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To cite this article: A Kohári and T Bárány 2022 *IOP Conf. Ser.: Mater. Sci. Eng.* **1246** 012001

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In situ–produced polyurethane-based thermoplastic elastomers: the effect of the acrylonitrile content of the rubber phase

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Abstract. We prepared thermoplastic dynamic vulcanizates (TDVs) with an in situ–produced thermoplastic polyurethane (TPU) matrix. We used unfilled acrylonitrile butadiene rubber (NBR) with different acrylonitrile contents and investigated the effect of the polarity of the rubber phase on the properties of the TDV samples. The results show that the acrylonitrile (AN) content of the rubbers affects the tensile strength and modulus slightly but the strain at break of the TDVs only negligibly. The results of TDVs are in between those of TPU and unfilled NBRs, demonstrating the feasibility of the TPU/NBR combination.

1. Introduction

The first thermoplastic elastomers (TPEs) appeared on the market more than 60 years ago. Since then, they have become more widely used, with demand growing rapidly for various applications, such as automotive, sports and leisure goods, medical devices, technical and utility articles, and coatings with a pleasant touch. The main reason for this is that TPEs have properties similar to those of vulcanized rubbers but can be processed with processes similar to those used for thermoplastic polymers. TPEs, therefore, form a bridge between thermoplastic polymers and vulcanized rubber [1-3].

TPEs are essentially two-phase systems, with one phase being rigid at the temperature of use; the hard phase provides the strength of the material. The other is the soft phase providing flexibility and elasticity. Increasing the mass fraction of the soft phase makes the TPE softer and more elastic. Their cross-linked structure, which is responsible for their elastic properties, is not formed by irreversible chemical reactions. Instead, they are formed physically and reversibly, due to a significant reduction in the mobility of the molecular chains or molecular chain segments that form the hard phase while the melt cools (e.g. glass transition, crystallization), while their elasticity is essentially due to the mobility of the molecular chains or chain segments forming the soft phase [1, 4].

Thermoplastic polyurethanes (TPUs) belong to thermoplastic elastomers, including block copolymers. The hard segment of TPU is made up of diisocyanate and chain extender, a low molecular weight diol. The soft segment is a long-chain diol, the so-called polyol. The different segments are linked by covalent bonds in the chain, creating the structure typical of block copolymers. They can be produced in one- or two-shot processes. In the first case, all three components (isocyanate, polyol, and chain extender) are mixed, and polyaddition occurs under appropriate conditions. In the second case, the polyol is first reacted with an excess of diisocyanate in an inert atmosphere, and in the second step, the



resulting isocyanate-terminated prepolymer units are linked with a chain extender. The latter is also called the prepolymer method [5, 6].

Another important group of thermoplastic elastomers is thermoplastic dynamic vulcanizates (TDVs). These materials consist of a continuous thermoplastic matrix and dynamic vulcanized rubber particles dispersed in it. The term dynamic vulcanization refers to the way the rubber is produced, as the vulcanization of the rubber and the compounding of the components take place simultaneously. The best known TDV is Santoprene, which is made of polypropylene and ethylene-propylene-diene rubber [7, 8].

For multi-phase blends, such as TDVs, the connection between the phases is vital, as it largely determines their properties. Commercially available polymers are rarely miscible or compatible, leading to poor mechanical properties. It can be improved by various compatibilisation methods. The aim of improving compatibility is to produce stable and reproducible dispersion with the desired structure and properties [9, 10].

We prepared thermoplastic dynamic vulcanizates with an in situ-synthesized polyurethane matrix. Due to the polar nature of TPU, we chose acrylonitrile butadiene rubber (NBR) as a rubber phase of the TDVs, which is also polar. During the experiment, we used unfilled NBR rubber mixes with different acrylonitrile content.

2. Experimental

2.1. Materials

The thermoplastic polyurethane matrix was prepared by the prepolymer method. For this purpose, we used the prepolymer brand Suprasec 2008, manufactured by Huntsman Co. (Texas, USA), which contained 10.2% free isocyanate groups. The chain extender was 1,6-hexanediol produced by Lanxess GmbH (Cologne, Germany). Acrylonitrile-butadiene rubbers with different acrylonitrile content were used as the rubber phase of the TDVs (Table 1).

Table 1. Types of rubber used in the experiment.

Brand name	Producer	Acrylonitrile content (%)	Mooney viscosity (ML, 1+4, 100 °C)
Perbuban 1846F		18	45
Perbunan 3445F	Arlanxeo Deutschland GmbH (Dormagen, Germany)	34	45
Perbunan 4066F		40	65

The component of the sulphur-based vulcanization systems and their suppliers were: zinc oxide (Werco Metal, Zlatna, Romania), stearic acid (Oleon, Ertvelde, Belgium), N-Cyclohexyl-2-benzothiazole sulphenamide (CBS) (Rhein Chemie, Mannheim, Germany), and sulphur (Ningbo Actmix Polymer, Ningbo, Zhejiang, China).

2.2. Preparation of thermoplastic dynamic vulcanizates

The rubber phase of the TDVs was prepared in a Brabender Plasti-Corder internal mixer (W 350 EHT, 370 cm³) (Brabender GmbH, Duisburg, Germany). The chamber temperature was 70 °C, and the recipe is summarized in Table 2.

The TDV samples were also prepared in the above-mentioned internal mixer. The initial temperature of the chamber was set to 150 °C, the rotor speed to 50 rpm, and the mixing time to 27 min. The ratio of free isocyanate groups (NCO) in the prepolymer to hydroxyl groups (OH) from the chain extender was chosen to be 1.05. The required amounts of TPU components were measured with a syringe on a scale to the nearest hundredth of a gram. First, the matrix components (prepolymer and chain extender) were added to the internal mixer chamber, and after 8 min, the rubber mixtures were added. In all cases, the ratio of TPU to rubber mixture was 60:40 wt%.

Table 2. Formulation of the rubber mixtures.

Ingredient	Quantity (phr)
Rubber	100
Zinc oxide	5
Stearic acid	2
CBS	1.5
Sulphur	2

From the produced TDVs, we prepared 2 mm thick plates between Teflon sheets at 200 °C for 4 min after preheating for 4 min at a pressure of 2 MPa using a Teach-Line Platen Press 200E (Dr. Collin GmbH, Ebersberg, Germany). 2 mm thick plates of the rubber mixtures were also prepared with the above press. The sheets were vulcanized at 160 °C, under a pressure of 2 MPa, for the vulcanization time (t_{90}) + 1 min of the related rubber mixes.

2.3. Test methods

The vulcanization properties of rubber mixtures were determined on a MonTech D-RPA 3000 Rubber Process Analyzer (MonTech GmbH, Buchen, Germany) under isothermal (160 °C, 1.67 Hz frequency, and 1° amplitude) conditions.

The mechanical properties of the TDV specimens were determined with a Zwick Z005 (Zwick GmbH, Ulm, Germany) tensile testing machine equipped with a 5 kN load cell. The TDV specimens were Type 1 dumb-bell shape test pieces according to MSZ ISO 37:2003. They were tensile tested at room temperature at a crosshead speed of 100 mm/min, with a grip length of 60 mm. The tear test was also carried out at room temperature on an angle test piece die (ISO 34 1:2015) at a crosshead speed of 100 mm/min and with a grip length of 56 mm. We made a 1 mm notch on the inner edge of the test pieces with a blade. In each case, the mechanical properties are the average of 5 measurements.

The Shore A hardness of the sheets was determined with a Zwick H04.3150.000 (Zwick GmbH, Ulm, Germany) hardness tester according to ISO 7619-1:2010, at 10 points per sample.

The dynamic mechanical properties of the prepared samples were determined with a TA Q800 (TA Instruments Ltd., New Castle, DE, USA) instrument. The dimensions of the samples cut out from the sheets were 2.0 x 2.5 x 10 mm (thickness x width x clamped length). The test was carried out between -90 °C and +150 °C at a heating rate of 3 °C/min, a frequency of 10 Hz, a superimposed 0.1% sinusoidal strain, and a preload of 0.01 N under tensile loading.

3. Results

3.1. Production of TDVs

In this study, we investigated the effect of the acrylonitrile content of the rubber phase. Before preparing the TDVs, we determined the isothermal vulcanization curves of the rubber mixtures (Figure 1 and Table 3). The results show that NBR 1846F and NBR 3445F rubbers with the same Mooney viscosity (45 MU) exhibited similar behaviour. In contrast, the NBR 4066F rubber, which has a higher Mooney viscosity, has a shorter scorch time (t_{10}) and a longer vulcanization time (t_{90}).

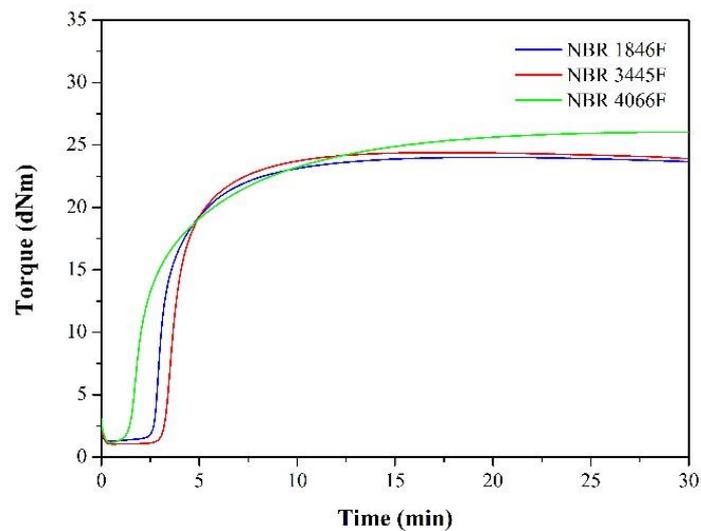


Figure 1. Isothermal vulcanization curves of the rubber mixtures.

Table 3. Isothermal vulcanization properties of the rubber mixtures.

Rubber mixtures	Scorch time, t_{10} (min)	Vulcanization time, t_{90} (min)	Max. torque (dNm)
NBR 1846F	2.75	7.00	24.01
NBR 3445F	3.28	6.81	24.40
NBR 4066F	1.56	10.7	26.04

During mixing, the internal mixer recorded the variation of the temperature of the material and the torque applied as a function of time (Figure 2). These curves provide useful information about the processes taking place in the chamber. An intense increase in the torque curves is observed after the addition of the rubber mixture, followed by a decrease. This decrease is due to the softening of the rubber mixture by kneading and high temperature. Subsequently, an intense increase in the curves is observed again due to the polymerization of the TPU and vulcanization of the rubber compounds. Finally, after reaching a maximum, the torque curves show a decrease again due to the fragmentation of the vulcanized rubber islands and the softening of the material.

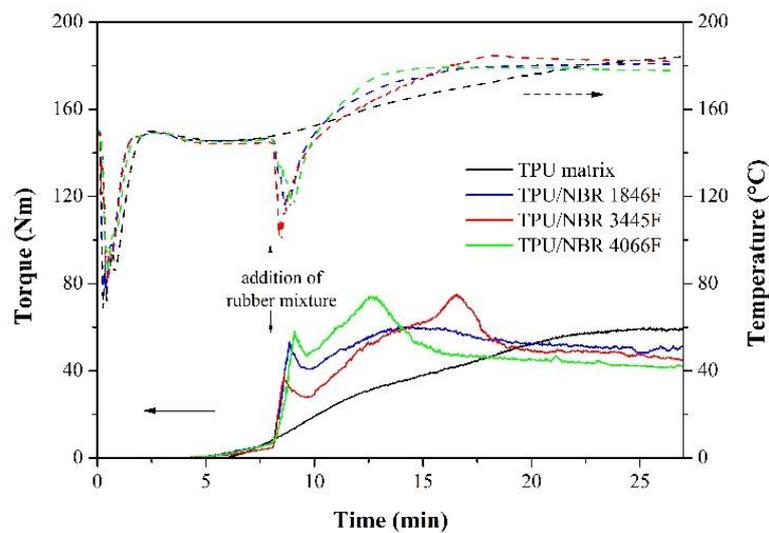


Figure 2. Torque and temperature curves recorded during the production of TDVs.

3.2. Mechanical properties

Based on the results of the tensile test (Figure 3 and Table 4), the mechanical properties of the vulcanized rubbers are far below those of the TPU matrix. Generally, the mechanical properties of TDVs are between those of the TPU matrix and (unfilled) rubber compounds. Of the rubbers, the two with higher AN content (NBR 3445F and NBR 4066F) have almost identical mechanical properties, while NBR 1846F has lower tensile strength, elongation at break, and stress at 100% and 200% elongation (M100 and M200). A comparison of the results of the TDVs does not show this, the effect of the AN content being smoothed into the scattering field. Please note that the rubber phase does not contain any reinforcement or filler. In practice, rubbers are rarely used without a filler—tests show that they have poor mechanical properties on their own.

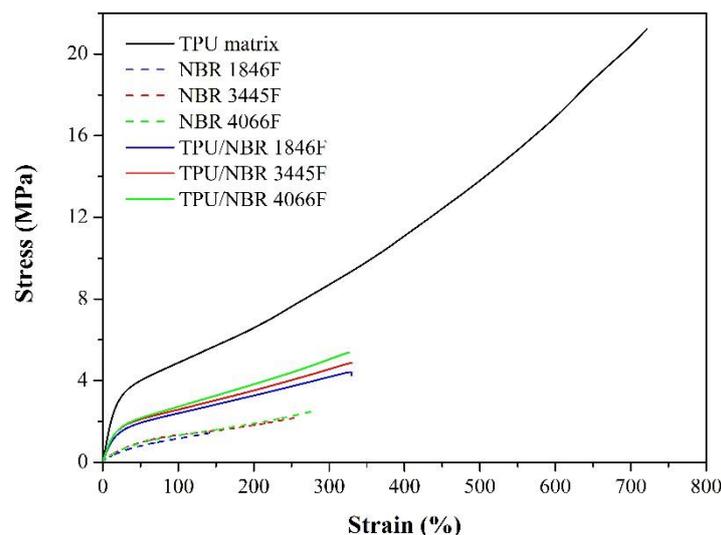


Figure 3. Typical tensile curves of the TPU matrix, the rubbers, and the TDVs.

Table 4. Mechanical properties of the TPU matrix, the rubbers, and the TDVs.

Sample	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)
TPU matrix	20.53±1.95	722.0±9.6	4.92±0.08	6.58±0.17
NBR 1846F	1.55±0.09	150.1±9.2	1.22±0.05	—
NBR 3445F	2.40±0.19	281.5±21.6	1.34±0.01	1.81±0.01
NBR 4066F	2.52±0.19	280.2±28.8	1.30±0.02	1.89±0.03
TPU/NBR 1846F	4.45±0.15	325.7±15.9	2.44±0.04	3.33±0.08
TPU/NBR 3445F	4.92±0.37	337.3±33.2	2.55±0.03	3.47±0.07
TPU/NBR 4066F	5.45±0.33	326.0±16.5	2.74±0.04	3.87±0.09

The tear strength of the rubbers (Table 5) increased with acrylonitrile content, but this trend was again not observed for TDVs. Their tear strength is between that of the two phases, closer to that of rubber. NBR 3445F and NBR 4066F have almost identical Shore A hardness, while NBR 1846F with a lower AN content is slightly softer. This trend is also observed for the hardness of TDVs.

Table 5. Tear strength and Shore A hardness of TPU matrix, rubbers, and TDVs.

Sample	Tear strength (kN/m)	Shore A hardness
TPU matrix	45.33±1.89	84±0.3
NBR 1846F	3.97±0.14	50±0.3
NBR 3445F	4.79±0.38	54±0.2
NBR 4066F	5.79±0.41	54±0.3
TPU/NBR 1846F	14.92±0.10	68±0.5
TPU/NBR 3445F	15.98±0.41	73±0.5
TPU/NBR 4066F	15.10±0.76	72±0.4

3.3. Dynamical mechanical analysis

On the $\tan\delta$ curves (Figure 4a) of the TPU matrix, there are two different glass transitions. The two glass transitions are due to the phase-separated structure of the thermoplastic polyurethane, as the soft and the hard phases have separated glass transition temperatures ($T_{g\text{ soft}}$ and $T_{g\text{ hard}}$). The rubbers have only one glass transition (Figure 4b), and their T_g ($T_{g\text{ rubber}}$) increased with acrylonitrile content, resulting in a deterioration of their cold resistance. This is because as the polar fraction of the polymer chain increases, the energy required for segment movements also increases, as the chains become stiffer due to the large polar nitrile groups.

Two glass transitions are observed in the thermomechanical curves of the TDVs (Figure 4a). In the case of the TPU/NBR 1846F sample, instead of $T_{g\text{ soft}}$ and $T_{g\text{ rubber}}$, one glass transition temperature and the T_g of the hard segment of the TPU are visible. For the other two TDVs, the T_g of the soft segment of the TPU and of the rubber phase can be seen.

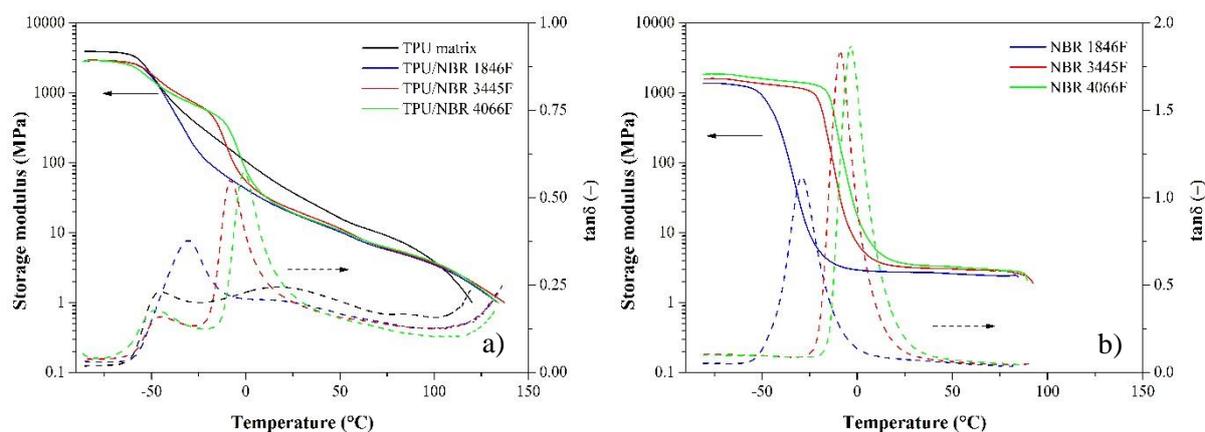


Figure 4. Thermomechanical curves of a) the TPU matrix and the TDVs, and b) the rubbers.

The room temperature storage modulus ($E'_{20^{\circ}\text{C}}$) of the rubbers also increased with acrylonitrile content, for the reasons described earlier (Table 6). The modulus of the produced TDVs is lower than the modulus of the matrix TPU due to the softer rubber islands. These findings are consistent with the results of the mechanical tests.

Table 6. The glass transition temperatures (T_g) and room temperature storage modulus of the TDVs ($E'_{20^{\circ}\text{C}}$).

Sample	$T_{g \text{ soft}}$ ($^{\circ}\text{C}$)	$T_{g \text{ rubber}}$ ($^{\circ}\text{C}$)	$T_{g \text{ hard}}$ ($^{\circ}\text{C}$)	$E'_{20^{\circ}\text{C}}$ (MPa)
TPU matrix	-45.12	—	17.62	44.90
NBR 1846F	—	-28.89	—	2.74
NBR 3445F	—	-9.05	—	3.33
NBR 4066F	—	-3.42	—	3.89
TPU/NBR 1846F		-30.59	25.59	21.60
TPU/NBR 3445F	-44.68	-7.93	—	24.37
TPU/NBR 4066F	-47.62	-0.63	—	22.42

4. Conclusions

We prepared thermoplastic dynamic vulcanizates with a TPU matrix and acrylonitrile butadiene rubber. In the experiment, we investigated the effect of the polarity of the rubber phase and the acrylonitrile content of the NBR on the properties of the TDVs produced. The properties of the rubbers were influenced by their acrylonitrile content, but this was not observed for TDVs. The properties of TDVs produced with unfilled rubber compounds are between those of the TPU matrix and those of the rubber phase. We hope to improve these results further by filling the rubber phase with carbon black or with silica. In the future, we will investigate the effect of the quantity and quality of the filler used in the samples produced.

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Acknowledgments

This work was supported by the National Research, Development and Innovation Office, Hungary (K128268). The research reported in this paper is part of project no. BME-NVA-02, implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021 funding scheme.