Structure and properties of NR- and XNBR-toughened polypropylene produced with latex by melt compounding

I Lendvai and J Karger-Kocsis

1 Budapest University of Technology and Economics, Faculty of Mechanical Engineering, Department of Polymer Engineering, Budapest, Hungary

E-mail: lendvai@pt.bme.hu; karger@pt.bme.hu

Abstract. Binary blends composed of polypropylene (PP) and natural rubber (NR) or carboxylated acrylonitrile butadiene rubber (XNBR) were produced in batch-type melt compounding process. The rubbers used as toughening agents were introduced into PP in up to 20 wt% in their dry and latex forms. Structure-property relationships of the blends were studied. Both NR and XNBR were homogenously dispersed in the PP matrix: XNBR in microscale, NR in the submicronic scale. Fracture toughness and energy, determined on notched Charpy specimens, were improved by rubber toughening, however, at the cost of stiffness and strength, determined in tensile tests. NR toughened blends were superior to blends containing XNBR with respect to impact resistance. The introduction of rubbers in latex form resulted in slightly better mechanical performance compared to addition in dry form.

1. Introduction

Nowadays great efforts are made to improve the mechanical, thermal and other properties of polymers. Among those, the development of rubber-toughened polymers (RTP) has been a subject of active research in the last decades to extend their range of applications [1]. Polypropylene (PP) is a thermoplastic polymer, mostly used in the packaging and textile industries. It exhibits, however, a relatively poor impact resistance, especially at room temperature (close to its glass transition temperature, $T_g$) and below. Two methods are used to improve its toughness: copolymerization with suitable monomers [2] and blending with various elastomers [1, 3, 4]. The elastomer particles in both cases should be finely and homogeneously dispersed and their interparticle distance (matrix ligament - controlled by the elastomer amount) should be adjusted to the matrix [5, 6]. These are the prerequisites of efficient toughening, the mechanism of which is as follows: stress concentration at the particles, followed by their cavitation/break-up/elongation, accompanied with massive shear yielding and/or crazing of the matrix [7]. It is noteworthy that rubber toughening – albeit via a somewhat different mechanism – also works in thermosts [8]. To get the suitable dispersion is, however, a challenging task. During melt blending the dispersion characteristics mainly depend on two controlling parameters: the viscosity ratio and the capillary or Weber number [9]. The closer the viscosity of the rubber modifier to that of the matrix under the melt blending conditions (temperature, shear rate), the finer the resulting dispersion is. The physical meaning of the Weber number is the balance between the shear stress acting locally on the particle and the deformation resistance of the particle. The elongated rubber particle breaks up when the Weber number exceeds a critical value, which also depends on the viscosity ratio [9]. Besides melt compounding and “reactor blending” (copolymerization involved), there is another possibility for the rubber modification of thermoplastics. Many rubbers are available in latex form,
which is an aqueous dispersion of the micron- or submicron-scaled elastomer particles. Therefore, it is reasonable to assume that by evaporating the water content of the latex during melt compounding, we may incorporate the elastomer particles for the level of dispersion required for toughening in the actual thermoplastic matrix [10]. It should be born in mind that a further requirement to this water-assisted melt compounding is the resistance of the corresponding matrix to hygrothermal decomposition. This concept has already been used for the toughening of polymers, such as polyamide [11, 12] and polystyrene [13]. Attempts have also been made to produce toughened and nanoparticle-reinforced thermoplastics in this way [10].

The objective of this paper was the toughening of polypropylene (PP) by blending it with uncured rubbers by latex-mediated and traditional melt compounding. The method followed would enable the preparation of PP-based materials with good impact resistance and thus broaden their application range. As modifiers, natural rubber (NR) and carboxylated acrylonitrile butadiene rubber (XNBR) were incorporated in PP. Their amount was varied between 0 and 20 wt%. The morphology, tensile mechanical and dynamic mechanical properties were determined and the related structure-mechanical property relationships deduced.

2. Experimental

2.1. Materials

A polypropylene of medium molecular weight, PP H 543 F, supplied by MOL Petrolkémiai Zrt, Tiszajjváros, Hungary was used as matrix (MFR = 4 g/10 min at 230 °C and 2.16 kg). Note that PP does not degrade hygrothermally. Two different types of uncured rubbers were introduced as toughening agents: a natural rubber (NR) and a carboxylated acrylonitrile butadiene rubber (NBR). The NR latex (G-TEX LATZ) with 60 wt% dry content was obtained from Variachem Kft., Budapest, Hungary. XNBR latex (Chemigum Latex 550) with 41 wt% solid content was kindly supplied by OMNOVA Solutions Inc., Beachwood, OH, USA. A laser diffraction particle analyser Malvern 2000 (Malvern Instruments Ltd., Malvern, UK) was used to determine the initial particle size distribution of the rubber particles in these two latices.

2.2. Preparation of the samples

Binary blends were produced by melt compounding of PP with rubbers added in their dry and latex forms. The rubber content in the corresponding blends was set to 0, 5, 10 and 20 wt%. Table 1 shows the composition of each sample. Firstly, the PP pellets were masticated in a counter rotating internal batch mixer PL2000 Plasti-Corder (Brabender GmbH., Duisburg, Germany) at a temperature of 180 °C and 60 rpm. Subsequently, the rubber additives were introduced. When adding rubber in its latex form to the PP melt, we followed the fast evaporation mixing method described by Gao et al [14]. Therefore, the latex was dosaged dropwise. The compound was mixed for a further 5 min to achieve a fine dispersion and to eliminate the residual water. Then, the compound was dumped from the mixing chamber and allowed to cool to room temperature.

Afterwards, the prepared PP/rubber blends were compression molded to sheets of 2 mm thickness in a hot press (Teach-Line Platen Press 200E, Dr. Collin GmbH., Munich, Germany) for 3 mins at 200 °C. Specimens for testing were cut out of the compression molded sheets with a Mutronic Diadisk cutter (Mutronic GmbH, Rieden, Germany).
Table 1. Composition of NR- and XNBR-toughened polypropylene samples

| Sample code    | PP [wt%] | NR [wt%] | XNBR [wt%] | Rubber [latex/dry] |
|----------------|----------|----------|------------|-------------------|
| PP             | 100      | -        | -          | -                 |
| 5NR            | 95       | 5        | -          | latex             |
| 10NR           | 90       | 10       | -          | latex             |
| 20NR           | 80       | 20       | -          | latex             |
| 5XNBR          | 95       | -        | 5          | latex             |
| 10XNBR         | 90       | -        | 10         | latex             |
| 20XNBR         | 80       | -        | 20         | latex             |
| 10NR_DRY       | 90       | 10       | -          | dry               |
| 10XNBR_DRY     | 90       | -        | 10         | dry               |

2.3. Characterization and testing
The static mechanical properties were determined with tensile tests performed on a universal testing machine (Zwick Z005, Ulm, Germany) at a crosshead speed of 5 mm/min at room temperature. Tests were stopped at 150% elongation in the case of the very ductile specimens. The average value was calculated from five measurements.

Charpy tests were performed at room temperature (RT) on notched specimens. The notch length to width ratio of the Charpy specimens was constant, viz. 0.5. The notch was made with a V-type saw blade (Mutaric GmbH, Rieden, Germany). The impact test was performed on an instrumented pendulum (Ceast Spa, Pianezza, Italy), equipped with a data acquisition unit (DAS 8000 of Ceast). For the tests, the edge of the hammer (impact energy: 2 J) was cushioned with plasticine to suppress vibrations. The given test results represent average values of five tests.

Dynamic mechanical analysis (DMA) was performed in dual-cantilever mode at a frequency of 1 Hz with a DMA Q800 analyzer (TA Instruments, New Castle, USA). The storage modulus and the mechanical loss factor were determined as a function of the temperature (T = -50 °C ... + 75 °C). The amplitude was set to 0.02% of deformation. DMA curves were registered at a heating rate of 3 °C/min.

The morphology of the prepared samples was studied in a scanning electron microscope (SEM; JEOL JSM 6380LA, Tokyo, Japan). Fracture surfaces, produced in the impact tests, were sputter-coated with gold/palladium alloy prior to their inspection.

3. Results and discussion
3.1. Particle characteristics
The particle size distribution of the rubbers within the latices used are displayed in Figure 1. Figure 1 clearly demonstrated the large differences in both the mean particle sizes and size distributions of the latices. The distribution curves peaked at about 190 nm and 620 nm for the XNBR and NR latices, respectively. Particle size distribution also differs: NR particles have a considerably broader distribution than XNBR particles.
Figure 1. Particle size distribution of the rubber particles in the NR and XNBR latices used. Note: the abscissa in the diagram is in a logarithmic scale.

3.2. Tensile mechanical properties
The tensile mechanical properties (tensile strength, Young’s modulus and elongations) are listed in Table 2. The addition of rubber particles markedly reduced both the strength and stiffness compared to neat PP. This is due to the “soft” rubbery character of the incorporated NR and XNBR. The incorporation of NR decreased the initial 29.9 MPa tensile strength of PP to 27.3, 24.8 and 19.7 MPa at 5, 10 and 20 wt% loading, respectively. The presence of XNBR had the same effect on strength. NR reduced the Young’s modulus to a lesser extent than XNBR, suggesting a higher stiffness for NR compared to XNBR. This is supported by the elongation at maximum load ($F_{\max}$) values, which were always below those of PP/XNBR in the case of NR toughening. Necking only appeared for neat PP and PP/NR blends. The possible reason behind this fact may be linked with the dispersion state of the rubber particles within the PP (see later in the morphology analysis).

The type of rubber introduction (latex/dry) makes no significant difference in strength, stiffness and elongation at $F_{\max}$, although samples prepared through dry addition exhibited no necking (by breaking before it could occur), showing the advantage of using the aqueous media.

Table 2. Tensile mechanical properties of rubber-toughened polypropylene samples with the use of natural rubber and acrylonitrile butadiene rubber. Note: 150+ means higher than 150%

| Sample     | Tensile Strength [MPa] | Young's Modulus [GPa] | Elongation at $F_{\max}$ [%] | Elongation at break [%] |
|------------|------------------------|-----------------------|-------------------------------|------------------------|
| PP         | 29.9 ± 0.5             | 1.21 ± 0.04           | 11.8 ± 1.4                    | 150+                   |
| 5NR        | 27.3 ± 0.9             | 1.14 ± 0.03           | 10.3 ± 0.6                    | 150+                   |
| 10NR       | 24.8 ± 0.4             | 1.05 ± 0.01           | 9.6 ± 0.5                     | 150+                   |
| 20NR       | 19.7 ± 0.1             | 0.86 ± 0.01           | 7.7 ± 0.4                     | 150+                   |
| 5XNBR      | 27.2 ± 1.6             | 1.09 ± 0.06           | 11.8 ± 0.4                    | 37.9 ± 7.9             |
| 10XNBR     | 22.9 ± 0.5             | 0.97 ± 0.02           | 11.8 ± 0.6                    | 33.3 ± 7.5             |
| 20XNBR     | 18.4 ± 1.3             | 0.77 ± 0.07           | 12.8 ± 1.3                    | 43.6 ± 9.1             |
| 10NR_DRY   | 23.5 ± 0.8             | 0.92 ± 0.03           | 11.2 ± 0.4                    | 35.5 ± 8.3             |
| 10XNBR_DRY | 22.7 ± 0.6             | 0.98 ± 0.02           | 10.5 ± 0.5                    | 21.4 ± 4.1             |
3.3. Dynamic mechanical analysis

DMA results, i.e. storage modulus and loss factor versus temperature traces, are shown in Figure 2. It is well resolved that with increasing content of both NR and XNBR, stiffness is monotonously reduced. Storage modulus values of the PP/rubber blends above -10 °C are identical irrespective of rubber type. At lower temperatures, however, the moduli of the XNBR-toughened samples are markedly higher than those of samples containing NR because of the vitrification of XNBR (T_g at about -28 °C). The glassing of NR domains occurs at temperatures below the analysed temperature range.

![Figure 2. Storage modulus and loss factor as a function of temperature for the rubber-toughened PPs containing NR (a) and XNBR (b)](image)

3.4. Impact performance

Figure 3 displays characteristic force-time traces of PP, PP/NR and PP/NBR blends registered at room temperature. The incorporation of rubber particles in PP resulted in a maximum force increment along with increased fracture time. This confirms that both rubbers acted as toughening agents for PP thereby increasing fracture energy. The largest fracture time was observed when NR was incorporated in a water-assisted way.

![Figure 3. Characteristic force-time curves registered on PP/rubber (NR, XNBR) blends produced by latex and melt compounding. Note: comparison of the methods is given only for the PP with 10 wt% NR](image)
The dependence of fracture toughness on rubber content is depicted in Figure 4 (a). It can be seen that the presence of both NR and XNBR leads to increased fracture energy values. For the PP/NR blends this increment is more significant than for PP/XNBR. For 5, 10 and 20 wt% NR loading the initial 5.2 kJ/m² fracture energy of PP increased to 8.1, 9.3 and 11.9 kJ/m², respectively. Samples containing XNBR exhibited slightly lower toughness values reaching a fracture energy of 8.8 kJ/m² at 20 wt% XNBR. Figure 4 (b) shows the differences in the fracture energy of the blends prepared by traditional and latex-mediated melt compounding methods. PP/rubber blends produced with latex dosage exhibited higher Charpy impact values than those with dry rubber, though the difference was practically within the scatter range.

\[ \text{Fracture energy [kJ/m}^2\text{]} \]

\[ \text{Rubber content [m\%]} \]

**Figure 4.** The fracture energy of rubber-toughened polypropylene samples with natural rubber and acrylonitrile butadiene rubber as a function of loading (a) and differences depending on the preparation method (b)

3.5. **Morphology**

SEM images taken of sample 10NR and 10XNBR are shown in Figure 5. Figure 5 (a) shows that NR particles within PP are in the size range of 500 nm to 2 μm. Compared to the initial particle size distribution of NR (cf. Figure 1), it means little to no increment. As a consequence, the original particle size of the NR latex also remained after compounding. By contrast, Figure 5 (b) shows that XNBR particles agglomerated to much larger domains compared to the original particle size in this latex. The initial size of XNBR increased from 190 nm to 3-8 μm, due to blending. It is well-known that in the presence of larger domains, resulting in larger matrix ligaments, there is no stress overlapping between the particles during deformation. This leads to a more brittle type of fracture in the case of PP/XNBR compared to the NR-toughened PP. This finding also supports our explanation when interpreting the measured mechanical properties (cf. Table 2).
Figure 5. SEM pictures from the fracture surface of rubber-toughened PP samples with NR (a) and XNBR (b) at a magnification of 2500x

4. Conclusions
Rubber-toughened PP-based blends, containing 0, 5, 10 and 20 wt% rubber were prepared in batch type melt compounding process. NR and XNBR rubbers were incorporated in their dry form by traditional or by latex-assisted melt compounding. Both NR and XNBR decreased the strength and stiffness of PP. This was in good agreement with a significant improvement in the notched Charpy impact energy. PP/NR blends outperformed the PP/XNBR blends with respect to Charpy toughness. Besides the better compatibility between PP and NR than between PP and XNBR, this was traced to the large differences in the dispersion characteristics of the rubber particles. XNBR particles were found in the range of 3 - 8 μm, by contrast to those of the NR particles, which were in the range of 0.5 - 2 μm. It is noteworthy that the particle size of the NR in the PP/NR blends agreed with that of the original latex. Opposed to that, the XNBR particles underwent a 15-40 fold size agglomeration upon blending compared to the parent latex. The static and dynamic mechanical properties of the PP/rubber blends prepared through dry rubber addition were inferior to those produced by latex mediation.

Acknowledgements
The work reported here was supported by the Hungarian Research Fund (OTKA) through the project K 109409. The authors thank Dr. J. Móczó for the particle size distribution measurements.

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