



The Application Development of Plant-Based Environmental Protection Plasticizer

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Authors' contributions

This work was carried out in collaboration between all authors. Authors WJ and WX designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors GL, LY, PW, CJ and ZL managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Present research is aimed towards designing and development of environmental protection plasticizers using the fractionation heavy component in the industrial production of corn stalks as raw material. The plant-based rubber oil (PBRO) plasticizers are the reactants of the dihydric alcohols (Polyols) in heavy component with phthalic anhydride (PA) (the molar ratio of Polyols/PA as 2 : 1) at the temperature range of 180 -190°C. The main advantage is that this substance does not contain any of the sixteen hazardous substances of PAHs (polycyclic aromatic hydrocarbons) and 38 hazardous substances of PAHs (polycyclic aromatic hydrocarbons) recorded in EU REACH regulation. In plasticization of NBR, the dosage of PBRO can reach 25 phr (parts per hundreds of rubber), but the plasticizing effects of PBRO is inferior to common rubber oil (paraffin oil, naphthenic oil, aromatic hydrocarbon oil and Dioctyl phthalate). In plasticization of SBR, the maximum amount of PBRO is 20 phr. Although the mechanical properties decrease; the aging resistance and thermal stability (the temperature of maximum weight losses of PBRO as 302°C) are slightly higher than that of common rubber oil.

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1. INTRODUCTION

As the leading enterprise of the Chinese bio-chemical industry, Changchun Dacheng Group was selected as the world's 50 most innovative companies by U.S. Fast Company magazine in 2011, ranking 46 [1]. The reason is that Dacheng firstly realizes large-scale industrial production of plant-based polyols from corn straw in the world, which is a milestone after the invention of bio-energy (bio-ethanol, bio-diesel), and bio-Ethylene glycol (EG) / Propylene glycol (PG) from corn in the post-oil era to reduce the dependence on oil. To finish this pioneering work, Dacheng begins a two-step strategy. The first step, at the end of 2007, the world's first 200,000 tons production line of plant-polyols based on corn starch successfully went into operation. After three years running, the plant-EG and plant-PG have been recognized by the domestic and international chemical market and in short supply. The second step, Dacheng has completed a 10,000 tons production line of plant-polyols based on corn straw in 2011. Dacheng will have an annual output of 200,000 tons of plant-polyols put into domestic and overseas chemical market in 2015, which will help to reduce the dependence of China's chemical industry on oil.

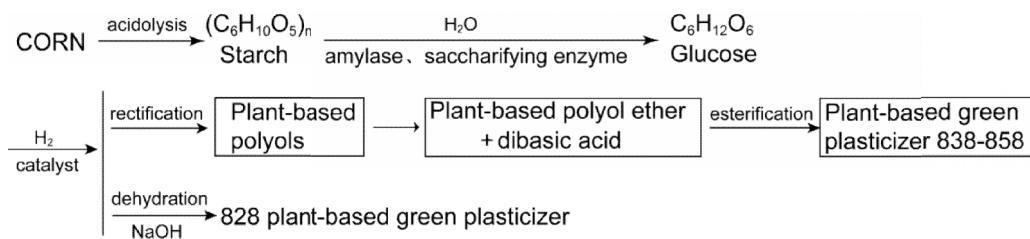
However, common problems are the application development of the fractionation heavy component encountered in large-scale industrial production of biomass raw materials to replace petroleum chemical products [2]. The same as in petrochemical route, the fractionation heavy component (condensate) of plant-based polyols production line seems to be able to be used as the materials of plasticizer. The most notable feature is that the fractionation heavy component is consistent with the requirements of environmental protection (green). In 2012, Changchun Dacheng Group has more than 10 million tons of fractionation heavy components to be developed into rubber plasticizer accorded with environmentally sound technology. The purpose of this paper is to initially introduce the performance, strongpoint and shortcoming, of those heavy component and plant-based plasticizers and hope researchers can jointly participate in the development of environmentally sound plasticizers using Dacheng biomass raw materials.

2. MATERIALS AND METHODS

At present, the plant-based green plasticizers of Changchun Dacheng Group are polyols - polyether (labeled 828) and polyol esters (labeled 838-858), of which 828 is mainly used in the area of amylose-based plastics and reclaimed rubber while 838-858 are used in the field of rubber products.

2.1 The Production of Plant-Based Green Plasticizer

The production line of plant-based polyols with annual output of 200,000 tons is put into operation in 2007. As shown in Fig. 1. the raw material is corn starch which is hydrolyzed to glucose and then the mixture of C2-4 alcohols and polyols is obtained by catalytic hydrogenation and dehydration of glucose; after distillation and purification, two series of products come into being. One is plant-based alcohols and polyol ether and the other is 828 plant-based original fractionation heavy components. 838-858 esterified plasticizers are obtained after the esterification of 828 plant-based polyol ethers with different dicarboxylic acids.

**Fig. 1. Production process**

2.2 Components of Fractionation Heavy Component

Different from the traditional petro-rubber oil, 828A (one of different fractionation techniques in 828) plant-based green rubber plasticizer is mainly composed of three types of groups: polyols (35 ~ 45%) of small molecules (2, 3-butanediol, pentanediol, PG, EG and so on), organic acid (20 ~ 30%) and polyether polyols (25 ~ 35%). Product indicators are as follows in Table 1.

Table1. The Indicators of 828A fractionation heavy component

| Item | Unit | Reference Value |
|-----------------------------|---------------------------------|-----------------|
| Appearance | — | Dark-Brown |
| Relative Density (20°C) | $\text{g}\cdot\text{cm}^{-3}$ | 1.300-1.400 |
| Kinematic Viscosity (100°C) | $\text{mm}^2\cdot\text{s}^{-1}$ | 500-600 |
| Pour Point | °C | ≤28 |
| Flash Point (COC) | °C | ≥230 |
| Volatility (163°C, 3h) | % | ≤1 |
| Moisture | % | ≤1 |
| Aromatic Content | % | ≤10 |
| Polyol Content | % | 35-45 |
| Polyether Polyol Content | % | 25-35 |
| Organic Acid Content | % | 20-30 |

828A plasticizer is mainly used for the development and application of recycled rubber, because it can reduce the proportion of coal tar or waste engine oil, greatly improve the workshop environment and smell and play a role of plasticizer to some degree. 828A contains polar groups with the hydroxyl which leads to precipitation phenomena when added in the non-polar rubber with additive of more than 20 phr. In order to increase its compatibility with the rubber and get better effect, it can be used with the original plasticizer after mixed evenly with 5% to 10% of the fatty acid or rosin heated to high temperature.

2.3 Effect of the Chemical Modification on the Properties of PBRO

A plasticizer of rubber can be obtained by esterification of phthalic anhydride (PA) with the dihydric alcohols (Polyols) in 828 fractionation heavy component.

2.3.1 Effect of alcohol acid mol ratio

Fixed reaction temperature of 190°C and the mass fraction of the catalyst (tetra-n-butyl titanate) as 0.3%, for different molar ratios of Polyols (the average molecular weight of the

dihydric alcohols in 828 is taken as 300) and PA (1: 1; 1.5: 1; 2: 1; 2.5: 1), reactions were carried out to give a series of different products, and their acid number and esterification rate were measured in Table 2.

Table 2. Acid number and esterification rate in the different Polyols/PA ratio

| Polyols/PA (mol/mol) | 1 : 1 | 1.5 : 1 | 2 : 1 | 2.5 : 1 |
|-------------------------|-------|---------|-------|---------|
| Acid value (mg KOH/g) | 34.2 | 27.3 | 25.6 | 27.3 |
| Esterification rate (%) | 82.9 | 85.2 | 85.4 | 82.9 |

The experimental results show that the molar ratio of Polyols / PA should be selected as 2: 1 in order to obtain a product of low acid value and a higher esterification rate.

2.3.2 The influence of esterification temperature

Fixed the molar ratio of Polyols/PA as 2:1 and the mass fraction of the catalyst (tetra-n-butyl titanate) as 0.3%, changing the reaction temperature, a series of products can be obtained at 170, 180, 190, and 200°C respectively, the acid number and the esterification rate of the products were measured shown in Table 3.

Table 3. The acid number and the esterification rate at the different temperature

| Reaction temperature (°C) | 170 | 180 | 190 | 200 |
|---------------------------|------|------|------|------|
| Acid value (mg KOH/g) | 37.2 | 20.5 | 25.8 | 33.6 |
| Esterification rate (%) | 79.9 | 88.9 | 86.1 | 81.9 |

Table 3 shows that the reaction temperature should be selected as 180°C.

2.4 Characteristics of PBRO Plasticizer

838-858 green plasticizers are developed by the method similar in References [3-9], aiming at synthetic rubber products. It has a high flash point, high boiling point and high temperature volatilization. It also has many characteristics as good compatibility with polar rubber and can commix with DOP and reduce DOP content.

2.4.1 Properties of plant-based plasticizer

838-858 plasticizers are compounds of aromatic esters, in which the ester content is more than 90%. Product indicators are as follows

Table 4. The Indicators of 838-858 plant-based green plasticizers

| Item | Unit | Reference value | | | | | |
|-----------------------------|----------------------------------|-------------------|-------------------|--------------------|-------------------|--------------------|----------------------|
| | | 838A | 838B | 848A | 848B | 858A | 858B |
| Appearance | | Dark-brown | Dark-brown | Pale yellow | Dark-brown | Pale yellow | Reddish brown |
| Relative density (20°C) | g·cm ⁻³ | 1.2-1.3 | 1.200-1.300 | 1.200-1.300 | 1.200-1.300 | 1.200-1.300 | 1.200-1.300 |
| Kinematic viscosity (100°C) | mm ² ·s ⁻¹ | 200-230 | 2750-2800 | 550-580 | 150-180 | 1200-1250 | 2400-2450 |
| Kinematic viscosity (40°C) | mm ² ·s ⁻¹ | 5-15 | 45-55 | 20-25 | 8-15 | 25-35 | 40-50 |
| Pour point | °C | ≤20 | ≤8 | ≤6 | ≤20 | ≤6 | ≤0 |
| Flash point | °C | ≥165 | ≥175 | ≥210 | ≥180 | ≥195 | ≥180 |
| Boiling point | °C | ≥210 | ≥245 | ≥250 | ≥255 | ≥215 | ≥245 |
| Ester content | % | ≥90 | ≥90 | ≥90 | ≥90 | ≥90 | ≥90 |
| Polyether polyol | % | ≤10 | ≤10 | ≤10 | ≤10 | ≤10 | ≤10 |

2.4.2 Measurement of the toxicity of PBRO

The production of Dacheng's plant-based green plasticizer is a combination of bio-chemical and rational chemical technologies. The preliminary route is bio-fermentation and the latter part is catalytic cracking, fractionation and distillation. The whole process route is short, less energy consumption, low emissions of "three wastes" and raw materials are renewable. The content analysis is carried out by authority according to the relevant laws and regulations for the plasticizer toxicity [10] such as Germany, polycyclic aromatic hydrocarbons (PAHs) 16 hazardous substances, EU REACH Regulation (No 1907/2006) Annex XVII PAHs8 entry of harmful substances, as well as 38 kinds of great concern substances (SVHC) and there is no toxicity is detected, seen in Table 5.

Table 5. Hazardous substances in plant-based plasticizer test results

| Test item | CAS | MDL | Test Results |
|------------------------------|------------|------------|---------------------|
| Naphthalene (Nap) | 91-20-3 | 0.2 | N.D.(QT) |
| Acenaphthylene (AcPy) | 208-96-8 | 0.2 | N.D.(QT) |
| Acenaphthene (AcP) | 83-32-9 | 0.2 | N.D.(QT) |
| Fluorene (Flu) | 86-73-7 | 0.2 | N.D.(QT) |
| Phenanthrene (PA) | 85-1-8 | 0.2 | N.D.(QT) |
| Anthracene (Ant) | 120-12-7 | 0.2 | N.D.(QT) |
| Fluoranthene (FL) | 206-44-0 | 0.2 | N.D.(QT) |
| Pyrene (Pyr) | 129-00-0 | 0.2 | N.D.(QT) |
| Benzo(a)anthracene (BaA) | 56-55-3 | 0.2 | N.D.(QT) |
| Chrysene (CHR) | 218-01-9 | 0.2 | N.D.(QT) |
| Benzo(b)fluoranthene (BbF) | 205-99-2 | 0.2 | N.D.(QT) |
| Benzo(k)fluoranthene (BkF) | 207-08-9 | 0.2 | N.D.(QT) |
| Benzo(a)pyrene (BaP) | 50-32-8 | 0.2 | N.D.(QT) |
| Indeno(1,2,3-cd)pyrene (IND) | 193-39-5 | 0.2 | N.D.(QT) |
| Dibenzo(a,h)anthracene (DBA) | 53-70-3 | 0.2 | N.D.(QT) |
| Benzo(g.h.i)perylene (Bghip) | 191-24-2 | 0.2 | N.D.(QT) |
| Total | - | | N.D.(QT) |

Remark: 1. Unit: mg/kg. 2. N.D. = Not detected (<MDL);
MDL = Method Detection Limits; QT= Quantitative Testing Methods

2.5 Sample Preparation

The compounding formulation of nitrile-butadiene rubber and styrene butadiene rubber are presented in 2.5.1 and 2.5.2. All mixing ingredients were used as received. Initially, polymers and other ingredients (except curatives) were mixed in an internal mixer. The dump temperature was about 64°C. After mixing, the compounds were sheeted on a two-roll mill and left at room temperature for 24 hours prior to mixing with the curatives in the second mixing stage. After curing test, the compounds were then extruded into a sheet form using a single screw extruder and finally vulcanized employing either hot air oven. For hot air vulcanization, the extrudates were preheated at 140°C for 12 minutes and then fully vulcanized at 160°C for 12 minutes.

2.5.1 Nitrile-butadiene rubber (NBR)

Experimental recipe: NBR 100 phr, ZnO 5 phr, Stearic acid, 1.5 phr, Carbon black N-550 80 phr, DM (Rubber Accelerator) 1 phr, M (Rubber Accelerator) 0.8 phr, Sulfur 1.5 phr, PBRO 0~30 phr.

2.5.2 Styrene butadiene rubber (SBR)

Experimental recipe: SBR 100 phr, ZnO phr, Stearic acid 1.5 phr, Carbon black N-550 40 phr, DM (Rubber Accelerator) 0.8 phr, M (Rubber Accelerator) 0.8 phr, CZ (Rubber Accelerator) 0.4 phr; Sulfur 1.2 phr, CaCO₃ 40 phr, PBRO 0~30 phr.

3. RESULTS AND DISCUSSION

3.1 The Application of 828A in Rubber Products

Naphthenic oil, engine oil and 828A are mixed with EPDM at the same proportioning respectively and Table 6 and Table 7 show the physical and mechanical properties of different fillers. It firstly can be seen from the data that the addition of 828A increases the hardness of rubber to some degree. Secondly, vulcanizates have excellent anti-heat-aging properties and anti-aging effect is very obvious. This may be due to the organic acid composition in 828A, which combines with rubber reinforcing agent like carbon black or silica particles to play the role of filling and reinforcing in the rubber mixing stage. The polyether polyol is a kind of good surfactant, whose polar group at one end combines with the polar groups like -COOH, RO-R '-of NH₂ of carbon black or silica particles by hydrogen bonding, while its non-polar groups has good compatibility with the rubber molecules, thereby increasing the binding force of the reinforcing particles and rubber molecules to achieve the purpose of improving the tensile stress and hardness of the rubber and raising anti-aging properties.

828A is alkaline, with significant help to improve curing efficiency, and it contains ester, hydroxyl and other alkaline groups, which can also play the role of the active agent. Due to this feature of 828A, the consumption of accelerating agent and stearic acid will be reduced by about 20 phr in the process. Currently, the price of the ordinary accelerating agent and stearic acid is about 16,000 yuan / ton and 6000 yuan / ton respectively. If the dosage of accelerating agent and stearic acid is calculated in accordance with 1% and 5% of the weight of raw rubber, cost savings of raw materials is at least about 460 yuan / ton.

Using formulation of 828A is over 15 phr, precipitation phenomena will occur at the surface of the product; therefore, the plasticizer must be modified if the using formulation increases. 838-858 series of plant-based rubber plasticizer is a modified plasticizer which is designed according to the characteristics of different types of plastic.

3.2 The Application of 828A in Reclaimed Rubber

Using 828A instead of 50% of pine tar or coal tar in producing reclaimed rubber by scrap rubber has been successfully accomplished in large-scale test line, in which 10-15 phr of rosin is added to play the role of thickener and the performance of products meet the requirements in all aspects. Now Dacheng Group is cooperating with some reclaimed rubber manufacturers in research and development of increasing the dosage of 828A in order to completely replace coal tar and pine tar.

Table 6. Comparison test for SBR

| No. | Item | Naphthenic oil | Engine oil | 828A | Detection methods |
|-----|---|----------------|------------|------|-------------------|
| 1 | Shore hardness (HA) | 61 | 60 | 67 | GB/T531-1999 |
| 2 | Tensile strength (Mpa) | 21.2 | 21.0 | 24.5 | GB/T528-1998 |
| 3 | Breaking elongation (%) | 451 | 419 | 377 | GB/T528-1998 |
| 4 | Tension set (%) | 8 | 12 | 10 | GB/T528-1998 |
| 5 | Hot air aging (70°C×72h) | | | | GB/T5312-2001 |
| 5.1 | Shore hardness (HA) | 67 | 67 | 72 | GB/T531-1999 |
| 5.2 | Tensile strength (Mpa) | 23.8 | 19.1 | 24.2 | GB/T528-1998 |
| 5.3 | Breaking elongation (%) | 340 | 286 | 272 | GB/T528-1998 |
| 5.4 | Brittleness temperature T _g (°C) | -60 | -66 | -63 | GB/T1682-1994 |

Table 7. Comparison test for EPDM

| No. | Item | Naphthenic oil | Engine Oil | 828A | Detection Methods |
|-----|------------------------------|----------------|------------|------|-------------------|
| 1 | Shore Hardness (HA) | 65 | 67 | 69 | GB/T531-1999 |
| 2 | Tensile strength (Mpa) | 19.6 | 23.0 | 21.1 | GB/T528-1998 |
| 3 | Breaking elongation (%) | 472 | 512 | 484 | GB/T528-1998 |
| 4 | Tension set (%) | 10 | 20 | 15 | GB/T528-1998 |
| 5 | Hot Air Aging (70°C×72h) | | | | GB/T5312-2001 |
| 5.1 | Shore Hardness (HA) | 77 | 78 | 79 | GB/T531-1999 |
| 5.2 | Tensile strength (Mpa) | 16.6 | 17.5 | 18.9 | GB/T528-1998 |
| 5.3 | Breaking elongation (%) | 189 | 196 | 223 | GB/T528-1998 |
| 5.4 | Brittleness Temperature (°C) | -70 | -70 | -70 | GB/T1682-1994 |

In current marketing, the costs factor is the largest obstacle. Due to the higher price of rosin, the production cost of green reclaimed rubber by 828A is higher than that of coal tar or pine tar. But it is not suitable to bracket these green plasticizers with coal tar which is being obsoleted. It is well known that coal tar indeed plays an important role in improving the performance of reclaimed rubber. However, coal tar as softener is inevitable to be obsoleted with the development of green reclaimed rubber products. Therefore, the use of biological green products will be the developing direction of the reclaimed rubber softeners.

3.3 The Application of PBRO in NBR

The main component of 838-858 plant-based green plasticizers is esters, whose adding amount can be improved to more than 30 phr in SBR, NBR, EPDM, etc., according to the different compositions. 838 plasticizers have better compatibility with polar rubber and it can partly take the place of DOP with great plasticization effect in nitrile rubber. 848 plasticizers have a unique composition and chemical structure with a wide application, especially in SBR. 858 plasticizers are particularly suitable for EPDM.

3.3.1 Effect of PBRO on properties of vulcanized NBR

The different dosage of PBRO (respectively 0, 10, 20, 25 and 30 phr) is added to the raw NBR to prepare a series of vulcanized rubber and Shore HA hardness, stress at 300% elongation, stress at 500% elongation, tensile strength, breaking elongation and tear strength are shown in Table 8.

Table 8. Effect of PBRO on mechanical properties of vulcanized NBR

| PBRO (phr) | 0 | 10 | 20 | 25 | 30 | Criterion* |
|-------------------------------------|------|------|------|------|------|------------|
| Shore hardness (HA) | 76 | 72 | 67 | 67 | 63 | 65~75 |
| Tensile stress at 300% | 4.26 | 3.57 | 3.35 | 3.28 | 3.26 | |
| Elongation (MPa) | | | | | | |
| Tensile stress at 500% | 8.13 | 6.18 | 5.79 | 5.21 | 5.18 | |
| Elongation (MPa) | | | | | | |
| Tensile strength (MPa) | 13.4 | 10.8 | 10.8 | 10.0 | 7.61 | 8~11 |
| Breaking elongation (%) | 627 | 700 | 727 | 742 | 748 | 700~900 |
| Tear strength (KN·m ⁻¹) | 54.1 | 45.5 | 43.1 | 41.3 | 31.2 | 35~45 |

Remark: criterion is a reference criterion of control quality*

It is seen from Table 8 that along with the increase of PBRO, Shore HA hardness, stress at 300% elongation, stress at 500% elongation, tensile strength and tear strength all decrease, while breaking elongation continuously increases. The results show that the mechanical properties of vulcanized rubber decrease, but it still can be used.

3.3.2 Effect of PBRO dosage on hot air aging properties of NBR

The different dosage of PBRO (respectively 0 phr, 10 phr, 20 phr, 25 phr, 30 phr) is added to the raw NBR to prepare a series of vulcanized rubber. After 24h aging test in 100°C oven, Shore HA hardness, stress at 300% elongation, stress at 500% elongation, tensile strength, breaking elongation and tear strength are shown in Table 9.

Table 9. Effect of PBRO dosage on hot air aging properties of vulcanized NBR

| PBRO (phr) | 0 | 10 | 20 | 25 | 30 | Criterion* |
|---|------|------|------|------|------|------------|
| Shore hardness (HA) | 80 | 75 | 71 | 71 | 67 | 70~80 |
| Tensile stress at 300% elongation (MPa) | 4.64 | 3.93 | 3.79 | 3.87 | 4.24 | |
| Tensile strength (MPa) | 13.9 | 11.7 | 12.0 | 11.6 | 9.59 | 8~13 |
| Breaking elongation (%) | 589 | 651 | 640 | 638 | 636 | 600~700 |

Remark: criterion* is a reference criterion of control quality

It is seen from Table 9 that compared with the vulcanized rubber without adding rubber oil, the tensile strength, stress at 300% elongation and hardness decrease while breaking elongation ratio increases. Table 8 and Table 9 show that the tensile strength, stress at 300% elongation and hardness of vulcanized NBR with hot-air-aging increase while breaking elongation ratio decreases compared with vulcanized NBR without hot-air-aging. This is because there are a large number of unsaturated double bonds in the molecular structure of NBR, which will make further crosslink reaction with rubber molecules during the hot air aging process. It is seen from Table 9 that the mechanical properties of vulcanized rubber with 10-25 phr PBRO meet the standard requirements.

3.3.3 Effect of PBRO on cold resistance of NBR

The different dosage of PBRO (0Phr, 10Phr, 20Phr, 25Phr, 30Phr) is added to the raw polar NBR to prepare a series of vulcanized rubber. The glass transition temperatures are measured by the differential scanning calorimeter and the results are shown in table 10.

Table 10. The glass transition temperature of NBR with different PBRO dosage

| PBRO (phr) | 0 | 10 | 20 | 25 | 30 |
|------------------------|-----|-----|-----|-----|-----|
| Onset of T_g (°C) | -25 | -30 | -34 | -36 | -44 |
| Midpoint of T_g (°C) | -20 | -25 | -29 | -31 | -36 |

It is seen from Table 10 that the glass transition temperature of vulcanized NBR decreases after PBRO is added. The glass transition temperature of vulcanized rubber with 30 phr PBRO is 15.8°C lower than that of vulcanized rubber without rubber oil. It means that PBRO can reduce the minimum using temperature of NBR and improve the cold performance.

3.3.4 Comparison of mechanical properties with common rubber oils

The 25 phr of PBRO, paraffin oil, aromatic hydrocarbon (AH) oil, naphthenic oil and DOP is added to NBR to prepare a series of vulcanized NBR and the Shore A hardness, stress at 300% elongation, stress at 500% elongation, tensile strength, breaking elongation and tear strength are shown in Table 11.

3.3.5 Comparison of hot air aging properties with common rubber oils in NBR

The 25 phr of PBRO, paraffin oil, aromatic hydrocarbon oil, naphthenic oil and DOP is added to NBR to prepare a series of vulcanized NBR. After 24h aging test in 100°C oven, Shore A hardness, stress at 300% elongation, tensile strength and tear strength are shown in Table 12.

Table11. Comparison of mechanical properties with common rubber oils

| Types of rubber oil | --- | PBRO | Paraffin oil | Naphthenic oil | AH oil | DOP | Criterion* |
|---|------|-------------|---------------------|-----------------------|---------------|------------|-------------------|
| Shore hardness (HA) | 76 | 72 | 58 | 62 | 65 | 67 | 65~75 |
| Tensile stress at 300% elongation (MPa) | 4.26 | 3.28 | 2.61 | 2.94 | 3.01 | 3.21 | |
| Tensile stress at 500% elongation (MPa) | 8.13 | 5.21 | 4.14 | 4.47 | 4.53 | 4.83 | |
| Tensile strength (MPa) | 13.4 | 10.0 | 8.94 | 9.45 | 9.87 | 10.3 | 8~11 |
| Breaking elongation (%) | 627 | 742 | 831 | 800 | 797 | 767 | 700~900 |
| Tear strength (KN·m ⁻¹) | 54.1 | 43.3 | 41.3 | 42.1 | 43.1 | 44.7 | 35~45 |

Remark: criterion is a reference criterion of control quality*

Table12. Comparison of hot air aging properties with common rubber oils in NBR

| Types of rubber oil | --- | PBRO | Paraffin oil | Naphthenic oil | AH oil | DOP | Criterion* |
|---|------|-------------|---------------------|-----------------------|---------------|------------|-------------------|
| Shore hardness (HA) | 80 | 71 | 61 | 67 | 69 | 71 | 70~80 |
| Tensile stress at 300% elongation (MPa) | 4.64 | 3.74 | 3.55 | 3.65 | 3.82 | 3.79 | |
| Tensile strength (MPa) | 13.9 | 11.4 | 10.8 | 11.3 | 11.6 | 12.0 | 8~13 |
| Breaking elongation (%) | 589 | 690 | 707 | 696 | 662 | 698 | 600~700 |

Remark: criterion is a reference criterion of control quality*

It is seen from Table 11 and 12 that the changes in mechanical properties of vulcanized NBR with PBRO is less than that of vulcanized NBR with other rubber oils which means the aging performance of vulcanized NBR with PBRO is better than that of other rubber oils. The reason is that the molecular weight of PBRO is large and not easy to volatilize which leads to the less volatilization and weight loss of PBRP in aging process.

3.3.6 Effect of PBRO on thermal stability of vulcanized NBR

The 25 phr of PBRO, paraffin oil, aromatic hydrocarbon oil, naphthenic oil and DOP is added to NBR to prepare a series of vulcanized NBR. After hot weight loss test in TGA thermogravimetric analysis, the DTG curves of this series of vulcanized NBR are shown in Fig. 2.

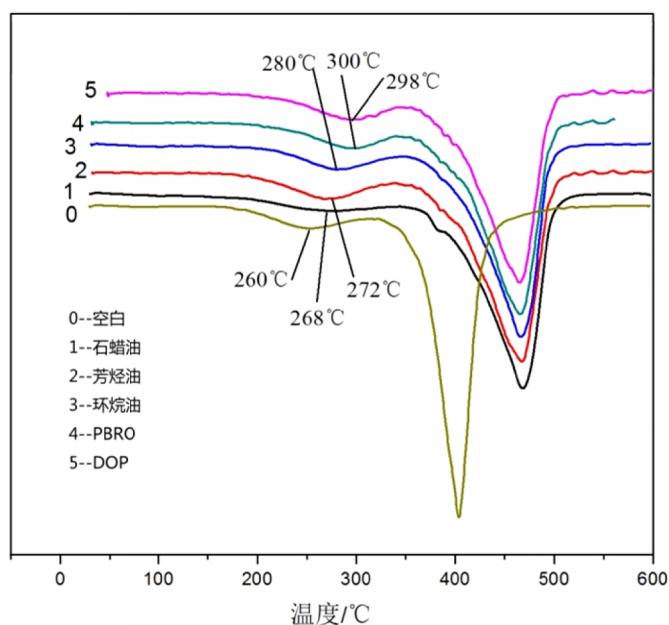


Fig. 2. The influence of different plasticizers on DTG curves of vulcanized NBR
0—blank assay, 1-- paraffin oil, 2-- aromatic hydrocarbon oil, 3-- naphthenic oil, 4—PBRO, 5—DOP

It can be seen from the DTG curves in Fig. 2 that the maximum weight loss temperatures of paraffin oil, aromatic hydrocarbon oil, naphthenic oil, DOP and PBRO are respectively 268°C, 272°C, 280°C, 298°C and 300°C among which PBRO is the highest. The thermal stability of rubber oil is related to the molecular weight. As a kind of ester rubber plasticizer, PBRO contains benzene ring and relative large molecular weight which leads to the high decomposition temperature.

3.3.7 Oil resistance of PBRO

The 25 phr of PBRO, paraffin oil, naphthenic oil, aromatic oil and DOP is respectively added to the NBR to prepare a series of vulcanized NBR and after 72h in the constant temperature (120°C) oil bath, the volume change rate in the two standard Oil (ASTM 1 # oil and ASTM 3 # oil) and mass change rate to investigate the oil resistance of PBRO are shown in Table 13.

Table13. Oil resistance of PBRO

| Types of rubber oil | --- | PBRO | Paraffin oil | Naphtha-nic oil | AH oil | DOP |
|----------------------------|-------------|-------------|---------------------|------------------------|---------------|------------|
| Volume change rate (%) | ASTM 1# oil | -1.8 | -6.9 | -14.0 | -8.0 | -7.0 -6.8 |
| mass change rate (%) | ASTM 3# oil | 25.9 | 14.1 | 12.0 | 12.5 | 13.8 15.0 |
| | ASTM 1#油 | -1.4 | -6.5 | -11.0 | -7.0 | -6.5 -5.7 |
| | ASTM 3#油 | 20.0 | 10.6 | 10.3 | 8.7 | 9.0 11.4 |

Seen from Table 13, PBRO and DOP in ASTM 1 # oil cannot be easily extracted, which shows the PBRO has a better oil resistance in polar NBR.

3.4 The Application of PBRO in SBR

3.4.1 Effect of PBRO on the mechanical properties of vulcanized SBR

The different dosage of PBRO (0Phr, 10Phr, 20Phr, 25Phr, 30Phr) is added to the raw nonpolar SBR to prepare a series of vulcanized rubber and the Shore A hardness, stress at 300% elongation, stress at 500% elongation, tensile strength, breaking elongation and tear strength are shown in Table 14.

Table14. Effect of PBRO on the mechanical properties of vulcanized SBR

| PBRO (phr) | 0 | 10 | 20 | 25 | 30 | Criterion* |
|---|----------|-----------|-----------|-----------|-----------|-------------------|
| Shore hardness (HA) | 73 | 70 | 67 | 62 | 60 | 60~70 |
| Tensile stress at 300% elongation (MPa) | 6.35 | 5.49 | 5.01 | 4.64 | 3.82 | |
| Tensile stress at 500% elongation (MPa) | 8.65 | 8.14 | 7.43 | 6.08 | 5.61 | |
| Tensile strength (MPa) | 10.8 | 9.29 | 9.07 | 8.93 | 7.13 | 8~10 |
| Breaking elongation (%) | 534 | 603 | 627 | 777 | 829 | 600~800 |
| Tensile strength (MPa) | 41.6 | 35.8 | 33.4 | 29.2 | 26.4 | 25~35 |

Remark: criterion is a reference criterion of control quality*

It is seen from Table 14 that with the increase of PBRO dosage, the mechanical properties of vulcanized rubber impairs. When the dosage is 20 phr, the mechanical properties of vulcanized SBR can meet the normal requirements of rubber product.

3.4.2 Effect of PBRO dosage on hot air aging properties of vulcanized SBR

The different dosage of PBRO (respectively 0Phr, 10Phr, 20Phr, 25Phr, 30Phr) is added to the raw nonpolar SBR to prepare a series of vulcanized rubber. After 24h aging test in 100°C oven, Shore HA hardness, stress at 300% elongation, stress at 500% elongation, tensile strength, breaking elongation and tear strength are shown in Table 15.

Table 15. Effect of PBRO dosage on hot air aging properties of vulcanized SBR

| PBRO (phr) | 0 | 10 | 20 | 25 | 30 | Criterion* |
|--|------|------|------|------|------|------------|
| Shore hardness (HA) | 77 | 72 | 71 | 68 | 66 | 65~75 |
| Tensile stress at 300% elongation(MPa) | 6.97 | 5.76 | 5.36 | 5.43 | 4.55 | |
| Tensile strength (MPa) | 11.4 | 9.75 | 9.70 | 10.1 | 8.20 | 8~12 |
| Breaking elongation (%) | 513 | 560 | 558 | 660 | 697 | 500~600 |

Remark: criterion* is a reference criterion of control quality

Table 15 shows that the Shore HA hardness, tensile stress and tensile strength increase when PBRO is added to vulcanized rubber while breaking elongation decreases. This is because the SBR will continue to crosslink during the aging process. It is more appropriate that the dosage of PBRO to SBR reach 20 phr.

3.4.3 Effect of PBRO dosage on cold resistance of SBR

The glass transition temperature is measured by DSC (different scanning calorimeter) analysis of vulcanized SBR and the dosage of PBRO and glass transition temperature (T_g) of vulcanized SBR is shown in Table 16.

Table16. Effect of PBRO dosage on glass transition temperature of SBR

| PBRO (phr) | 0 | 10 | 20 | 25 | 30 |
|---------------|-----|-----|-----|-----|-----|
| Oneset (°C) | -38 | -43 | -48 | -48 | -49 |
| Midpoint (°C) | -32 | -38 | -44 | -45 | -46 |

It can be seen from Table 16 that the addition of PBRO will increase the cold resistance of vulcanized SBR, which also means reducing the minimum using temperature.

3.4.4 Comparison of mechanical properties with common rubber oils in SBR

The 20 phr of PBRO, paraffin oil, aromatic hydrocarbon oil, naphthenic oil and DOP is added to SBR to prepare a series of vulcanized SBR and the Shore A hardness, stress at 300% elongation, stress at 500% elongation, tensile strength, breaking elongation and tear strength are shown in Table 17.

Table17. Comparison of mechanical properties with common rubber oils in SBR

| Types of rubber oil | --- | PBRO | Paraffin oil | Naphthenic oil | AH oil | DOP |
|---|------|------|--------------|----------------|--------|------|
| Shore hardness (HA) | 73 | 67 | 65 | 64 | 62 | 68 |
| Tensile stress at 300% elongation (MPa) | 6.35 | 5.01 | 4.87 | 4.56 | 4.46 | 5.13 |
| Tensile stress at 500% elongation (MPa) | 8.65 | 7.43 | 7.09 | 6.88 | 6.54 | 7.41 |
| Tensile strength (MPa) | 10.8 | 8.07 | 8.75 | 8.44 | 9.11 | 8.13 |
| Breaking elongation (%) | 535 | 627 | 664 | 681 | 721 | 617 |
| Tensile strength (MPa) | 41.8 | 32.4 | 33.1 | 33.2 | 35.4 | 32.7 |

It can be seen from Table 17 that the addition of PBRO cannot improve the mechanical properties of vulcanized SBR and the plasticizing effect is relatively poor.

3.4.5 Comparison of thermal stability of NBR with common rubber oils and PBRO

The thermo-gravimetric tests are carried out by using TGA thermo-gravimetric analyzer manufactured by Germany Netzscht Instruments Manufacturing Co., Ltd. in order to study the thermal stability of vulcanized SBR with different rubber oils. The DTG curves of vulcanized SBR with different rubber oils are shown in Fig. 3.

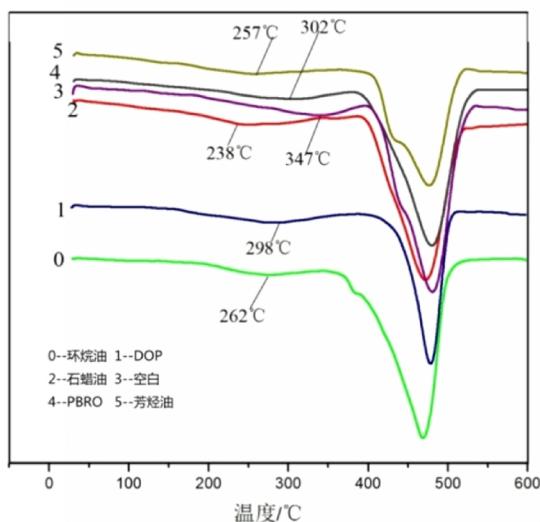


Fig. 3. The influence of different plasticizers on DTG curves of vulcanized SBR
0-- naphthenic oil, 1—DOP, 2-- paraffin oil, 3--blank assay, 4--PBRO, 5-- aromatic hydrocarbon oil

It can be seen from Fig. 3 that in N_2 atmosphere, vulcanized SBR has two major mass loss: the first mass loss happens at the temperature between 200°C ~ 300°C , mainly due to the volatile of rubber oil or other organic additives; the second mass loss happens at the temperature between 400°C ~ 550°C , mainly due to the thermal decomposition of SBR. The maximum weight losses of PBRO, paraffin oil, aromatic hydrocarbon oil, naphthenic oil and DOP happen respectively at the temperature of 302°C , 238°C , 257°C , 262°C and 298°C . It is concluded that the thermal stability of vulcanized SBR with PBRO is better.

3.4.6 Effect of PBRO on cold resistance of vulcanized SBR

Glass transition temperature is used to measure the cold resistance of vulcanized SBR. The DSC curves of vulcanized SBR with different rubber oils are shown in Fig. 4 and the glass transition temperature (T_g) of vulcanized SBR with different rubber oils are shown in Table 18.

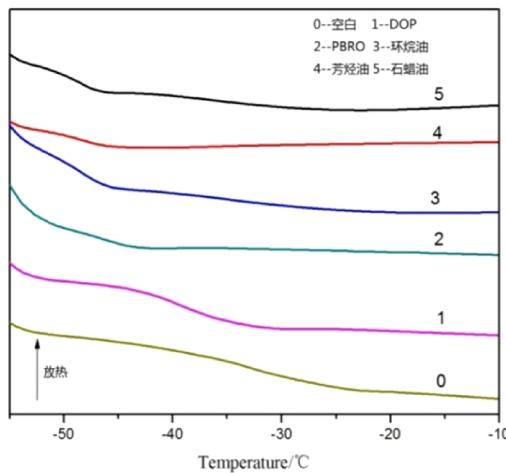


Fig. 4. DSC curves of different plasticizers in SBR
0-- blank assay, 1-DOP, 2-PBRO, 3-Naphthenic oil, 4-AH oil, 5-Paraffin oil

Table 18. The glass transition temperature of different plasticizers in SBR

| Types of rubber oil | --- | PBRO | Paraffin oil | Naphthe-nic oil | AH oil | DOP |
|---------------------|-----|------|--------------|-----------------|--------|-----|
| Oneset (°C) | -38 | -47 | -50 | -50 | -50 | -44 |
| Midpoint (°C) | -31 | -43 | -47 | -47 | -47 | -40 |

It can be seen from Fig. 3 and 4 that the effect of PBRO on the cold resistance of rubber is similar to that of other rubber oils.

4. CONCLUSION

The experimental results submitted in this paper preliminary indicate that plant-based green plasticizer can be applied in the fields of reclaimed rubber production, NBR and SBR partly. Although the current development of performance is insufficient, the plant-based green plasticizer is a new type of raw materials, which is possibly a new impetus to promote the development of our new low-carbon, green rubber plasticizer.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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