Design and multiobjective optimization of a novel reactive extrusion process for the production of nanostructured PA12/ PDMS blends

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ABSTRACT

This work deals with the manufacture, by reactive extrusion, of Polyamide 12 (PA12)/Polydimethylsiloxane (PDMS) nanostructured blends, with the purpose of improving the mechanical properties of PA12. The originality of the process is based on the simultaneous anionic synthesis of both PA12 and a compatibilizer (PA12-PDMS-PA12) in the presence of the dispersed phase (PDMS).The process was studied owing to an adapted experimental strategy which allowed elaborating empirical models able to predict the effect of the main operating variables on the corresponding blends properties. These models were then used in a multiobjective optimization procedure which allowed, determining the best operating conditions for the production of blends for which all specific properties were maximized except the diameter of the dispersed phase which was minimized.
This work led to a significant improvement of the mechanical properties of PA12, particularly its impact energy at low temperature.

Keywords: nanostructured blends, PA12, PDMS, reactive extrusion, multiobjective optimization

1 INTRODUCTION

The concept of physically combining two or more polymers via blending to enhance mechanical properties of materials, has received a lot of attention [1], [2].

Traditionally, the elaboration of these blends is carried out by mixing, at the melt state, the polymers in the presence of a compatibilizer [3]. Usually, under these conditions, this leads to a micrometric scale dispersion of the minor phase and it is known that at this scale of dispersion the mechanical properties of the final materials are not optimal, whatever the method of compatibilization. By contrast, this work sets out a new process of elaboration of polymers blends, through a typical example: the manufacture, by reactive extrusion, of PA12/PDMS nanostructured blends. In this process, the continuous phase (*PA12)* is synthesized in the extruder in the presence of: (i) the dispersed phase (*PDMS)*, (ii) a new and particularly efficient catalytic system (*aluminium hydride* as catalyst *and MDI caprolactam* as activator and (iii) a macro-activator *(functionalized PDMS*: *α,ω–dicarbamoyloxy-caprolactam-PDMS)* well suited to develop *in situ* a tri-block (PA12-PDMS-PA12) copolymer acting as compatibilizer. The originality of the process is based on the simultaneous synthesis of both PA12 and the compatibilizer by activated anionic polymerization of lauryl lactam (LL). The final goal is to obtain blends in which the elastomer particles *(PDMS)* are dispersed and stabilized at a nano-scale and with mechanical properties better than those of PA12.

This research comprises (i) the synthesis, the kinetic study and the modeling of the activated anionic polymerization of LL (AAPL). This was preceded by the synthesis of both the macro-activator and a catalytic system giving rise to complete conversion of LL in a short and controlled reaction time, (ii) the complete design, modeling and optimization of the reactive extrusion process.

2 STUDY AND MODELING OF THE ANIONIC POLYMERIZATION

Prior to the study of this polymerization, the catalytic system and the macro-activator were synthesized. The efficiency of the catalytic system was tested according to methods described in previous papers [4], [5], which clearly showed that the total conversion of LL can be achieved, at 220°C, in a reaction time comparable to classical residence times in the extruder (3-4 minutes). This result was confirmed owing to experiments carried out in the extruder and followed by the construction of a kinetic model for the syntheses of both the matrix (PA12) and the interfacial agent (PA12-PDMS-PA12) [5].

2.1 Elementary chemical reactions

The chemistry of AAPL is complex in nature. However, the process is of high interest, particularly, owing to (i) its fast reaction rate and (ii) the interesting mechanical properties of the resulting polymer. AAPL involves several reversible and irreversible reactions in which the active species are consumed and regenerated. The general reaction scheme responsible for the polymer chains formation has long been established. It comprises:

- an initiation step (reaction between the activator and the catalyst),
- a propagation step consisting of a proton transfer followed

by a nucleophilic addition,
- side reactions, mainly Claisen's reactions characterized by the formation of enols and condensation reactions.

2.2 Main assumptions

The establishment of the model requires the use of several assumptions to enhance the speed of convergence. These assumptions can be summarized as following:
- initiation is very fast and is considered as irreversible,
- the reaction giving rise to enols will not be taken into account because it is analytically similar to the proton transfer reaction. Therefore, its kinetic parameter will be included into that of the proton transfer,
- proton transfer, propagation and Claisen's reactions rate are supposed to be independent of the chain-length,
- the reactor is isothermal and ideally mixed.

2.3 Mathematical model

Thanks to the above mechanisms and assumptions, the model is based on material balances expressed for each species (activator, catalyst, monomer, active species and macromolecules). It consists of a system of differential algebraic equations involving 18 parameters which were determined through the minimization of the maximum likelihood criterion, J, with the experimental data:

$$J = \sum_{data} (X^{experimental} - X^{simulated})^2 \qquad (1)$$

where X is LL conversion. This minimization was obtained using an evolutionary algorithm previously developed in our laboratory [6], [7]. These 18 parameters were identified thanks to batch polymerizations carried out at 180°C and 220°C with the same initial concentrations of monomer: $[M]_0$=4.55 mol.l^{-1}, catalyst: $[C]_0$=3.10^{-2} mol.l^{-1} and activator: $[A]_0$=3.10^{-2} mol.l^{-1}). Monomer conversion, X, was determined for reaction times varying between zero and around 15 minutes, through a Soxhlet extraction of the residual monomer during 24 hours, followed by weighting the resulting polymer sample previously dried under vacuum at 80°C during 24 hours.

2.4 Validation of the model

Figure 1 shows the time evolution of X for experiments carried out (i) at 180 and 220°C with the same recipe ($[M]_0$=4.55mol.l^{-1} and $[C]_0$=$[A]_0$=4.55.10^{-2}mol.l^{-1}), (ii) at 200°C for two different activator and catalyst concentrations.

The results clearly show the good agreement between simulated and experimental data. Moreover, as expected, X is higher when the temperatures and the catalytic system concentrations are increased.

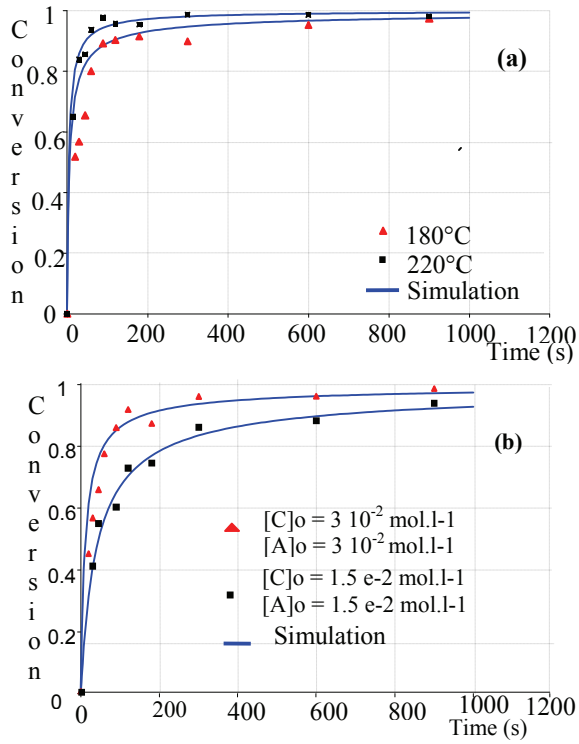

Figure 1: Effect of temperature (a) and catalytic system concentration (b) on lauryl lactame conversion

3 BLENDS ELABORATION

3.1 Preliminary experiments

Blends were synthesized in a conical intermeshing counter-rotating twin screw extruder. Melting of LL, PDMS, functionalized PDMS and activator was carried out in an electrically heated flask mechanically stirred under a nitrogen atmosphere. This mixture and the catalyst were pumped separately by controlling the mass flow into the extruder hopper. Connections between the flask and the extruder were accomplished by a heated metal tube. The resulting materials were then pelletized, dried at 80°C and injection-molded in the form of test bars for tensile and strength measurements. Preliminary experiments allowed to analyze the effects of the macro-activator concentration, [MA], the [PDMS]/[MA] ratio and PDMS number average molar mass, Mn, on blends morphology and mechanical properties. The results clearly showed that the average diameter of the dispersed phase decreased while the corresponding impact energy increased significantly when [MA] and Mn were increased.

3.2 Process modeling

An experimental design was then carried out in order to elaborate a model able to predict the effect of the main process operating variables [*Screw rotation speed (N),*

PDMS feed rate (Q), concentration (F) and number average molar mass (Mn)], on the corresponding blends properties [*LL conversion (X), average diameter of the dispersed phase (D_n), Young modulus (E), melting temperature of the matrix (T_m) and Charpy impact energy (E_{imp})].*

In order to obtain a model with correct specification and well determined parameters, a series of 30 runs were carried out. Given the fact that the expected responses do not vary in a linear manner with the selected variables, a D-optimal plan, where the response could be modeled in a quadratic manner, was selected to enable the quantification of the prediction of the responses.

An optimal number of 20 experiments were obtained using an evolutionary algorithm [6], [7].

The rotatability method was then used to complete the experimental design in order to increase the degree of freedom and to choose 6 more experiments to validate the model.

4 repetition experiments were also performed in order to validate the statistical significance of the chosen experimental plan.

The proposed mathematical equations were complete second degree polynomials using the normalized values of N, F, Q, and Mn, respectively.

The different steps used for the calculation of the model coefficients (a_i), together with their confidence intervals are summarized here only for Young's modulus. The final polynomial equations of the other properties were obtained using the same method.

By applying a multiple regression analysis on 20 experimental data, the coefficients of equation (1) were estimated.

The quality of the estimations needs to be checked out. The confidence interval for each coefficient with a risk of 5% was then estimated. If the confidence interval of a coefficient is large and include zero, the parameter must be discarded (its effect being negligible). So, a total of 7 coefficients were deleted which led to a model containing 8 coefficients.

The final structure of the model was then defined by:

$$E = 520 - 34x_2 - 189x_3 - 113x_4 + 53x_1x_2 - 60x_2x_4 + 128x_3^2 + 132x_4^2 \quad (1)$$

It was then necessary to check out the absence of correlation between the coefficients of the model.

The degrees of correlation between two coefficients were evaluated using the variance-covariance matrix. In the present case no correlation between the different coefficients was found.

The validity of the polynomial equation was finally verified by use of Fischer-Snedecor's test based on the ratio of the variances applied to identification, validation and repetition experiments.

Figure 2 shows, as examples, the validation of the model equations obtained for D_n and E_{impact} for which a fairly good agreement was observed between simulated and experimental data.

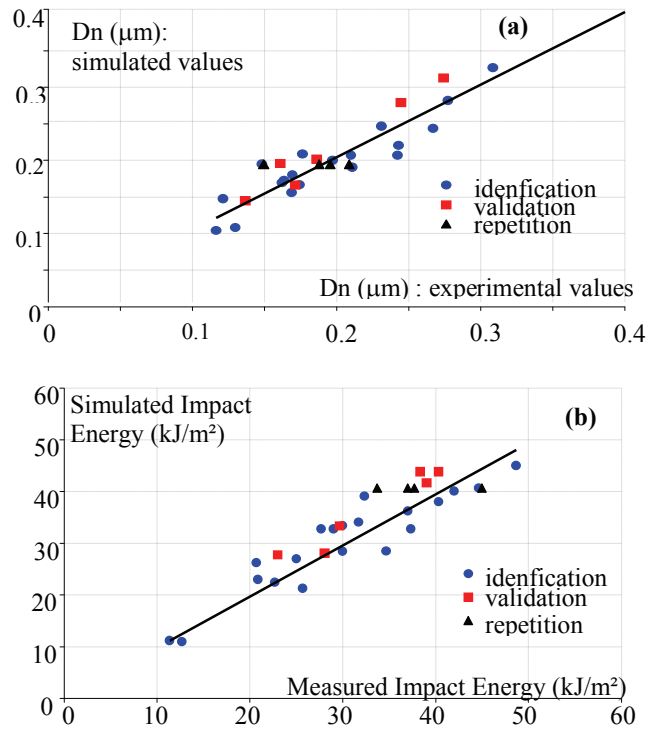

Figure 2: Validation of the model: simulation versus experiments (a): Average particles diameters; (b): Impact energy

3.3 Multiobjective optimization

The model thus obtained was then used in a multiobjective optimization procedure which allowed, owing to the use of the concept of domination, obtaining a set of non-dominated solutions called Pareto's domain.

A specific decision engineering tool was then set up to classify all these solutions taking into account the preferences defined by a decision maker in order to determine the best operating conditions for the production of nanostructured blends characterized by a high impact energy at low temperature.

The concept of domination used to select a solution, is defined in such manner that a solution (compromise or vector) z_1 dominates another solution z_2 if it is better or equal for all criteria and strictly better for at least one criterion [8]. The input variables constitute Pareto's domain while the output criteria constitute Pareto's front. In the present study, this domain was defined by an infinite number of solutions obtained using an evolutionary algorithm [7].

Among the different methods developed to classify the non-dominated solutions, we used the Net Flow Method [9] based on a decision-maker's choice defined for each property by 4 parameters: weight and preference, indifference and veto thresholds. Table 1 gives the values of the 4 parameters used in this investigation. The selection of

a proper level of each threshold is not a trivial task. It is based on a good knowledge of the process and on the range spanned by each criterion of Pareto's front.

Decision-maker's choice	T_m	D_n	X	E_{impact}	E
Weight	0.10	0.30	0.15	0.30	0.15
Indifference threshold	0.5	0.005	0.005	2	5
Preference threshold	1	0.01	0.01	5	20
Veto threshold	2.6	0.03	0.03	10	40

Table 1. Decision-maker's choice for each criterion

The final objective of this work was to maximize T_m, X, E_{impact} and E, and to minimize Dn. According to the decision maker's choice, an example of visualization of the results is given through an input-input graph (Figure 3a): F, versus N and an output-output graph (Figure 3b): $E_{impact)}$, versus Dn. This example clearly shows that N covers all the range of its use, while (F) is limited in a restricted range**.** On each figure are represented 5000 non-dominated solutions constituting Pareto's domain -figure 3(a)- and Pareto's front -figure (3b)-, respectively. The 20% best and the preferred solutions are also indicated in grey and by a red triangle respectively.

These results show that, for the proposed decision-maker's choice, the recommended operating conditions are: N=75.6 rpm, F=3.43%, Q=20.1 g/min and Mn=62,700 g/mol. The corresponding values of the blends properties are: X=1, D_n=128 nm, T_m=167.6°C, E=485 mPa and E_{impact}=43 kJ/m^2. This proves that the chosen decision-maker's preferences allowed well to minimise Dn and to maximize E_{impact}. This was a deliberate choice to obtain a nanostructured blend with high impact energy.

To validate these results, an experimental run was carried out using the following operating conditions: N=80 rpm, F=3.30 g/min., Q=20 g/min. and Mn=62700 g/mol. The corresponding blend properties were: X=0.95, D_n=115 nm, T_m=167.4°C, E=490 mPa and E_{impact}=42 kJ/m^2. They correspond to an actual improvement of pure PA12 properties which are: E_{impact}=7 kJ/m^2 (at 23°C) and 6 kJ/m^2 (at -30°C), T_m=178°C and E=1100 mPa.

4 CONCLUSION

The objective of this work was to determine the optimal operating conditions of a reactive extrusion process for the production of nanostructured PA12/PDMS blends. In this process, the matrix (PA12) and the compatibilizer (PA12-PDMS-PA12) were simultaneously synthesized in the presence of the dispersed phase (PDMS). The optimization is a multiobjective procedure using: (i) Pareto's concept, to determine a large number of non-dominated solutions, (ii) ranking of these solutions according to decision-makers' preferences. This method allowed selecting the optimal operating conditions giving rise to the best properties of the corresponding blends and confirmed the importance of their nanostructured morphology.

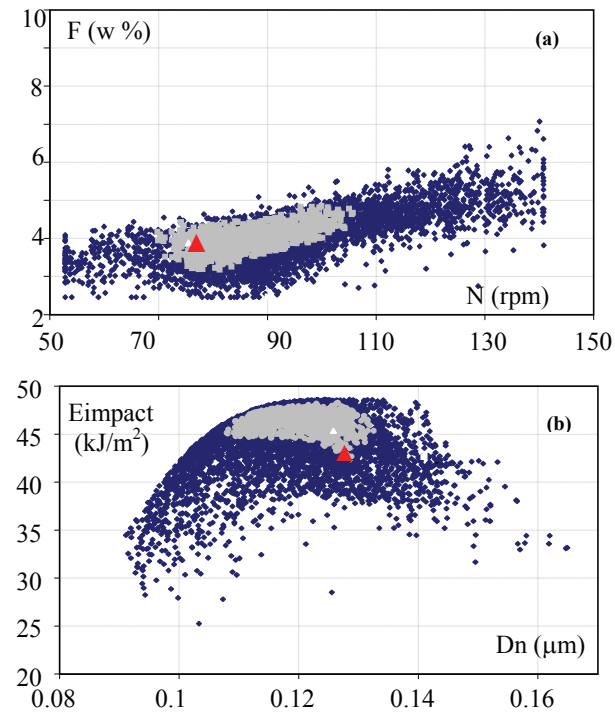

Figure 3: Ranked set of non dominated solutions:
(a) F versus N ; (b) E_{impact} versus Dn

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