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Study on the Interface Reaction and Properties of Carboxynitrile Rubber/Blended Polyurethane

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Abstract

Millable polyurethane (MPU) is widely used in the field of sealing and wear-resistant components due to its excellent solvent resistance and dimensional stability. However, its inherent drawbacks of high rigidity and low elasticity limit its application in complex working conditions. Carboxylated nitrile butadiene rubber (XNBR) contains reactive carboxyl groups (-COOH) in its molecular chain, which can chemically interact with the isocyanate groups (-NCO) of MPU, providing a new approach to improve the mechanical properties of MPU. At present, research on the blending of XNBR with thermoplastic polyurethane (TPU) has been reported, but studies on the interfacial reaction mechanism, process regulation, and mechanical property synergy rules of the XNBR/MPU system are rarely conducted. In this study, an integrated technical route of "molecular simulation - experimental verification - performance characterization" was adopted, focusing on the correlation between the interfacial reaction and mechanical properties of the XNBR/MPU system: 1) Molecular dynamics simulations were used to confirm that the amidation reaction between XNBR and MPU proceeds spontaneously at 80°C, and the interfacial cross-linking mechanism of amide bonds was revealed; 2) The optimal formula was determined through orthogonal experiments, and mechanical property tests were carried out. This study provides theoretical support for the development of high-performance XNBR/MPU blended materials and has application value in the fields of automotive sealing and shock absorption.

Keywords

Carboxynitrile rubber; Blended polyurethane; Interface response; Mechanical performance testing

1. Introduction

As a class of polymer materials with highly designable molecular structures, polyurethane (PU) enables precise regulation of mechanical properties and environmental resistance through the step-growth polymerization reaction between polyols and isocyanates. It has been widely applied in fields such as automotive manufacturing, electronic packaging, and high-end equipment [1-2]. According to differences in

processing characteristics, PU can be further divided into millable polyurethane (MPU) and thermoplastic polyurethane (TPU). MPU requires molding via traditional rubber vulcanization processes and exhibits excellent solvent resistance and dimensional stability, thus having been extensively used in harsh scenarios including wear-resistant liners for mining machinery and gaskets for automotive engines. However, MPU inherently possesses high rigidity and low elastic recovery rate, making it prone to failure due to insufficient mechanical properties when subjected to dynamic loads. This limits its application in complex working conditions that demand vibration damping and impact resistance [3-4].

Blending rubber with polyurethane is an effective approach to achieve performance complementarity. Nitrile butadiene rubber (NBR) contains acrylonitrile segments, which endow it with better polarity matching with polyurethane compared to natural rubber and styrene-butadiene rubber. Nevertheless, the blending of NBR and MPU is merely a physical mixing process, resulting in poor interfacial compatibility and a high tendency for phase separation. This ultimately leads to the deterioration of tensile and tear properties of the blended materials [5-6]. Carboxylated nitrile butadiene rubber (XNBR) is a functionalized modified product of NBR. The carboxyl groups introduced into its molecular chain can undergo amidation reactions with the isocyanate groups in polyurethane, forming chemically cross-linked interfaces and significantly enhancing the bonding strength between the two phases. Jindal et al. [7] prepared thermoplastic vulcanizates (TPVs) by blending XNBR with TPU. Through the interfacial reaction between carboxyl groups and -NCO groups, the oil-swelling volume ratio of the material was reduced by 25%, and the tensile strength was increased by 30%. Mahmood et al. [8] incorporated nano-clay into the XNBR/TPU system. Utilizing the coordination interaction between carboxyl groups and hydroxyl groups on the clay surface, the dispersion of the filler was further improved, and the tear strength was enhanced by 28%.

Compared with TPU, MPU molecular chains contain more reactive -NCO groups and require high-temperature vulcanization molding (160-180°C). This not only provides more favorable conditions for the interfacial chemical reaction between XNBR and MPU but also brings about process challenges: at high temperatures, the reaction between carboxyl groups in XNBR and -NCO groups in MPU tends to generate CO_2 gas, leading to the formation of bubbles inside the blended material; meanwhile, the vulcanization system of MPU (e.g., dicumyl peroxide, DCP) is prone to inducing premature cross-linking of XNBR molecular chains at high temperatures, resulting in scorch [9]. Currently, research on the XNBR/MPU system mainly focuses on the exploration of simple formulations. For instance, Liu et al. [10] investigated the effect of XNBR on the mechanical properties of polyether-based MPU and found that the hardness of the blend decreased by 15% when the XNBR content was 60%. However, in-depth analysis of the interfacial reaction mechanism and control of process defects was not conducted.

Based on the above, this study focuses on the XNBR/MPU blending system. Molecular simulation was employed to reveal the interfacial reaction mechanism, process parameters were optimized to address process defects, and microscopic characterization combined with mechanical testing was carried out to establish a correlation model of "interfacial cross-linking - microstructure - mechanical properties". This work aims to provide technical references for the development of high-performance XNBR/MPU blended materials.

2. Molecular Dynamics Simulation

2.1. Model Construction

The monomer models of MPU, XNBR, and their corresponding reaction products were constructed using the Visualizer module in Materials Studio software, as shown in Fig. 1, Fig. 2, and Fig. 3. In the models, red represents oxygen atoms, blue represents nitrogen atoms, gray represents carbon atoms, and white represents hydrogen atoms. The molecular structure model of the reaction is as follows:

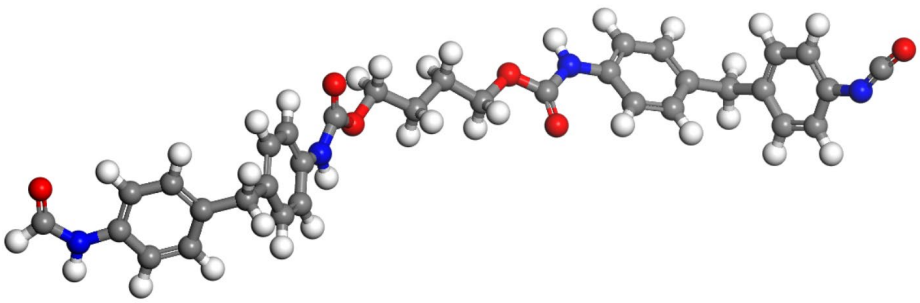

Fig 1. MPU molecular dynamics monomer models

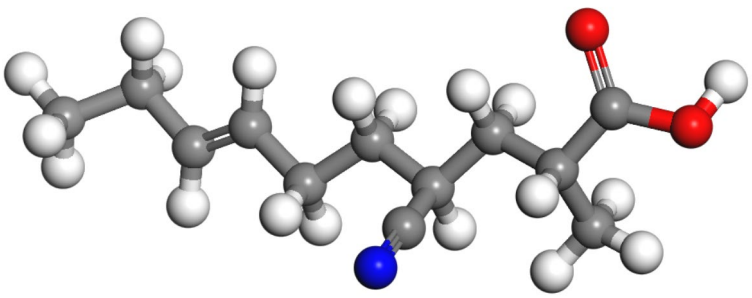

Fig 2. XNBR molecular dynamics monomer models

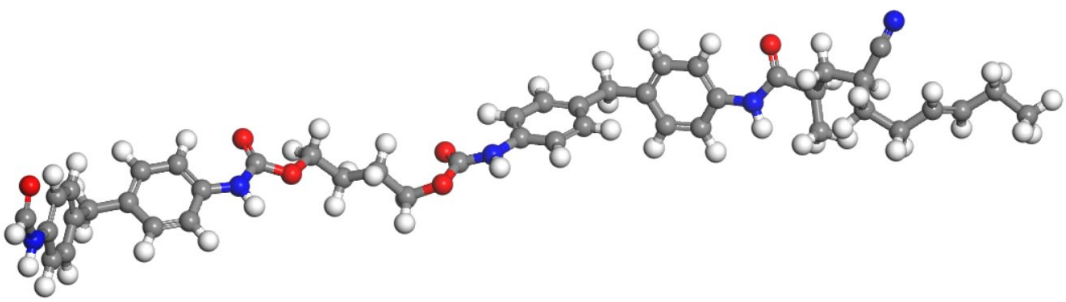

Fig 3. Co-curing reaction products of MPU and XNBR

2.2. Free Energy Calculation

Before calculating the free energy, it is necessary to optimize the molecular structure. The Geometry Optimization task was performed using the Dmol3 module in MS software. The purpose of optimization is to find the lowest energy point on the total potential energy surface of the molecular model and obtain the molecular model in the lowest energy state. After optimization, the BLYP functional in GGA was used to describe the exchange-correlation energy in the entire molecular model system, and the DNP basis set was selected to ensure that the accuracy was within an acceptable calculation range. The free energy at 80°C was derived from the output file of Dmol3, and the data from the last step of the algorithm were selected. The Etotal value of XNBR was -485.2 Hartree, the Etotal value of MPU was -1985.36 Hartree, and the Etotal value of their reaction product was -2470.67 Hartree.

In the outmol file, the G correction value of the product of XNBR and MPU at 353.15 K can be found to be approximately +452.04 kcal/mol. By converting the Gtotal value, the Gtotal of the product is calculated to be approximately +0.7 Hartree. Similarly, the Gtotal of XNBR is approximately +0.2 Hartree, and the Gtotal of MPU is approximately +0.46 Hartree.

The calculation results are shown in Tab. 1. Finally, the free energy value of the entire co-curing reaction stage is calculated to be -0.07 Hartree, i.e., -44 kcal/mol. The negative sign indicates that the reaction can proceed spontaneously at the experimental temperature, which provides a theoretical basis for the experimental preparation of XNBR and MPU-based composite materials.

Tab 1. Thermodynamic properties (Unit: Hartree)

	Reactant	Reaction products
E_{total}	-2470.56	-2470.67
G_{total}	0.66	0.7
$E_{Tcorr}^{458.15K}=E_{total}+G_{total}$	-2469.9	-2469.97

3. Experimental Section

3.1. Raw Materials and Instruments Required for Experiments

Materials：

Millable Polyurethane (MPU): Grade 85A, supplied by BASF (China) Co., Ltd.;

Carboxylated Nitrile Butadiene Rubber (XNBR): Grade 1072CG, with an acrylonitrile content of approximately 26 wt%, a Mooney viscosity [ML (1+4) at 100°C] of 35, and a carboxyl mass fraction of 0.075, provided by Nan-Ti Chemical Co., Ltd. (Taiwan, China);

Cross-linking agent TAIC (Triallyl Isocyanurate): purchased from Shanghai Dunmei New Material Technology Co., Ltd.;

Carbon black: obtained from Qingdao Degussa Chemical Co., Ltd.;

Precipitated silica: supplied by Qingdao Solvay Co., Ltd.

Instruments：

Open mill: Model X(S)K-160, manufactured by Shanghai Shuangyi Rubber & Plastic Machinery Co., Ltd.;

Rotorless vulcanizer: Model GT-M2000-A, produced by Taiwan Gaotie Testing Instrument Co., Ltd.;

Flat vulcanizing machine: Model LCM-3C2-G03-LM, supplied by Shenzhen Jiaxin Electronic Equipment Technology Co., Ltd.;

Electronic universal testing machine: Model AI-7000, manufactured by Gaotie Testing Instrument (Dongguan) Co., Ltd.;

Shore hardness tester: Model LX-A, provided by Xijing Co., Ltd.

3.2. Experimental Procedure

3.2.1. Carboxylated Nitrile Butadiene Rubber and Millable Polyurethane

The carboxyl functional groups in XNBR tend to undergo amidation reaction with the isocyanate groups in MPU at 80°C. The components of the XNBR/MPU blend were designed via orthogonal experiments, as shown in Tab. 2.

Tab 2. XNBR/MPU rubber-plastic ratio component design

Component/g	1#	2#	3#	4#	5#
XNBR	50	60	70	80	90
MPU	50	40	30	20	10
SA	0.5	0.5	0.5	0.5	0.5
N330	30	30	30	30	30
CaO	3	3	3	3	3
Antioxidant RD	1	1	1	1	1
TAIC-70	1.5	1.5	1.5	1.5	1.5
DCP	2.5	2.5	2.5	2.5	2.5
ZnO2	5	5	5	5	5
CTP	0.5	0.5	0.5	0.5	0.5

Experimental Operations

Mastication: XNBR was masticated on an open mill at room temperature to break the rubber macromolecular chains, thereby improving the adhesion of the rubber compound and facilitating the uniform dispersion of other materials in the rubber. Subsequently, MPU powder was added for mixing, and the mixture was sheeted out once sufficient mixing between the two components was observed.

Mixing: The temperature of the open mill was raised to 80°C, and the roll gap was adjusted to 1 mm. The premix was fed into the mill, followed by the sequential addition of antioxidant RD, stearic acid (SA), carbon black N330, and calcium oxide (CaO). Finally, TAIC-70, dicumyl peroxide (DCP), zinc dioxide (ZnO_2), and scorch retarder CTP were added. Before each addition, it was ensured that the mixture was uniformly mixed. The minimum roll gap was maintained, and the mixture was folded into a triangular packet more than ten times. Afterward, the roll gap was adjusted to 2 mm, and the mixture was sheeted out.

Vulcanization: Vulcanization enables rubber to form a three-dimensional network structure through chemical cross-linking of linear macromolecular chains. A 5 g

portion of the mixed rubber was cut and placed in a rotorless vulcanizer to test the vulcanization curve. Then, a 25 g portion of the mixed rubber was cut and placed in a mold of the vulcanizing machine for vulcanization. After vulcanization, the test sheets were stored for 24 hours to release internal stress before subsequent tests.

A rubber rotorless vulcanizer (Model ZL-3001), as shown in Fig. 4, was used to test the vulcanization performance parameters of the thermoplastic elastomer at 160°C, with the results presented in Tab. 5; the vulcanization characteristic curve is shown in Fig. 5, where the abscissa represents vulcanization time and the ordinate represents torque. It can be seen from the curve that the torque increases continuously from the start up to 20 minutes and reaches the maximum value at approximately 20 minutes. Therefore, the vulcanization time in actual vulcanization process can be set to 20 minutes. As shown in Tab. 3: Formulation 3 exhibits the smallest minimum torque (ML), indicating the best fluidity of the rubber compound; the largest maximum torque (MH) implies the highest shear modulus or hardness of the rubber compound; the largest MH-ML value indicates the highest cross-linking degree of the rubber compound. Meanwhile, Formulation 3 has the longest scorch time (tc10), and a longer scorch time corresponds to better processing safety under high-temperature conditions.

Fig 4. Rotorless vulcanizer

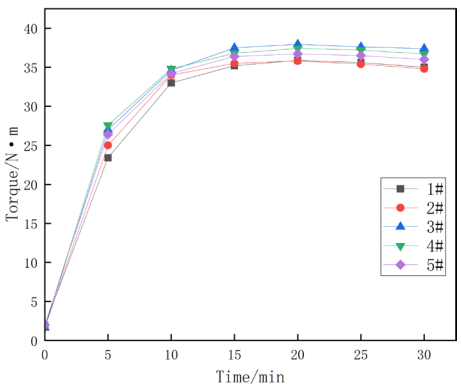

Fig 5. XNBR/MPU vulcanization characteristic curve

Tab 3. XNBR/MPU vulcanization performance parameters

Parameter	1#	2#	3#	4#	5#
MH-ML/ dN·m	33.99	34.05	36.32	35.66	34.78
MH/ dN·m	35.78	35.75	37.91	37.31	36.64
ML/dN·m	1.79	1.70	1.59	1.65	1.86
tc10/min	0.78	0.82	0.90	0.81	0.78
tc90/min	8.11	9.02	8.1	8.65	9.03

Note: M_L = Minimum Torque; M_H = Maximum Torque; M_H-M_L = Degree of Polymer Cross-linking; tc10 = Scorch Time; tc90 = Optimal Vulcanization Time.

3.3. Testing and Characterization

3.3.1. Static Mechanical Property Testing

The instrument shown in Fig. 6 was used to conduct tensile property testing, tear

property testing, and Shore hardness testing on the rubber-plastic materials. The Shore hardness test was performed in accordance with the standard GB/T 531.1-2008, the tensile property test followed GB/T 528-2009, and the tear strength test complied with GB/T 529-2008. The tensile rate was set to 500 mm/min.

Fig 6. Tensile testing machine (left) and rubber shore hardness tester (right)

3.3.2. Microscopic Morphology Testing

Perform microscopic analysis on TPV and use a scanning electron microscope (Hitachi S-3400N SEM) to analyze the interfacial bonding of the composite material, as shown in Fig.7.

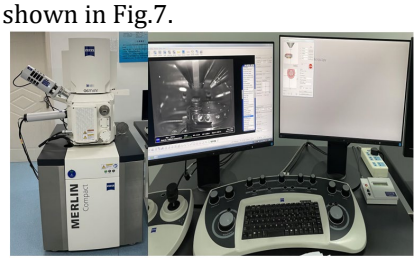

Fig 7. Electron microscope equipment

4. Results and Discussion

4.1. Static Mechanical Properties

Static mechanical properties are core indicators for evaluating the engineering application potential of thermoplastic vulcanizates (TPVs), and their variation patterns are directly related to the interfacial bonding state and microstructure of rubber-plastic blends. The mechanical property test results of the XNBR/MPU blend are shown in Fig. 8.

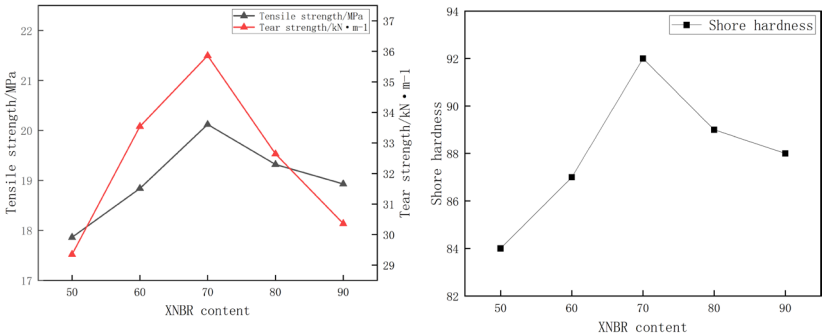

Fig 8. XNBR/MPU tensile tear performance (left) and shore hardness (right)

Fig. 8 presents the performance data of the XNBR/MPU thermoplastic elastomer at room temperature. Among Formulations 1# to 5#, the tensile strengths are 17.86 MPa, 18.84 MPa, 20.12 MPa, 19.32 MPa, and 18.93 MPa, respectively. Formulation 3# exhibits the highest tensile strength; simultaneously, it also has the maximum tear strength of 35.86 MPa, while the tear strengths of the other four formulations are 29.35 MPa, 33.54 MPa, 32.64 MPa, and 30.36 MPa, respectively. The Shore hardness of Formulation 3# is 92. These results indicate that the thermoplastic elastomer of Formulation 3# possesses the optimal mechanical properties. The underlying reason is that when the XNBR content is 70%, MPU forms a continuous matrix phase, and XNBR is uniformly dispersed as nano-sized particles within this matrix. This structure results in the highest interfacial chemical cross-linking density and optimal stress transfer efficiency.

4.2. Microscopic Morphology Analysis

Fig. 9 shows the cross-sectional SEM micrograph of the XNBR/MPU blend. It can be observed from the figure that the blend exhibits a distinct two-phase structure: MPU serves as the continuous matrix phase, and XNBR is uniformly distributed as the dispersed phase. The interface between the two phases is blurred, with no obvious debonding or voids. This phenomenon confirms that the -COOH groups in the XNBR molecular chains have undergone an amidation reaction with the -NCO groups in MPU, forming a covalent bond interface layer. This layer effectively inhibits phase separation and enhances the interfacial bonding strength. When the material is subjected to external forces, stress can be efficiently transferred to the MPU matrix and XNBR dispersed phase through the interfacial chemical bonds, avoiding strength loss caused by interfacial debonding. This observation is consistent with the relatively high tensile and tear strengths of Formulation 3#.

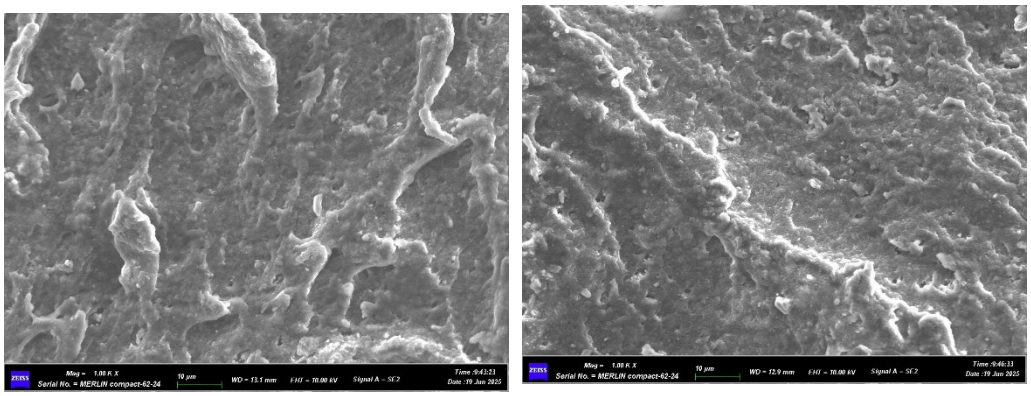

Fig 9. XNBR/MPU SEM

5. Conclusions

This study focuses on the preparation of high-performance thermoplastic vulcanizates (TPVs) via blending carboxylated nitrile butadiene rubber (XNBR) with millable polyurethane (MPU). By integrating molecular simulation, experimental optimization, and multi-scale characterization, the key conclusions are drawn as follows:

1.Molecular dynamics simulations confirm that the amidation reaction between XNBR and MPU at 80°C has a Gibbs free energy change (ΔG) of -49 kcal/mol, indicating that the reaction proceeds spontaneously. The formed amide bonds provide a chemical basis for strong interfacial bonding between the two phases.

2.Orthogonal experiments identify the optimal formulation for the XNBR/MPU blend: a rubber-plastic mass ratio of 70/30 (XNBR/MPU), 2.5 g of dicumyl peroxide (DCP), and 3 g of calcium oxide (CaO). Under this formulation, the blend exhibits a tensile strength of 20.12 MPa and a tear strength of 35.86 kN/m, with no scorch risk during processing.

3.Scanning electron microscopy (SEM) characterization verifies that the amidation reaction significantly improves the interfacial compatibility between XNBR and MPU. MPU forms a continuous matrix phase, while XNBR is uniformly dispersed as nano-sized particles within the matrix, with no interfacial debonding. This microstructure provides microscopic support for the enhanced mechanical properties of the blend.

This study clarifies the interfacial reaction mechanism and mechanical property regulation rules of the XNBR/MPU system. The developed blend material shows application prospects in the fields of automotive sealing and shock absorption, and provides technical references for the blending modification of functionalized rubbers with millable polyurethanes.

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