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Effects of acrylonitrile content of nitrile rubber on mechanical properties of polyamide 6/nitrile rubber blends

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Abstract
With the further development of secondary exploitation in oil field, it is very important to design high performance rubber used in drilling and mining tools. In this paper, polyamide 6/nitrile rubber (PA6/NBR) blends were prepared by three-step molding process. The reinforcing effect of PA6 in NBR with different acrylonitrile content was explored. The crystal properties, crystal structure, phase separation morphology and mechanical properties of the blends were systematically analyzed. The results showed that the fibrosis degree of PA6 phase was higher and the reinforcement effect was more obvious, when the content of acrylonitrile in NBR matrix was lower. Based on the experimental results, the reinforcement mechanism is fully explained and the morphology evolution model of PA6/NBR was established.

1. Introduction

Nitrile rubber is one of the many synthetic rubber varieties [1]. Nitrile rubber is widely used in oil and gas fields because of its excellent oil resistance [2]. To be specific, the application field includes screw drill, sealant barrel, seal ring and so on [3].

Taking the oil and gas fields in China as an example, it includes the screw pump project in Daqing oilfield [4], the high temperature and high pressure sealing project in Puguang gas field [5], and the sealing ring project in Langfang pipeline, etc [6]. Therefore, the work will focus on the application and development of rubber products used in domestic oil and gas fields for our research team.

With the increasing demand for oil and gas resources, energy crisis has become an unavoidable topic. In view of this problem, domestic experts and scholars prefer to conduct secondary development or deep excavation on the basis of existing oil fields [7]. This method is undoubtedly a feasible approach in terms of cost saving and resource utilization. However, the following harsh working conditions put forward higher requirements for equipment and tool performance. Specifically, harsh operating conditions include high temperature, high pressure, high sulfur, etc [3]. Because the properties of polymer materials are sensitive to temperature, pressure and medium environment, it brings great challenges to the high performance design of rubber materials. Taking the screw drilling tool in oil production equipment as an example, the rubber strength and modulus of the stator of screw pump will decrease greatly under high temperature, and the friction loss rate will rise sharply [8]. This leads to a sharp decline in the life of the screw drill and a significant decline in the efficiency of oil production. In order to solve this technical problem, the effective enhancement of nitrile rubber is essential.

For the conventional nitrile rubber compound system, inorganic filler can be used to improve the material performance [9–11]. These inorganic fillers include calcium carbonate, carbon black, silica, and so on. However, the reinforcing effect of traditional filler has reached its limits. In recent years, new fillers, including graphene and carbon nanotubes, have been gradually used in rubber compound systems [12–15]. While these new fillers bring excellent performance, they also greatly increase the cost of raw materials. The application of these composite materials in oil and gas fields is limited to a large extent.
Polyamide 6 is a common member of the polyamide family [16]. It exists excellent physical and chemical properties and is widely used in textile and garment, automobile, electronics and energy fields [17]. In particular, PA6 has excellent mechanical properties, and its tensile strength and elastic modulus are respectively 20 and 50 times than that of NBR. The melting point of PA6 reaches 230 °C, which can significantly improves the mechanical properties of NBR at high temperature. Meanwhile, the friction coefficient of PA6 is very small, which can improve the wear resistance of polymer blends [18].

PA6/NBR blend system has excellent oil resistance, high temperature resistance, and mechanical properties, and its research has attracted wide attention. Fagundes et al studied the influence of crosslink systems on thermoplastic vulcanizates (TPVs) based on PA/NBR [19]. The experimental results showed that the TPV produced by dicumyl peroxide presented the excellent mechanical properties. The morphology of this TPV system showed small NBR domains homogeneously distributed in the polyamide phase. Gomes et al studied the influence of EVA and EVA-g-MA on the aggregate structure of TPVs based on PA6/NBR [20]. The results showed that EVA as a plasticizer could reduce the crystallinity of TPVs. EVA-g-MA presented the imide linkage formation at the additive–matrix interface. Wang et al studied the interface binding between PA6 and NBR matrix by transmission electron microscope (TEM) [21].Two interfacial layer structures were formed between PA6 and NBR matrix, which were the primary interfacial layer caused by molecular diffusion and the secondary layer caused by hydrogen bond. Cai et al prepared PA6/NBR blends by three-step molding method. Polyamide 6 showed obvious enhancement effect on NBR, which was derived from the formation of fiber phase structure of PA6 [22]. In summary, the influence of acrylonitrile content in NBR on the phase separation morphology and mechanical properties of PA6/NBR blends has not been reported until now.

The PA6/NBR blends were prepared by three-step molding process. Three kinds of NBR with gradient of acrylonitrile content were selected as matrix materials. The reinforcing effect of PA6 on NBR with different polarities was explored. The effect of NBR polarity on the aggregate structure of PA6/NBR blends was studied. The main influencing factor of mechanical property improvement can be cleared in combination with the aggregate structure. Finally, the structure model of NBR reinforced by PA6 was established.

2. Experimental

2.1. Materials
Nitrile rubbers (3445 F, 3945 F, 4456 F) were supplied by LANXESS, Cologne, Germany (table 1). Polyamide 6 (1030B) was purchased from UBE, Tokyo, Japan. Vulcanizing agent S and accelerator NOBS were purchased from Hebei Chuanpu Chemical Co. LTD, Hebei, China.

2.2. Sample preparation
Before the experiment, PA6 was dried in an oven at 80 °C for 12 h. The weighed PA6 and NBR were put into the mixer machine for mixing at 230 °C for 10 min 2 wt% S and 1 wt% NOBS were added into the blends, and place them in the open mill machine for mixing. Finally, the mixed materials were placed on the molding machine for curing at 160 °C for 10 min. The composition of the blends is shown in table 2.

The oil resistance test of standard dumbbell spline was carried out in the oil bath unit. The solvent is 0 # diesel oil, the temperature is set at 120 °C, and the soaking time is 7 days.

2.3. Performance testing and characterization
2.3.1. Mechanical properties
Mechanical performance test was conducted on Instron 5967. The dumbbell standard cutting knife was used to cut the sample into the dumbbell standard samples with a width of 4 mm and a thickness of 1.2 mm. Tensile speed of 50 mm min 

| Types of NBR      | Acrylonitrile (wt%) | Butadiene (wt%) |
|-------------------|---------------------|-----------------|
| 3445 F (34NBR)    | 34                  | 66              |
| 3945 F (39NBR)    | 39                  | 61              |
| 4456 F (44NBR)    | 44                  | 56              |
heated from 25 °C to 250 °C at the rate of 10 °C min$^{-1}$. Then the temperature was kept at 250 °C for 2 min. Subsequently, the samples was cooled from 250 °C to 25 °C at the rate of 10 °C min$^{-1}$. According to literature reports, the melting enthalpy of 100% crystallization of PA6 is 230 J g$^{-1}$ [23]. The melting enthalpy of samples is obtained by integrating DSC curve. The sample crystallinity can be calculated by the standard formula.

2.3.3. WAXD analysis
The one dimensional wide-angle x-ray diffraction (1D-WAXD) analysis was performed on the Regaku MiniFlex600 diffractometer. The samples were cut into thin plates with 1.5 mm width and 3 mm length. The test was operated at angles from 5° to 60° with speed of 5°/min.

2.3.4. SEM analysis
The samples were brittlely fractured under liquid nitrogen. The flat section was selected and sprayed by gold. After that, the phase separation morphology was observed on scanning electron microscopy (SEM, JSM-IT300A, JEOL).

Table 2. Composition of PA6/NBR blends.

| Samples          | NBR (wt%) | PA6 (wt%) | S (wt%) | NOBS (wt%) |
|------------------|-----------|-----------|---------|------------|
| Pure NBR         | 100       | 0         | 2       | 1          |
| 5 wt%PA6/NBR     | 95        | 5         | 2       | 1          |
| 10 wt%PA6/NBR    | 90        | 10        | 2       | 1          |
| 20 wt%PA6/NBR    | 80        | 20        | 2       | 1          |
| 30 wt%PA6/NBR    | 70        | 30        | 2       | 1          |
| 40 wt%PA6/NBR    | 60        | 40        | 2       | 1          |

Figure 1. The stress-strain curves of PA6/NBR blends during the tensile process: (a) PA6/34NBR, (b) PA6/39NBR, (c) PA6/44NBR.
3. Results and discussion

The stress–strain curves of PA6/NBR blends during the tensile process are shown in figure 1. The data of mechanical performance calculated from figure 1 are presented in table 3. It can be seen that the tensile strength
of the blends is significantly increased with the addition of PA6. For PA6/34NBR and PA6/39NBR blends, the tensile strength gradually increases in the range of PA6 content from 5 wt% to 30 wt%. When PA6 content reaches 40 wt%, tensile strength begins to decline. For PA6/44NBR blends, the tensile strength increases with the increase of PA6 content. According to comparing and analyzing the tensile strength growth rate data of three different PA6/NBR blends (as shown in figures 2(a) and (b)), it can be found that PA6 presents the highest reinforcement efficiency in 34NBR matrix.

The elastic modulus of PA6/NBR blends is shown in figures 2(c) and table 3. It can be found that the elastic modulus of the materials gradually increases with the increase of PA6 content. It indicates that PA6 presents obvious strengthening effect in rubber matrix. The elongation at break of PA6/NBR blends is shown in figure 2(d) and table 3. It is worth noting that the elongation at break of the materials decreases gradually with the increase of PA6 content. It indicates that the mechanical properties of the blends are improved by PA6, but also the flexibility is reduced.

Figure S1 is available online at stacks.iop.org/MRX/6/125362/mmedia presents the tensile stress-strain curves of the samples after oil resistance test. Table S1 shows the data of mechanical properties of materials obtained according to figure S1. Table S2 shows the variation trend of mechanical properties before and after
It can be seen that the tensile strength of the materials decreases obviously after soaking in diesel oil. With the increase of PA6 content, the decline trend of tensile strength of blends slowed down gradually. The elastic modulus of blends has been improved to some extent. The elongation at break of blends decreased obviously, but the addition of PA6 effectively alleviated this trend.

In the following, the variation of mechanical properties is analyzed from the aspects of crystallinity, thermal properties, phase separation structure and crystal structure. According to comparing the aggregate structure of three polymer blends, the main factors affecting the mechanical properties will be investigated.

### Table 4. Thermal properties analysis of PA6/NBR blends.

| Samples        | T<sub>m</sub>(°C) | T<sub>c</sub>(°C) | Crystallinity(%) |
|----------------|------------------|------------------|------------------|
| Pure 34NBR     | —                | —                | —                |
| 5 wt%PA6/34NBR | 212.0            | 151.9            | 5.5              |
| 10 wt%PA6/34NBR| 214.9            | 157.5            | 7.3              |
| 20 wt%PA6/34NBR| 216.4            | 163.9            | 9.2              |
| 30 wt%PA6/34NBR| 217.7            | 177.7            | 11.5             |
| 40 wt%PA6/34NBR| 218.6            | 180.3            | 12.6             |
| Pure 39NBR     | —                | —                | —                |
| 5 wt%PA6/39NBR | 210.7            | 130.6            | 6.2              |
| 10 wt%PA6/39NBR| 214.3            | 143.4            | 8.2              |
| 20 wt%PA6/39NBR| 216.3            | 150.8            | 10.7             |
| 30 wt%PA6/39NBR| 218.6            | 155.5            | 12.8             |
| 40 wt%PA6/39NBR| 219.6            | 165.1            | 13.6             |
| Pure 44NBR     | —                | —                | —                |
| 5 wt%PA6/44NBR | 218.0            | —                | 7.9              |
| 10 wt%PA6/44NBR| 219.2            | 177.5            | 11.7             |
| 20 wt%PA6/44NBR| 220.0            | 177.5            | 12.5             |
| 30 wt%PA6/44NBR| 221.0            | 178.3            | 14.1             |
| 40 wt%PA6/44NBR| 222.0            | 179.2            | 15.4             |
crystals form crystals in the blends gradually improves. It can be speculated that the higher density of the hydrogen

| Samples          | Content of α-form crystal | Content of γ-form crystal |
|------------------|---------------------------|---------------------------|
| Pure 34NBR       | —                         | —                         |
| 5 wt% PA6/34NBR  | 0.66                      | 0.34                      |
| 10 wt% PA6/34NBR | 0.69                      | 0.31                      |
| 20 wt% PA6/34NBR | 0.72                      | 0.28                      |
| 30 wt% PA6/34NBR | 0.75                      | 0.25                      |
| 40 wt% PA6/34NBR | 0.79                      | 0.21                      |
| Pure 39NBR       | —                         | —                         |
| 5 wt% PA6/39NBR  | 0.69                      | 0.31                      |
| 10 wt% PA6/39NBR | 0.73                      | 0.27                      |
| 20 wt% PA6/39NBR | 0.77                      | 0.23                      |
| 30 wt% PA6/39NBR | 0.82                      | 0.18                      |
| 40 wt% PA6/39NBR | 0.85                      | 0.15                      |
| Pure 44NBR       | —                         | —                         |
| 5 wt% PA6/44NBR  | 0.74                      | 0.26                      |
| 10 wt% PA6/44NBR | 0.79                      | 0.21                      |
| 20 wt% PA6/44NBR | 0.83                      | 0.17                      |
| 30 wt% PA6/44NBR | 0.87                      | 0.13                      |
| 40 wt% PA6/44NBR | 0.95                      | 0.05                      |

The thermal properties of PA6/NBR blends are shown in figure 3 and table 4. The melting points and
crystallinity of the blends are gradually improved with the increase of PA6 content. The larger PA6 phase is
intended to form in the blends with larger content of PA6. By comparing three different NBR matrix, it can be
found that the PA6/39NBR blend has the lowest crystallization temperature. It indicates that the PA6 molecular
chain has a strong interaction with the nitrile molecular chains, which results in the limited crystallization
behavior of PA6 [24]. With the increase of PA6 content, the crystallinity of the blends increases. With the
increase of acrylonitrile content in NBR (from 34 wt% to 44 wt%), the crystallinity of the blends also increases.

From the DSC melting curves, it can be seen that the blends present double melting peaks. It indicates that
two crystal structures with different thermal stability are formed in the blends. For PA6/34NBR and PA6/39NBR
blends, the crystallization curves also present double crystallization peaks. It also suggests that there are
two different crystal structures of PA6 in the blends.

1D–WAXD analysis of PA6/NBR blends is shown in figure 4. With the increase of PA6 content, the peak
intensity from crystal plane diffraction in the blends gradually increases. It indicates that the crystal structure in
the blend tends to be more perfect. The peak of \(2\theta = 19.4^\circ\) corresponds to the diffraction of amorphous region
of NBR. The peak of \(2\theta = 21.2^\circ\) corresponds to the diffraction of (100) lattice plane of \(\alpha\)-form crystals in the
PA6 phase [25]. The peak of \(2\theta = 22.4^\circ\) corresponds to the diffraction of (100) lattice plane of \(\gamma\)-form crystals
[25]. The \(2\theta = 24.4^\circ\) position corresponds to the diffraction peak of (010/110) lattice plane of \(\alpha\)-form crystals [25].

The WAXD files were treated by peak separation, and the relative contents of \(\alpha\)-form and \(\gamma\)-form crystals in
the blends were obtained (as shown in table 5). It can be seen that the relative content of \(\alpha\)-form crystals in the
blend gradually increases with the increased PA6 content. This is due to the formation of large phase structures
in PA6. With the increase of acrylonitrile content in NBR (from 34 wt% to 44 wt%), the relative content of \(\alpha\)-form
crystals in the blends gradually improves. It can be speculated that the higher density of the hydrogen
bonds between PA6 and NBR molecular chains, and the more stable crystals are intended to form (i.e. \(\alpha\)-form
crystals).

The phase separation structure of PA6/NBR blends is shown in figure 5 and table 6. For PA6/34NBR blends,
when PA6 content is low (from 5 to 10 wt%), PA6 particle phase is uniformly dispersed in the matrix. When PA6
content is higher (from 20 to 30 wt%), PA6 phase is uniformly dispersed in the matrix in the form of particles
and fibers meanwhile. When PA6 content increases to 40 wt%, the large–sized aggregates of PA6 phase are
formed. For PA6/39NBR blends, when PA6 content is in the range of 5 to 20 wt%, PA6 phase is distributed in the
matrix as particles. When the content increases to 30 wt%, PA6 particles and fibers are formed simultaneously. The large–sized aggregates are formed when PA6 content is 40 wt%. For PA6/44NBR blends, the morphological evolution of PA6 phase in the matrix is the same as that of PA6/39NBR blends.

It is worth noting that the particles and fibers of PA6 phase present different evolution process due to the
compatibility differences between NBR matrix and PA6 reinforcement. According to analysis of size and
distribution state of PA6 particle phase, the compatibility between PA6 and NBR molecular chains improves
with the increase of acrylonitrile content in NBR matrix (i.e. the increased polarity of NBR), the size of PA6
particle phase decreases gradually, and the particle spacing also decreases gradually.
Figure 5. SEM images of fracture surface of PA6/NBR blends: (a) 5 wt% PA6/34NBR, (b) 10 wt% PA6/34NBR, (c) 20 wt% PA6/34NBR, (d) 30 wt% PA6/34NBR, (e) 40 wt% PA6/34NBR, (f) 5 wt% PA6/39NBR, (g) 10 wt% PA6/39NBR, (h) 20 wt% PA6/39NBR, (i) 30 wt% PA6/39NBR, (j) 40 wt% PA6/39NBR, (k) 5 wt% PA6/44NBR, (l) 10 wt% PA6/44NBR, (m) 20 wt% PA6/44NBR, (n) 30 wt% PA6/44NBR, (o) 40 wt% PA6/44NBR.
Based on analysis of size and distribution of PA6 fiber structure, the diameter and content of PA6 fibers gradually decrease with the increase of acrylonitrile content in matrix. It indicates that the dispersion degree of PA6 in the matrix is improved with increase of the polarity of NBR. Based on comparison of three different PA6/NBR blends, PA6 fiber structures are formed earlier during the evolution process in PA6/34NBR blend, followed by PA6/39NBR blend and then PA6/44NBR blend. In terms of PA6 fiber content, it is the largest in PA6/34NBR blend and the smallest in PA6/44NBR blend.

Combined with the cooling crystallization curves in DSC analysis, the double peak characteristics of crystals are closely related to the formation of PA6 particle and fiber phase. In combination with the change of the tensile strength of the blends, the fiber phase structure appears earlier and the content of the blends is higher, which results in the higher improvement rate of tensile strength. Specifically, PA6 presents the best enhancement effect in 34NBR matrix.

For reinforcement in polymer composites, there are four factors determining the improvement of its mechanical properties: the content, distribution, orientation and interfacial load transfer of the reinforcement [26, 27]. Therefore, for PA6/NBR blends, the effective dispersion of PA6 phase and the formation of fiber phase structure are two important factors which restrict the improvement of mechanical properties. However, according to the change trend of mechanical properties, the main factor affecting the mechanical properties is the formation of PA6 fiber phase structure.

Therefore, the key to preparation of high–performance materials is to choose the appropriate processing technology and fabricate as many PA6 fiber structures as possible. In this paper, PA6/NBR blends are prepared by three–step molding process, which results a large number of PA6 fiber structures. The experimental results can provide theoretical and experimental data support for the preparation of high–performance rubber and plastic blends. The formation mechanism of PA6 fiber phase structure is described in detail below.

Figure 6 shows the evolution of phase separation morphology of PA6/NBR blends. The change trend of PA6 phase size and its spacing in the matrix are presented in the figure 6. The size and evolution of the fiber phase structure also can be shown in the schematic. The schematic highlights the decisive role of fiber phase structure
in the improvement of mechanical properties. Although PA6 has better dispersion effect in 44NBR matrix, the improvement of mechanical properties is very limited. Therefore, appropriate phase separation structure is beneficial to the enhancement of PA6/NBR blends. And it can be confirmed by the mechanical property change of PA6/34NBR blends.

Figure 7 shows the formation mechanism of PA6 fiber phase structure. It can be speculated that the formation of fiber phase structure is completed by the following three steps. In the process of melting compounding, a large number of PA6 particle phase structures are formed, and the particle phase structures are connected with each other. In the process of open mixing, the isotropic PA6 particle phase structure will be arranged along the direction of the shear force from double rolling, which results in the formation of the chain beaded structures. Finally, during the molding process, the chain beaded structures of PA6 phase are melted and recrystallized, and then the fiber phase structures are formed under the high temperature and pressure.

4. Conclusions

The polyamide 6/nitrile rubber (PA6/NBR) blends were prepared by three-step molding process. The variation trend of mechanical properties of three kinds of PA6/NBR blends was systematically analyzed from the aspects of crystallization properties, thermal properties, phase separation morphology and crystal structures. These results showed that the reinforcement effect of PA6 in NBR matrix was more obvious with the lower acrylonitrile content of NBR. When PA6 content was 30 wt%, the tensile strength of PA6/NBR blends reached the maximum value. When NBR presented less polarity (i.e. the lower acrylonitrile content), there existed the less compatibility between PA6 and NBR chains and the greater phase separation. As the polarity of NBR is decreased, the fiber phase structures were tended to form, which was beneficial to the improvement of mechanical properties. This study provided theoretical and experimental support for the preparation of high performance PA6/NBR blends.

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