parameters of the process has been studied, and power consumption during the reaction has been monitored using two different techniques.

EXPERIMENTAL

Methanol, benzene, toluene, and *o*-xylene, of reagent grade, were used as received, *n*-Butanol was purified by azeotropic distillation and rectification in order to decrease the water content below 200 ppm concentration. PVAc (Doljchim S.A.) was received as a 47 mass-% methanol solution. It was diluted to the required concentration just before use.

The alcoholysis experiments were carried out in a Brabender-type micromixer equipped with 50 and 70 cm^3 mixing chambers or in a 90-cm^3 all-in-glass reactor fitted with a mechanical stirrer having arms from the bottom to the top of the reactor. The reactor was also fitted with an appropriate device for recording the variations of power consumed by the mechanical stirrer during PVAc alcoholysis. Recorded power represents a measure of the viscosity of the reaction medium. When alcoholysis was carried out in the micromixer, the variation of the shear effort during the process was recorded [7].

The reactions were performed by mixing the catalyst and the PVAc solution at room temperature, followed by introduction of the mixture into the mixing chamber of the mixer or into the reactor kept at the desired temperature. A 0.053 g/cm^3 NaOH solution in absolute methanol was used as catalyst. The alcoholysis reaction was terminated by adding a methanol–acetic acid mixture. The PVA obtained was recovered by filtration, vacuum dried, and analyzed to determine its degree of hydrolysis [8].

RESULTS AND DISCUSSION

The viscosity of the reaction medium increases during methanolysis of PVAc due to association of the newly formed alcohol groups through hydrogen bonds [4, 5]. Utilization of the mixing chamber of a Brabender mixer as the place in which to perform the process offers the possibility of monitoring the reaction by recording variations of the shear stress.

The recorded Brabender diagrams shown in Fig. 1 indicate the variation of viscosity of the reaction medium during methanolysis of PVAc, and they generally display two peaks.

An older interpretation of the significance of the two peaks [5] assumes that the alcoholysis of PVAc initially occurs in a homogeneous medium up to the conver-

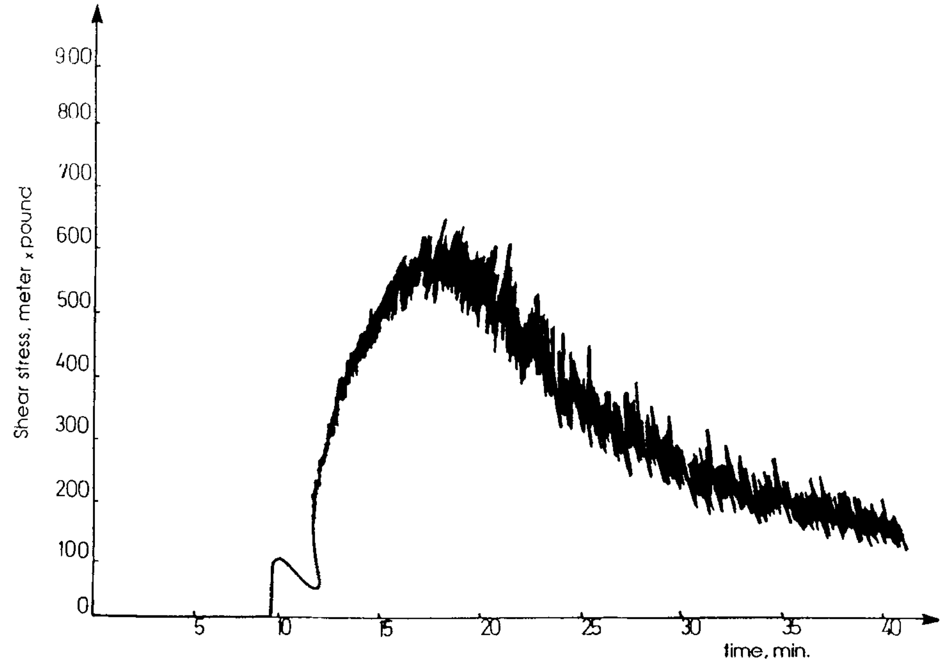

FIG. 1. Variation of shear effort during the methanolysis of PVAc. Mixing chamber volume 50 cm^3; [PVAc] = 28 wt%; concentration of catalyst [NaOH] = 0.4 wt%; temperature = 50°C; mixing rate (n) = 50 rpm.

sion indicated by the end of the first peak. Then the reaction medium becomes heterogeneous, and the second peak corresponds to the "breaking down" of the gel formed. However, visual observation of our samples just before and after the appearance of the first peak showed that the resulting PVA had already precipitated and the reaction medium was heterogeneous. Moreover, PVA samples taken at the beginning and at the end of the first peak displayed degrees of hydrolysis of 74 and 80 mol%, respectively, which is in good agreement with the widely accepted value of acetate group conversion corresponding to the formation of the gel (about 65 mol%) [9].

Based on these results, a new interpretation of the significance of the two peaks displayed in the Brabender diagrams is proposed: The alcoholysis process occurs initially in a homogeneous medium as long as the shear stress has a low and constant value. The increase of the shear effort, corresponding to the first peak, indicates the appearance and development of the gel, i.e., the beginning of the heterogeneous stage. After the first peak, the shear stress increases again and the curve displays significant momentary fluctuations due to intense shearing of the reaction mass. This second peak can be considered as an effect of the aggregation of the PVA particles. Methanol seems to favor aggregation because of its polar character.

The intensity and the time interval from the appearance to the disappearance of the peak on the diagram give information on energy consumption during that step and, therefore, information on the intensity of the physical process involved. Thus, the parameters of the PVAc alcoholysis process (polymer and catalyst con-

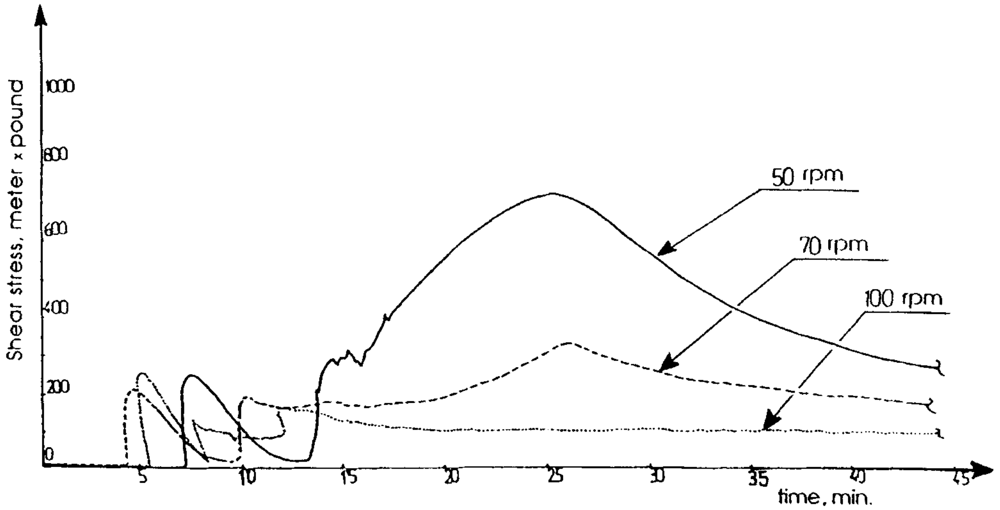

FIG. 2. Variation of shear effort during the methanolysis of PVAc for different mixing rates. Mixing chamber volume 70 cm^3; [PVAc] = 40 wt%; [NaOH] = 0.4 wt%; temperature = 35°C. The figure does not display the fluctuations due to shearing of the gel.

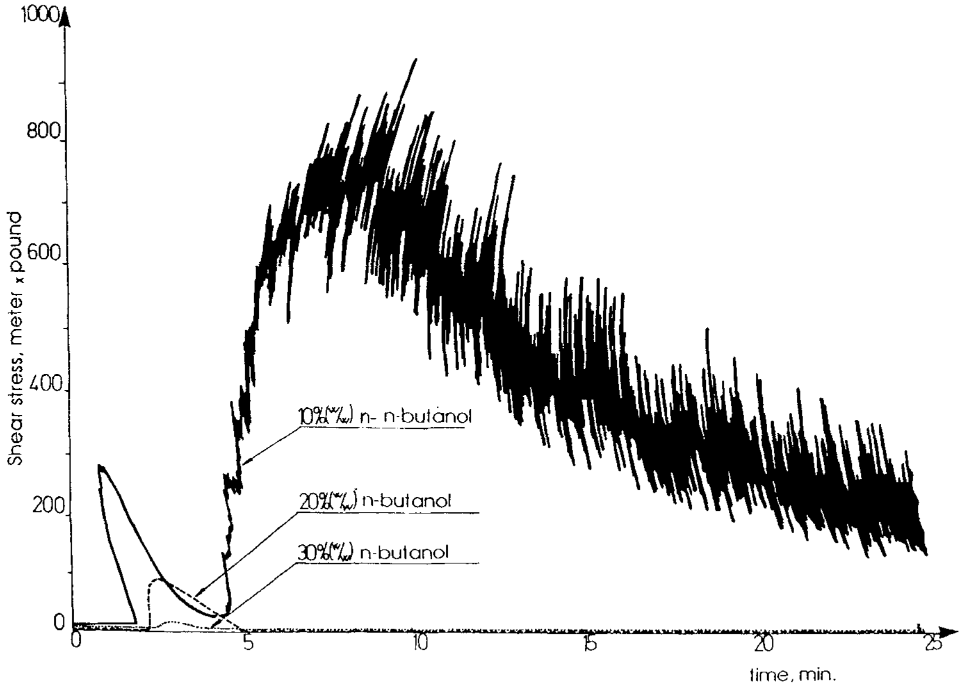

FIG. 3. Variation of shear effort during the alcoholysis of PVAc for different concentrations of *n*-butanol (*n*-BuOH). Mixing chamber volume 70 cm^3; [PVAc] = 40 wt%; [NaOH] = 0.4 wt%; temperature = 50°C; n = 70 rpm.

centration, temperature, and mixing rate) have a reasonable influence on the characteristics of the first peak but strongly influence the second one [7].

An increase of reaction temperature or of polymer or catalyst concentration enhances the aggregation of PVA particles, while an increase of the mixing speed has the opposite effect (Fig. 2).

Power consumption during the PVA synthesis process could be reduced by diminishing or completely eliminating the phenomena which determine the appearance of the two peaks on the Brabender diagram, i.e., gel formation and PVA particle aggregation. With this aim in view, increasing amounts of *n*-butanol were added to the reaction mixture (Figs. 3 and 4). The Brabender diagrams show a significant decrease of the second peak until it has completely disappeared, which means that PVA particle aggregation has been eliminated.

The above discussed results were obtained by using the Brabender micromixer. In order to check their reproducibility, alcoholysis experiments were carried out in an all-in-glass reactor fitted with a mechanical stirrer having arms from the bottom to the top of the reactor.

Based on the monitoring of the power consumed by the stirrer, PVAc alcoholysis in a methanol-*n*-butanol solvent mixture was investigated and compared with the reaction performed in pure methanol (Fig. 5).

The two alcoholysis processes had different evolutions. When the reaction was performed in a methanol-*n*-butanol mixture, precipitation of PVA occurred

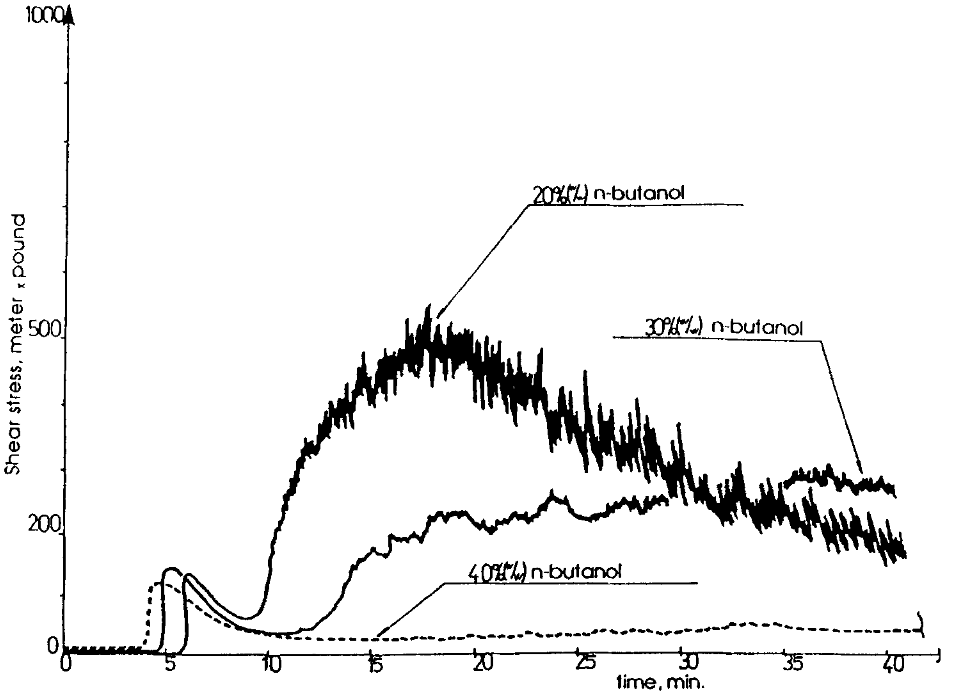

FIG. 4. Variation of shear effort during the alcoholysis of PVAc for different concentrations of *n*-butanol (*n*-BuOH). Mixing chamber volume 50 cm^3; [PVAc] = 28 wt%; [NaOH] = 0.4 wt%; temperature = 50°C; n = 50 rpm.

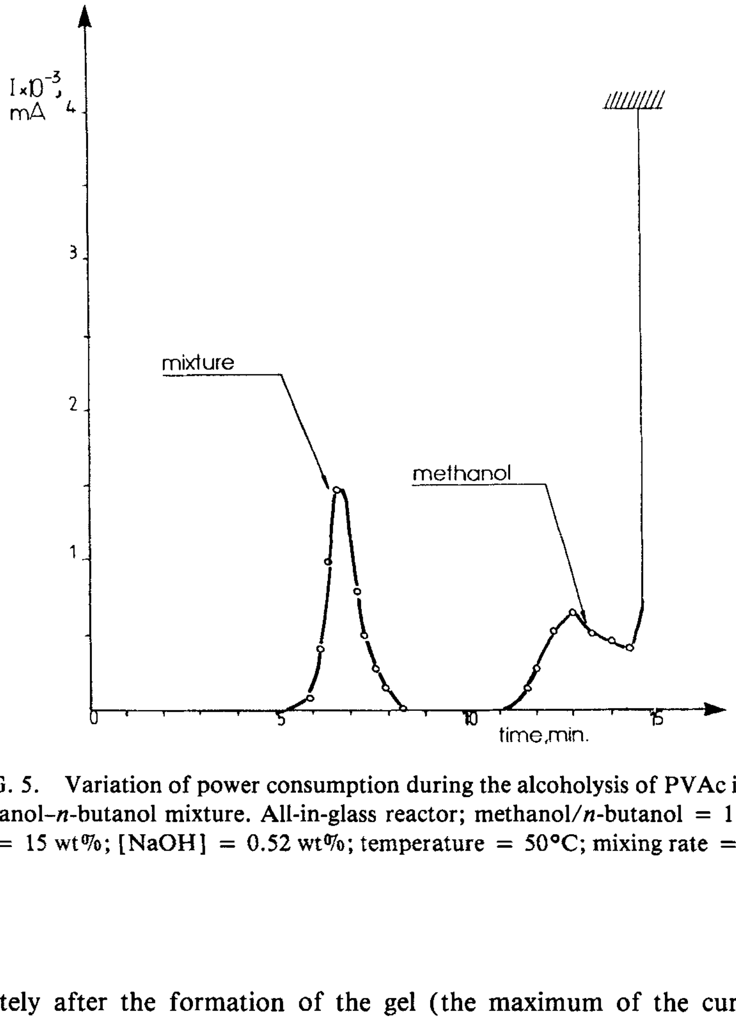

FIG. 5. Variation of power consumption during the alcoholysis of PVAc in methanol and methanol-*n*-butanol mixture. All-in-glass reactor; methanol/*n*-butanol = 11/6 (w/w); [PVAc] = 15 wt%; [NaOH] = 0.52 wt%; temperature = 50°C; mixing rate = 1280 rpm.

immediately after the formation of the gel (the maximum of the curve). PVA particles did not aggregate further, and the power consumption remained constant at a low level. In the case of pure methanol as solvent, a new increase of power consumption was recorded following the peak corresponding to the gel stage. This fact is ascribed to PVA particle aggregation which caused stirrer blocking and, eventually, the cessation of measurements. The two increases of power consumption correspond to the two peaks on the Brabender diagrams.

The effect of the addition of *n*-butanol on the aggregation of PVA particles was supposed to be due to the increase of the hydrophobic character of the reaction medium. In order to check this hypothesis, the reaction was performed in methanol-aromatic hydrocarbon mixtures and the power consumption was monitored. For this purpose the aromatic series benzene-toluene-*o*-xylene was considered (Fig. 6). The curves show that the intensity of the peak corresponding to the gel stage decreases in the order benzene > toluene > *o*-xylene, i.e., the reverse order of the number of carbon atoms contained in each hydrocarbon. Simultaneously, no aggregation of PVA particles was observed.

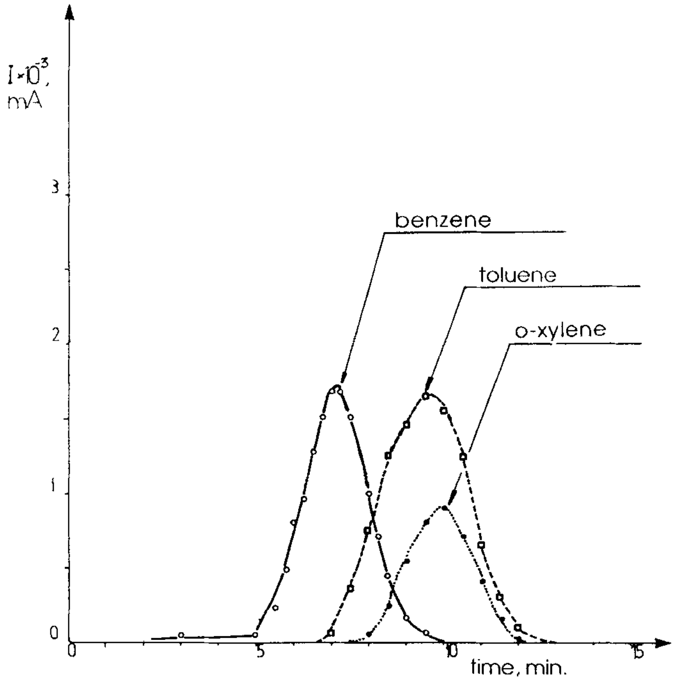

FIG. 6. Variation of power consumption during the alcoholysis of PVAc in methanol-aromatic hydrocarbon mixtures. All-in-glass reactor; methanol/aromatic hydrocarbon = 4/7 (w/w); [PVAc] = 12 wt%; [NaOH] = 0.52 wt%; temperature = 35°C; mixing rate = 1280 rpm.

CONCLUSIONS

1. Quantitative results concerning the evolution of the PVAc alcoholysis process were obtained by performing the reaction in the mixing chamber of a Brabender-type micromixer or in a all-in-glass reactor fitted with a mechanical stirrer having arms from the bottom to the top of the reactor. The information obtained in both cases led to the same conclusions.

2. The recorded Brabender diagrams displayed two peaks. The first one was ascribed to the gel phase while the second one was ascribed to the aggregation of PVA particles.

3. The increase of the hydrophobic character of the reaction medium by the addition of an alcohol with a longer hydrocarbon moiety (*n*-butanol) or of an aromatic hydrocarbon (benzene, toluene, *o*-xylene) determined the disappearance of the effect of agglomeration of PVA particles. The consistency of the gel was influenced by the nature of the aromatic hydrocarbon, and it decreased in the order benzene > toluene > *o*-xylene.

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