Impact modification of polyamide-12 through blending with liquid polybutadiene, 1
Binary blends of PA 12 and liquid polybutadiene

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Abstract: Blends of polyamide 12 (PA12) with liquid polybutadiene (HTPB) were prepared by melt blending over a composition range varying from 0 to 20% of polybutadiene. A study of the potential reactions led to the conclusion that the system undergoes no chemical reaction under the processing conditions used. Scanning electron micrographs of the blends showed a good dispersibility of HTPB in the PA12 matrix. Charpy impact tests and tensile tests demonstrated that the dispersion of HTPB in PA12 provides a good impact toughness enhancement but leads to a decrease of Young's modulus.

Introduction

In the past decades there has been a constant interest in studying the enhancement of impact properties of polyamides [1-53], since these are polymers showing very good mechanical properties but a relatively low resilience due to a poor resistance to the propagation of an existing crack under impact. For example, the un-notched Charpy impact strength of PA12 (ISO 179, 1eU at 23°C) is higher than 100 kJ m−2 (no break), whereas its notched Charpy impact strength (ISO 179, 1eA at 23°C) is about 5 kJ m−2. When considering the improvement of impact properties of a polymeric material, the general strategy consists in blending it with an other polymer, the modulus of which is at least about 10 times lower [3], so as to obtain a dispersion of spherical particles of the low-modulus polymer in a continuous matrix. The materials thus obtained generally exhibit enhanced impact properties combined with bulk mechanical properties (e.g., modulus) quite equivalent to those of the original material.

One can find in the literature several types of such blends that can be classified as follows: class I - the binary blends [1-8,30,34], and class II - the compatibilized blends [5,6,9-26,30-52,54-65]. The latter are blends in which a third component is added, that is usually a block-copolymer, one block of which shows a good compatibility towards the continuous phase and the other towards the dispersed particles.

While class I blends are mostly prepared the same way (i.e., melt mixing of the two components, either in an extruder or in an internal mixer), class II blends can be obtained through several processes. Those will be described in a following paper that
will deal with compatibilized blends of PA12 and HTPB. In this first paper, we will focus on binary blends of PA12 and a hydroxytelechelic liquid polybutadiene (HTPB).

Usually, impact toughened blends are obtained through melt blending of a ‘brittle’ thermoplastic matrix (here PA12) and a soft phase, which in most cases is an elastomer (EPDM, EPR, …) [1-29,54-56], even if good improvement can be obtained for PA6 or PA6-6 with polyolefins such as PE or PP [3,5,32,39-47,57-63]. One can also find in the literature examples where the impact modifier itself is a multiphase material like ABS or SEBS [19,20,30-38]. For binary blends, the size of the dispersed particles depends mostly on the viscosity ratio of the two phases during melt blending, on processing parameters such as shear rate or processing time, and on the weight ratio of the phases [1,4,18,55,66]. In this study, we intended to use, instead of a ready-made elastomer, a liquid oligomer precursor, HTPB. The choice of HTPB was mostly due to its functionality (Pham et al. have studied by $^1$H and $^{13}$C NMR and by titration the microstructure of HTPB and found 22% of 1,2-vinyl units and an average hydroxyl functionality of 2.4 [67-72]) that enables reactive compatibilization in the case of compatibilized blends that will be presented in a next paper.

PA12 and HTPB were characterized, and the reactions that are likely to occur during their melt blending were explored. Binary blends were prepared. Their morphology was studied by scanning electron microscopy (SEM). The blends were granulated and testing bars were melt injected. Notched Charpy impact tests, as well as tensile tests were performed on the latter.

**Results and discussion**

*Thermal analysis of the polymers*

Fig. 1 and Fig. 2 show the degradation curves obtained for PA12 and HTPB. It can be concluded from the results of those tests that both PA12 and HTPB seem to be thermally stable at 200°C. Indeed, the 2% weight loss points for PA12 and HTPB are, respectively, at 420°C and 400°C. In isothermal conditions, the weight loss of PA12 at 220°C after 45 min is less than 0.5%, and that of HTPB at 320°C after 45 min is less than 2%. It can hence be assumed that only little degradation of the materials should occur when preparing the blends for 20 min at 200°C.

*Mixing of pure PA12*

After introduction of the PA12 pellets in the mixer, the torque decreased quickly. This decrease is due to fusion of the pellets (Fig. 3). After complete fusion, the torque levels off at a constant value. This stability lets us assume that PA12 is thermomechanically stable under those conditions. Indeed, crosslinking or chain extension reactions would induce an increase of the torque, whereas chain scission reactions would be detected by a decrease of the torque. However, size exclusion chromatography (SEC) was needed to confirm this interpretation, since the torque stability could result from a competition between chain scission and chain extension.

*SEC of PA12*

Pure pellets of PA12 were trifluoroacetylated (cf. Exptl. part) as well as 18 min melt processed PA12. The samples were then dissolved in dichloromethane and analysed by SEC. If there had been concomitant chain scission and extension, the peak would
have been widened, but the two chromatograms are identical (Fig. 4). We can hence conclude that neither chain extension nor chain scission reactions occurred during processing.

![Thermogravimetrical analysis (TGA) curves of PA12 AECHVO](image)

**Fig. 1.** Thermogravimetrical analysis (TGA) curves of PA12 AECHVO (cf. Exptl. part). (a): Heating rate = 20°C/min, (b): isothermal degradation at 220°C

**Determination of the amine functionality of PA12**

First measurements on pure PA12 pellets led to a functionality of 0.5 NH₂ per chain. However, it appeared that after processing of PA12 at 200°C, this functionality decreased down to 0.25. This decrease in amine content occurred in the very first minutes of processing, and then the functionality levelled off. Further reprocessing did not reveal any new decrease, showing that the disappearing of amine functions could not be due to further condensation of PA12 chains. However, this hypothesis of further condensation is not relevant when it is considered that the torque remains stable (Fig. 3) and that SEC measurements showed that the chromatograms of pure pellets and of processed PA were just the same (Fig. 4).

Therefore, there has to be another explanation of that phenomenon. We assumed that the overestimation of amine content in the pure pellets could be an artifact due to the presence of residual monomer (lauryl lactam) in the commercial product. This lactam could indeed be opened during the titration or the preparation of the sample (Fig. 5), and the amine function of the aminododecanoic acid thus obtained could be taken for an amine end group of a PA12 chain in the conductometric titration of dissolved pellets. This lactam is besides likely to be opened, during melt mixing, by a carboxylic acid end group of a PA12 chain. It would thus get incorporated in the chain
as a further monomer unit (Fig. 6) and would no longer be detected by titration. Since reprocessing of PA12 did not lead to a further decrease of functionality, we can conclude that high temperature allows that reaction to be both total and fast.

Fig. 2. TGA curves of HTPB. (a): Heating rate = 20°C/min, (b): isothermal degradation at 320°C

Fig. 3. Evolution of the Brabender torque during mixing of PA12. 200°C, 10 rpm
Fig. 4. CH₂Cl₂ SEC curves obtained for crude and melt processed PA12

![SEC curves](image)

Fig. 5. Postulated opening of residual lauryl lactam in the presence of water (in phenol/water 90/10 at 90°C or during room temperature titration)

![Chemical reaction](image)

Fig. 6. Incorporation of lauryl lactam residual monomer during mixing at 200°C through ring opening by carboxylic end groups of PA12

The relevance of this hypothesis had to be checked. Caprolactam and lauryl lactam underwent the same treatment as PA12 samples prior to their conductometric titration. Just like in the case of polyamide, there is a discontinuity of the curve at the equivalence point. However, there is still a question here, since it requires under our experimental conditions 2 mol HCl instead of one for 1 mol of lactam. This could be due to kinetic problems, but this issue was not further investigated. However, it remains obvious that the presence of lactam can interfere during the titration, thus leading to an overestimation of the amine content in the polyamide.

If we assume that the real amine content of PA12 is about 0.25 per chain, considering that PA12 molar mass is 20,000 g mol⁻¹ (i.e., a degree of polymerization of 100), there is one amine end group for four PA12 chains, i.e., for 400 monomer units. Hence, only one lactam per 400 monomer units would be enough to estimate doubled amine functionality, i.e., 0.25% residual monomer. This proportion is not
irrelevant for an industrial product: according to the supplier, the residual monomer proportion after synthesis is about 5 - 10%. Moreover, this calculation does not take into account the excess of acid required for lactam titration that would lead to an even lower residual lactam proportion. Such a quantity of residual lactam, once incorporated as new monomer units, would lead to a chain extension of 1 unit per 8 chains. This extension is not large enough to be noticed by SEC measurements. The lactam hypothesis is therefore in good agreement with the non-evolution of the chromatograms (Fig. 4).

**SEC study of the thermal crosslinking of HTPB**

![SEC curves of HTPB](image)

**Fig. 7. CH₂Cl₂ SEC curves of HTPB. Evolution of HTPB in a glass reactor at 200°C**

**Tab. 1.** Evolution of the number- and weight-average molar masses and of the polymolecularity (I) of HTPB in a reactor at 200°C, determined by CH₂Cl₂ SEC

<table>
<thead>
<tr>
<th>Reaction time in min</th>
<th>$\bar{M}_n$ (g mol⁻¹, eq. PS)</th>
<th>$\bar{M}_w$ (g mol⁻¹, eq. PS)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6700</td>
<td>18100</td>
<td>2.7</td>
</tr>
<tr>
<td>45</td>
<td>6300</td>
<td>23200</td>
<td>3.7</td>
</tr>
<tr>
<td>60</td>
<td>6000</td>
<td>25700</td>
<td>4.3</td>
</tr>
<tr>
<td>75</td>
<td>5600</td>
<td>22600</td>
<td>4.0</td>
</tr>
<tr>
<td>120</td>
<td>5900</td>
<td>27500</td>
<td>4.7</td>
</tr>
</tbody>
</table>

The chromatograms obtained during heating of HTPB are shown in Fig. 7. The one obtained for untreated HTPB shows a bimodal molar mass distribution. As the polybutadiene is heated, a slow diminution of the low molar mass peak occurs, whereas a new high molar mass peak appears. This evolution reveals that some chemical degradation of HTPB occurs, resulting in an enhancement of weight average molar...
mass and polymolecularity, as shown in Tab. 1. However, it should be noticed that the peak area remains stable even for the last chromatogram, which implies that all samples were fully soluble. There is, therefore, no crosslinking of HTPB during this experiment, but only chain extension. Moreover, we can notice that the evolution of the chromatogram is not really significant before 1 h. When considering that the residence time in the Brabender mixer during blending is 20 min, we can conclude that there should be no thermal crosslinking of HTPB during the preparation of the blends.

_Esterification of hydroxyl functions of HTPB with carboxylic end groups of PA12_

According to the titration results obtained by Lê [73], the amount of carboxylic end groups in PA12 AECHVO is between 1.1 and 1.5 per chain. Since HTPB bears hydroxyl functions, we can wonder whether an esterification reaction between HTPB and PA12 is likely to occur in our blending conditions. Such a reaction would lead to the formation of a block PA-b-PB copolymer that could act as a compatibilizer in the blend.

 Bulk reactions of lauric acid (chosen as a model of PA12 carboxylic end groups) with HTPB were conducted at 200°C under nitrogen flushing for at least 2 h, with large excess of lauric acid \((r = [\text{COOH}] / [\text{OH}] = 2.5)\) and under stoichiometric conditions \((r = 1)\).

\(r = 2.5:\)

FTIR spectra were taken before and after the reaction (Fig. 8). Even if the peak at 1708 cm\(^{-1}\) remained after the reaction, a new peak in the ester region appeared at 1738 cm\(^{-1}\). This new peak shows that an ester was formed during the reaction.

![FTIR spectra of HTPB and of HTPB / lauric acid blends. Zoom in the carbonyl bands area](image)

_Fig. 8. FTIR spectra of HTPB and of HTPB / lauric acid blends. Zoom in the carbonyl bands area_
\( r = 1 \):

Samples were collected during the reaction. They were dissolved in a mixture of 2-
butanone, isopropyl alcohol and water (20/10/20 v/v/v), and the remaining acid
functions were titrated with aqueous NaOH 0.1 N. The disappearing of the carboxylic
functions is plotted against time in Fig. 9.

It appears that only a few 10\% of the acid functions have reacted after 20 min. Such
a proportion would however lead to the formation of enough compatibilizing
copolymer if the reaction in the polymer blends reaches such an extent. But it should
be noticed that this model reaction occurs in a homogeneous phase, whereas the
reaction during melt mixing of the two incompatible polymers would occur in a
multiphase system. In that case, the interfacial concentration of the reactive functions
will not be as high, and since the kinetics of the reaction seem to be slow, we can
assume that esterification during the processing of binary blends of HTPB and PA12
is negligible.

![Fig. 9. Disappearing of acid functions during the reaction between HTPB and lauric acid](image)

**Blending of the materials**

Two series of blends were prepared, with 5, 10, 15 or 20\% HTPB, ImPB or hmPB
(low and high molar mass polybutadienes), at rotation rates of the blades of 10 or 20
rpm. The compositions and the rotation rates for blends 1 to 8 are listed in Tab. 2.
The evolution of the torque during the preparation of blends 1 to 4 is shown in Fig.
10 and Fig. 11. The curves are classical curves of absorption of a liquid by a thermo-
plastic melt. The higher the weight ratio of HTPB, the lower the plateau torque.

Fig. 12 shows the morphology of blends 1 to 4 and of a processed PA12. The hole-
less fracture surface of the PA12 sample shows that the cavities observed on the
blends can be related to dispersed particles of polybutadiene. For blends 1 to 3, the
polybutadiene is well dispersed as fine spherical particles. Fig. 13 shows the size
distribution of these particles. In the 20\% blend 5, on the other hand, the dispersion
of HTPB is very much coarser. A finer dispersion can be achieved when enhancing
the rotation speed (20 rpm), so as to obtain a crude 20\% blend homogeneous
enough to be injection moldable (blend 6).
Tab. 2. Composition and mixing conditions of blends ① to ⑧

<table>
<thead>
<tr>
<th>Blend</th>
<th>Dispersed polybutadiene</th>
<th>wt.-%</th>
<th>Rotation rate in rpm</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>②</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>③</td>
<td>HTPB</td>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>④</td>
<td></td>
<td>20</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>⑤</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>⑥</td>
<td></td>
<td>20</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>⑦</td>
<td>ImPB</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>⑧</td>
<td>hmPB</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10. Mixing curves of PA12 and binary blends ① and ③

Fig. 11. Mixing curves of PA12 and binary blends ② and ⑥
Fig. 12. SEM micrographs of the cryofracture surfaces of melt processed PA12 (a), and of blends ① (b), ② (c), ③ (d) and ④ (e)

Fig. 13. Size distribution of the dispersed particles of polybutadiene in blends ① to ④
The particle sizes in the binary blends are already in the range for which good enhancement of impact properties can be expected. One can wonder how such a good dispersion is possible, and whether there is compatibilization in the binary blends, via esterification of HTPB with PA12, or not. Blend \( \mathbb{O} \) was therefore prepared with a non-hydroxy functional polybutadiene that exhibits a molar mass equivalent to that of HTPB (ImPB). Standard Charpy bars were injection molded from blends \( \mathbb{O} \) and \( \mathbb{O} \), then cryofractured. The fracture surfaces of those two materials are quite equivalent (Fig. 14), and the average diameters of the dispersed particles are equal in both cases, as it is shown in Tab. 3.

![Fig. 14. SEM micrographs of cryofractured Charpy bars injection molded from blends \( \mathbb{O} \) (a) and \( \mathbb{O} \) (b)](image)

<table>
<thead>
<tr>
<th>Blend</th>
<th>( \bar{D}_n/\mu m )</th>
<th>( \bar{D}_w/\mu m )</th>
<th>( l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathbb{O} )</td>
<td>0.78</td>
<td>1.02</td>
<td>1.57</td>
</tr>
<tr>
<td>( \mathbb{O} )</td>
<td>0.76</td>
<td>1.08</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Since no reaction can occur in blend \( \mathbb{O} \), it is obvious from the similarity of morphologies that the good dispersibility of HTPB in a PA12 matrix in the binary blends is only due to the processing conditions, and mainly to the viscosity ratio, and not to any compatibilization reaction. The importance of the viscosity ratio becomes obvious when comparing the morphologies of blends \( \mathbb{O} \) and \( \mathbb{O} \) (Fig. 15). Indeed, highly viscous hmPB cannot be well dispersed in PA12 under the same processing conditions as HTPB.

![Fig. 15. SEM micrographs of cryofractured samples of blends \( \mathbb{O} \) (a) and \( \mathbb{O} \) (b)](image)
It should be noticed here that the finer dispersion of polybutadiene in PA12 is obtained with HTPB. This result is not in agreement with the theory of dispersive mixing that says the closer the viscosity ratio, the finer the dispersion. In our case, melt PA12 and HTPB do not have similar viscosities ($\eta_{HTPB} / \eta_{PA12} \ll 1$). Moreover, according to the empirical rule of Jordhamo [74], HTPB should here be the continuous phase, and PA12 the dispersed one. Nevertheless, the blends we prepared show good dispersions of fine particles, and the cumulative fraction area of the particles (Tab. 4) shows that all the HTPB is dispersed in the matrix. (One can indeed allow the approximation that the surface area fraction of the dispersed particles is equal to the weight fraction of the dispersed phase). It seems then that those classical rules do not apply to such a case where the viscosities of the two phases are not comparable.

Tab. 4. Weight fraction and surface area fraction of the dispersed phase for blends ⑤ and ⑥

<table>
<thead>
<tr>
<th>Blend</th>
<th>HTPB weight fraction</th>
<th>Cumulative area of the dispersed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>⑤</td>
<td>10%</td>
<td>9%</td>
</tr>
<tr>
<td>⑥</td>
<td>20%</td>
<td>18%</td>
</tr>
</tbody>
</table>

![Fig. 16. Evolution of torque (a) and morphology (b) during melt blending of blend ⑤](image-url)
When preparing blend ⑤, samples were taken in order to check the evolution of the morphology (Fig. 16). It appears that the final morphology is already achieved a few minutes after the levelling off of the torque.

_Deformation of the testing bars under room temperature fracture_

It is known that the enhancement of impact properties in such blends is due to deformations of the matrix promoted by the dispersed particles. The deformation of the samples under room temperature impact was therefore investigated with SEM. The micrographs of the room temperature fracture surfaces of notched Charpy bars, injection molded from PA12 and blends ⑤ and ⑥, are reproduced in Fig. 17. The scheme under the micrographs shows the position in the bar where each micrograph was taken.

Fig. 17. SEM micrographs of room temperature fractured notched Charpy bars of PA12 (a, b, c), of blend ⑤ (d, e, f) and of blend ⑥ (g, h, i)
Pure PA12 fractures in a brittle way, with no massive deformation occurring. Two different deformation areas can be observed for blends $\odot$ and $\circ$. In blend $\odot$, the bar did not undergo bulk deformations. Whereas the side opposite to the impact exhibits high deformations, the core of the samples seems to be intact, as in the case of a cryofracture. In blend $\circ$, on the other hand, the whole sample was highly deformed.

That difference can be related to morphological parameters. The cryofracture surfaces of the two blends are shown in Fig. 18. The room temperature notched Charpy impact toughness and the morphological parameters are listed in Tab. 5. Even if the dispersion is finer in blend $\odot$ than in blend $\circ$, the impact toughness is less enhanced. Two factors can lead to that situation: the first one would be the existence of particles that are not fine enough to promote matrix deformations, the second one being the lower interparticle distance in blend $\circ$ that leads to a deformation mechanisms.

Moreover, it should be noticed that the effect of the cooling rate of injection molded bars after injection was not studied here. In our case, the bars were rather quickly cooled. Since the crystallinity of the matrix plays a role in the impact toughness and in toughening [75-78], one could expect that appropriate annealing could lead to an optimal crystallization, and therefore to enhanced impact properties.

![Fig. 18. SEM micrographs of cryofracture surfaces of Charpy bars made of blends $\odot$ (a) and $\circ$ (b)](image)

<table>
<thead>
<tr>
<th>Blend</th>
<th>wt.-% PBHT</th>
<th>Room temperature resilience in kJ m$^{-2}$</th>
<th>$D_n$/$\mu$m</th>
<th>ID in $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA12</td>
<td>0</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\odot$</td>
<td>10</td>
<td>9.9</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>$\circ$</td>
<td>20</td>
<td>21.1</td>
<td>1.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Tensile tests have been performed on half-standard injection molded test bars. Young's modulus and yield stress (obtained by Considère's construction) are given in Tab. 6. As it could be expected, the tensile properties of the blends are inferior to those of pure PA12. The incorporation of HTPB as spherical dispersed particles in the PA12 matrix leads then to a significant improvement of the impact properties, but this improvement is unfortunately counterbalanced by a decrease of Young's modulus and yield stress.
Tab. 6. Young's modulus and yield stress of PA12 and of blends ọ and ọ

<table>
<thead>
<tr>
<th>Blend</th>
<th>wt.-% PBHT</th>
<th>Young's modulus in MPa</th>
<th>Yield stress in MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA12</td>
<td>0</td>
<td>1090</td>
<td>36.3</td>
</tr>
<tr>
<td>ọ</td>
<td>10</td>
<td>920</td>
<td>32.2</td>
</tr>
<tr>
<td>ọ</td>
<td>20</td>
<td>800</td>
<td>31.0</td>
</tr>
</tbody>
</table>

**Experimental part**

**Materials**

The PA12 used in this study is a Rilsan 12 AECHVO supplied by ATOFINA ($\bar{M}_n = 20,000 \text{ g mol}^{-1}$). The polybutadiene is a PolyBd R45 HT, supplied by ATOFINA ($\bar{M}_n = 2800 \text{ g mol}^{-1}$, 22% 1,4 cis double bonds, 56% 1,4 trans double bonds and 22% vinyl double bonds [67-72]). Low molar mass polybutadiene (lmPB) was supplied by Degussa (Polyöl 130, $\bar{M}_n = 3000 \text{ g mol}^{-1}$, 77% 1,4 cis double bonds, 22% 1,4 trans double bonds and 1% vinyl double bonds). High molar mass polybutadiene (hmPB) was supplied by ATOFINA ($\bar{M}_n = 300,000 \text{ g mol}^{-1}$).

The blends were prepared in a Brabender internal mixer at 200°C. It was therefore important to characterize the materials and to explore the changes that they may undergo under those experimental conditions.

**Thermogravimetric study of the degradability of PA12 and HTPB**

Thermogravimetric analysis (TGA) experiments were conducted in order to evaluate the thermal resistance of PA12 and HTPB. The materials were first dried under reduced pressure (20 mm Hg, 80°C) for 24 h, as they would be prior to blending, in order to avoid hydrolysis reactions. Both isothermal tests and tests with temperature scanning were performed. The apparatus used is a Perkin-Elmer TGA7 with Pyris software. The tests were conducted under inert atmosphere (nitrogen, 100 mL min$^{-1}$) with a heating rate of 20°C min$^{-1}$.

**Amine functionality of PA12**

With a view to the compatibilization of further blends, the determination of the end-chain amine functionality of PA12 appeared necessary. A conductometric titration method was therefore developed, inspired by that proposed by Waltz [79]. PA12 was dissolved in boiling phenol/water (90/10), then the solution was allowed to cool to room temperature prior to conductometric titration with aqueous HCl (0.1 N).

**Evolution of HTPB during blending**

Since HTPB bears reactive double bonds (22% 1,2 monomer units), one could assume that it could undergo thermal crosslinking, even alone, during blending. In order to explore this possibility, the evolution of the molar mass of HTPB (200°C, 120 min, nitrogen purge gas) was followed by size exclusion chromatography (SEC).
**Processing of the blends and of pure PA12**

Prior to blending, PA12 pellets and liquid HTPB were dried in a vacuum oven (80°C, 2 mm Hg) for at least 12 h in order to eliminate any residual water that could lead to chain scission of PA12 through hydrolysis reaction. The mixing chamber was pre-heated at 200°C and flushed with nitrogen. PA12 was introduced in the mixer, with the rotation rate of the blades fixed at 10 or 20 rpm. HTPB was introduced in the mixer after the full fusion of the PA12 pellets, indicated by a stabilization of the torque. About 35 g were blended in each preparation. The mixing chamber was continuously flushed with nitrogen during processing. The internal mixer used was a Brabender PL2000 Plasticorder.

**SEC of PA12**

PA12 is insoluble in usual SEC solvents, such as tetrahydrofuran, CH₂Cl₂, toluene or water. SEC analysis of PA12 requires therefore a chemical modification step prior to injection. Pelisson [80] recommends the use of a large excess of trifluoroacetic anhydride (TFAA) that reacts with the amide linkages of the polyamide chain. The trifluoroacylation of polyamide breaks the intermolecular H-bonds between the chains, making thus the PA12 soluble in dichloromethane.

About 50 mg PA12 were added to 5 mL dried CH₂Cl₂. TFAA was added in large excess (about 0.5 g). After 1 h stirring, a clear solution was obtained. After vacuum extraction of the solvent, the excess TFAA and the formed trifluoroacetic acid (TFA), the trifluoroacylated PA12 is dissolved in 3 mL dichloromethane prior to SEC analysis (eluent: dichloromethane; flow rate: 1 mL min⁻¹; columns: 2 x PLgel 5 μm MIXED-C, 600 x 7.5 mm, Polymer Laboratories; detector: differential refractometric detector, Shimadzu RID-10A).

**FTIR**

FTIR spectra were obtained with a Perkin Elmer Spectrum 2000 apparatus.

**Morphological studies**

It has been widely shown that the morphology of the blend is a key factor in the toughness enhancement of a brittle matrix [1-4,11,12,19,20,23,28-32,44,56,81,82]. There is a diameter window out of which the reinforcement is not as good as it could be expected. The upper diameter limit is related to the interparticle distance criterion, postulated by Wu [2]. The particles act as stress concentrators in the matrix, thus promoting energy consuming plastic deformations in it. If the particle distribution is not fine enough, the interparticle distance will be higher, and there will be no overlapping of the stress fields. Therefore, energy dissipation by matrix deformation will be limited and the resilience of the material will be lower. A further explanation of the interparticle distance criterion was given by Muratoglu et al. [75,76], and later by Bartczak et al. [77,78], who have shown that, in the case where the matrix is semi-crystalline, there is in such biphasic materials a preferential orientation of the crystalline areas neighbouring the dispersed particles. Thanks to that orientation, the yield stress of these elements of the continuous phase is lower than that of the bulk, where there is a random orientation of the crystalline zones. Therefore, yielding can occur as an energy dissipating deformation process. Provided that the mean interparticle distance is short enough, those ‘easy yielding’ zones percolate, and the blends become tough.
The lower size limit is related to the particle cavitation phenomenon. This cavitation also promotes energy dissipating deformation mechanisms (yielding and crazing) that explain the toughness enhancement. However, under a certain critical size, cavitation cannot occur, and reinforcement is lower.

When computing the data proposed by various authors, it appears that, for polyamide based blends, the best improvement of resilience would be obtained with particle sizes between 0.1 and 1 \( \mu \text{m} \). However, the knowledge of the size distribution of the dispersed particles, or at least of the average size, is of high interest in the study of such blends. The morphology of the prepared blends was therefore studied with SEM. It was observed on either crude blend out of the mixer or on injection molded Charpy testing bars. This was done on cryofractured samples the surfaces of which were coated with gold by standard sputtering. The deformations occurring in the test bars during room temperature fracture were also observed by SEM on gold-coated fracture surfaces.

The size and the number of dispersed particles were determined with ArcView GIS software. A shape recognition algorithm was used to isolate spherical dispersed particles, the diameters of which were calculated from the surface area. Then, the number average diameter \( \bar{D}_n \), the weight average diameter \( \bar{D}_w \) and the polydispersity of particle diameters, \( I \), were determined for each sample according to Eqs. (1), (2) and (3):

\[
\bar{D}_n = \frac{\sum N_i D_i}{\sum N_i} \quad (1)
\]

\[
\bar{D}_w = \frac{\sum N_i D_i^2}{\sum N_i D_i} \quad (2)
\]

\[
I = \frac{\bar{D}_w}{\bar{D}_n} \quad (3)
\]

It is obvious that the observation of such dispersions on cryofracture surfaces or on microtomed sections leads to an error in the particle size. The diameter of the observed sections is indeed inferior to that of the spheres, unless each one would be sectioned through its equatorial plane. Only few articles seem to deal with this problem [9,18,64,82], some of them proposing statistical corrective methods. However, those methods are quite long and lead to a new error that is not much inferior to the first one. We therefore decided, like Scott [18], to ignore these correction problems, and the particle average diameters in this paper are calculated directly from the observed section diameters.

**Conclusions**

HTPB was easily dispersed as spherical particles in a PA12 matrix by melt blending in an internal mixer (except of the low-speed processed 20% blend). It was shown that no chemical reaction occurred during blending, and that the good dispersions obtained were only due to the experimental conditions of blending. The blends thus obtained exhibit impact properties that are significantly improved, with regards to those of the initial PA12. However, the dispersion leads besides to a decrease in other mechanical properties.
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