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Effect of Sulphur Content on Crystallization Characteristics and Mechanical Properties of *trans*-Polyisoprene†

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The effect of sulphur content on crystallization behavior of vulcanized *trans*-1,4-polyisoprene (TPI) was examined with optic microscope and differential scanning calorimetry. The dynamic mechanical properties were investigated with dynamic mechanical analyzer and the mechanical properties and shape memory performance were also determined. The results showed that crystallinity and spherulite size decreased with the increase of sulphur content. The crystals disappeared completely at sulphur content of 4 phr. The fusion heat and melting temperature of *trans*-1,4-polyisoprene crystals decreased with the increase of sulphur content. Dynamic mechanical analyzer revealed a striking change in the loss tangential as the sulphur content changed from 3-4 phr. When the sulphur content increased, the tensile strength, the modulus, the drum abrasion resistance and the shore A hardness of *trans*-1,4-polyisoprene decreased, while the resiliency increased. *trans*-1,4-Polyisoprene could maintain the performance of shape memory as the sulphur content was below 3 phr but the shape memory feature disappeared as the sulphur content was over 4 phr.

Keywords: Crosslinking, Crystallization, Rubber, Morphology, Mechanical properties.

INTRODUCTION

cis-1,4-Polyisoprene (CPI) has an excellent resilience, insulativity, water tightness and plasticity characteristics. It exhibits oil resistance, acid resistance, alkali resistance, heat resistance, cold resistance and wear resistance by appropriate treatment. Thus it is an important polymer widely used in the industrial and the automotive field. *trans*-1,4-Polyisoprene (TPI) has similar molecular structure with that of CPI and the main difference is that the configuration of TPI is *trans* structure. So TPI has some specific properties different from CPI[1].

trans-1,4-Polyisoprene can be obtained by extraction from plant tissues, such as balata in Brazil, gutta percha in Southeast Asia and Eucommia ulmodies gum in China or by synthesis. The British Dunlop Company, Canadian Polysar Company and Japanese Kuraray Company have researched TPI since 1960s to 1970s. Currently there are only two companies still producing and trading TPI. The first company is Kuraray, it employs solution polymerization using vanadium system or vanadium/titanium mixed catalyst system. The second one is from Qingdao and it uses a new method of bulk precipitation polymerization with titanium catalyst system supported by magnesium chloride[2]. *trans*-1,4-Polyisoprene has been used for telegraph hand sets, conveyors, golf balls, decoration items, chewing gums, root canal filling materials and adhesives[3].

Because of the regularity of TPI molecular structure, it can crystallize in two crystal forms, monoclinic (α-form) and orthorhombic (β-form)[4]. The α-form has a monoclinic cell with two chains, which containing two repeat units. The β-form has an orthorhombic unit cell with four chains, which containing one repeat unit.

Yan[5] proposed that the activity of molecular chain of TPI could be controlled through crosslink thereby to control its crystallinity. By varying the crosslinking degree, TPI can show three different properties, *i.e.*, thermoplastic material, shape memory material and elastic material, which would extend the application field of TPI.

Recently, structure and dynamical behavior of TPI crystal has been reported by several researchers. Inomata *et al.*[4] studied the influence of conversion temperature and the crystallization conditions on the crystal form and the melting temperature. Pathak *et al.*[6] investigated the crystal vibrational dynamics of

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TPI. Zong and Li[7] studied the nonisothermal crystallization behaviour of TPI. Du *et al.*[8] discussed the TPI crystal performance treated by chlorination. Zhao *et al.*[9] studied the TPI crystal performance treated by epoxidation. It is supposed that the degree of crystallinity decreased with the increase of the chlorine groups and the epoxy groups. Zhang and Xu[10] had a comparative study on the properties of Eucommia ulmoides gum and synthetic TPI.

However, the effect of crosslink on TPI crystallization behaviour and mechanical properties has not been clarified systematically so far. Therefore, the effects of crosslink on the crystallization characteristics, dynamic properties and mechanical properties of TPI were investigated in this work. Furthermore, the relationship between the properties and crystallization behaviour was also clarified.

EXPERIMENTAL

trans-1,4-Polyisoprene (TP-301, Kuraray, Japan), M_n = 7.0×10^4. The content of *trans*-structure is over 98 %. Commercial curing agents and additives including sulphur, stearic acid, zinc oxide and accelerator (N-*tert*-butylbenzothiazole-2-sulphenamide) were used without purification.

Sample preparation: *trans*-1,4-Polyisoprene compounds were prepared using two-roll mill(XK-160) with the roll temperature of 60 ºC. The formula was TPI 100 phr, zinc oxide 5 phr, stearic acid 2 phr, accelerator 1 phr and sulphur variable. The compounds were vulcanized according to the cure time predicted by the vulkameter after they kept for 24 h. Then compounds were crosslinked in corresponding mould by compression moulding at 150 ºC and the moulding pressure at 15 MPa, the vulcanized time was tc90.

Crystallinity behaviour of TPI with different sulphur content: The NETZSCH 204FE differential scanning calorimetry(DSC) instrument was used to study the crystallinity behaviour of TPI. The samples were heated from 0-90 ºC at a heating rate of 10 °C/min. The degree of crystallinity (Xc) was calculated by formula (1)[10]:

$$Xc = Xc_\alpha + Xc_\beta = \left(\frac{\Delta H}{\Delta H_\alpha} \times A_\alpha\% + \frac{\Delta H}{\Delta H_\beta} \times A_\beta\% \right) \times 100\ \% \quad (1)$$

where ΔH was melting enthalpy of sample, ΔH_α was the melting enthalpy of pure α-form crystals, the value was 12.8 kJ/mol; ΔH_β was the melting enthalpy of pure β-form crystals, the value was 9.6 kJ/mol; Xc_α was degree of crystallinity of the α-form structure; Xc_α was degree of crystallinity of the β-form structure; A_α % was percentage of the α-form melting peak area; A_β % was percentage of the β-form melting peak area in the DSC curves[11].

In addition, the percentages of the α-form and β-form crystals were calculated according to formula (2-3)[10]:

$$\alpha\ \% = \frac{Xc_\alpha}{Xc_\alpha + Xc_\beta} \times 100\ \% \quad (2)$$

$$\beta\ \% = \frac{Xc_\beta}{Xc_\alpha + Xc_\beta} \times 100\ \% \quad (3)$$

Dynamic mechanical properties of TPI with different sulphur content: The NETZSCH DMA240DC dynamic mechanical analyzer (DMA) was used to investigate the dynamic mechanical properties of TPI. The samples were rapidly cooled down to -90 ºC and then heated at a rate of 5 ºC/min to 80 ºC at a fixed frequency of 1 Hz. The samples for the test were rectangular in shape having width of 6 mm, thickness of 2 mm and length of 8 mm.

Measurement of shape memory properties: Dumbbell-shaped sample with length L_1 was stretched to twice, kept the length and put it into ice water to make it be fixed and then put it into oven at 70 ºC for 3 min, removed it to room temperature. The length was again measured denoted by L_2. The strain recovery ratio (R) was calculated by formula (4).

$$R = \left(1 - \frac{L_2 - L_1}{L_1} \right) \times 100\ \% \quad (4)$$

Dumbbell-shaped sample was stretched to twice, kept the length and put it into ice water to make it fixed and then put it into room temperature water, heated the water at 2 ºC/min, recorded the temperature of the sample recovery ratio of 50 %. The temperature was thermal response temperature.

Mechanical properties: Mechanical properties were tested according to the interrelated China national standard. Each result was obtained from the averaged value of the data obtained from measurements of three specimens.

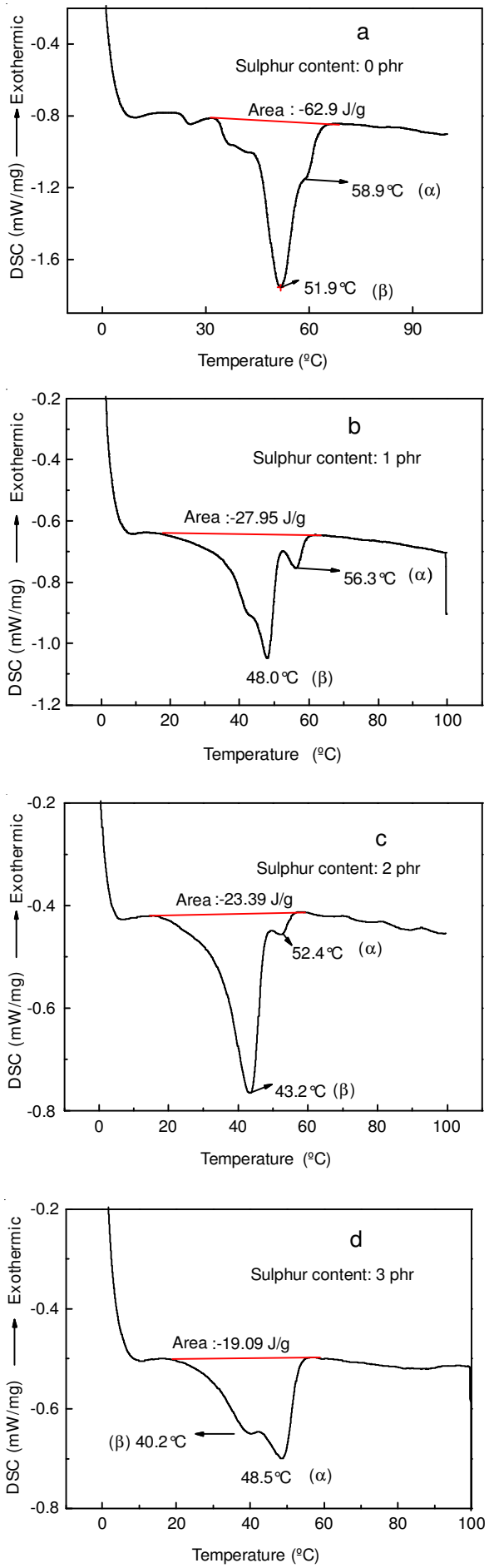
Polarizing microscope analysis: The polarizing microscope model was Nanjing Jiangnan Novel Optics Co. Ltd. XP-201. The samples were prepared by ultrathin section.

RESULTS AND DISCUSSION

Effect of sulphur content on crystallinity behaviour of vulcanized TPI: Fig. 1(a-e) and Table-1 showed the variation of TPI crystalline characteristics with the change of sulphur content from 0-4 phr. It could be seen that there were two melting peaks which correspond to α-crystal and β-crystal when the sulphur content changed from 0-3 phr [Fig. 1(a-d)], however, it had no obvious melting peak in the DSC curve when the sulphur content reached 4 phr [Fig. 1(e)]. The melting enthalpy of TPI crystal decreased with the increase of sulphur content, indicating that the degree of crystallinity of TPI vulcanizates decreased when the sulphur content increased. According to formula 1, the degree of crystallinity of TPI vulcanizates decreased from 36.3 to 12.1 % when the sulphur content changed from 0 to 3 phr. However, when the sulphur content was 4 phr, the degree of crystallinity was very low.

TABLE-1
CRYSTALLINE CHARACTERISTICS OF TPI WITH DIFFERENT SULPHUR CONTENT

Sulphur content (phr)	0	1	2	3	4
Peak number	2	2	2	2	0
Tm_1 (ºC)	51.9	48.0	43.2	40.2	–
Tm_2 (ºC)	58.9	56.5	52.4	48.5	–
ΔH (J g^{-1})	62.90	27.95	23.39	19.09	–
A_α (%)	23.8	17.3	8.5	57	–
A_β (%)	76.2	82.7	91.5	43	–
Xc_α (%)	10.6	3.4	1.4	7.7	–
Xc_β (%)	25.7	12.4	11.5	4.4	–
Xc (%)	36.3	15.8	12.9	12.1	–
α (%)	29.2	21.7	10.9	63.7	–
β (%)	70.8	78.3	89.1	36.3	–



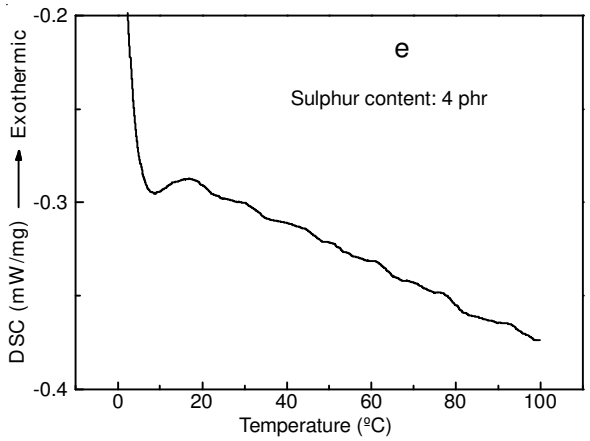


Fig. 1. Effect of sulphur content on the TPI crystalline characteristics

This was because of the vulcanization destroyed the regularity of the molecular chain and limited the mobility of the molecular chain.

As can be seen from Table-1, the degree of crystallinity of the β-form was higher than that of the α-form when the sulphur content changed from 0 to 2 phr. However, the degree of crystallinity of the α-form was higher than that of the β-form when the sulphur content was 3 phr. Similar crystal phase transitions have been reported by other researchers[12-14]. According to Mandelkern *et al.*[11], α-form was a stable crystalline structure, while β-form was a metastable crystalline structure. It was easy to grow β-form crystals for the regular macromolecular chains which were in a metastable state. However, the irregular macromolecular structure had to grow the more stable α-form crystals. When the sulphur content changed from 2 to 3 phr, a qualitative change of the regularity of molecular chain occurred, which affected the crystal phase transition.

In addition, Tm_1 and Tm_2 decreased gradually with the increase of sulphur content. This was because crystallizing at room temperature from the molten state created a large number of crystals defects, which would in turn decrease the melting temperature.

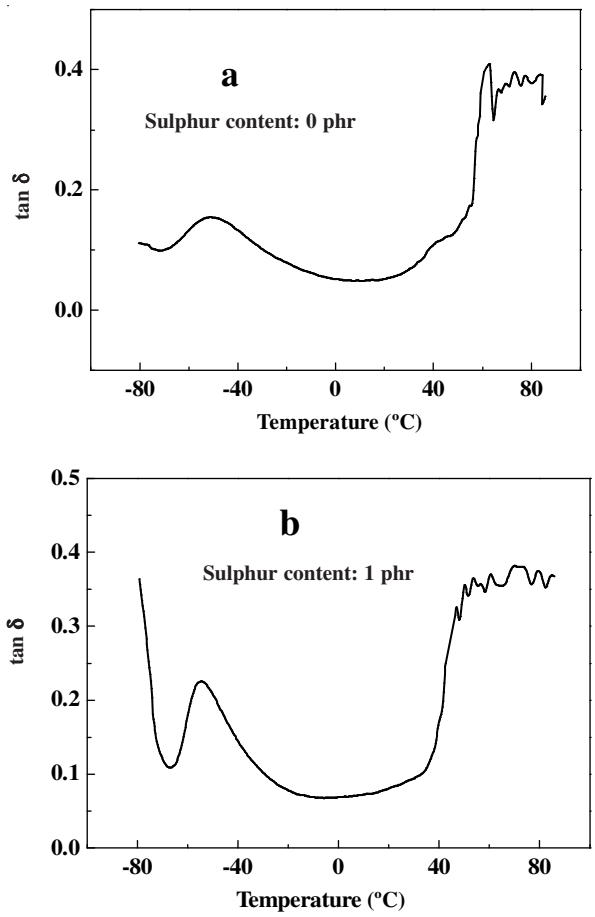
Effect of sulphur content on vulcanization characteristics of vulcanized TPI: As shown in Table-2, with the increase of sulphur content, scorch delay time (tc10) of TPI vulcanizates increased gradually. The variation tendency of optimum curing time (tc90) was complex. Maximum torque M_H and DT (M_H-M_L) increased gradually. The reason was that M_H and DT were related to the crosslink density of the compounds, which affected by the sulphur content. The values of M_H and DT became larger with the increase of sulphur content.

TABLE-2
EFFECT OF SULPHUR CONTENT ON THE TPI VULCANIZATION CHARACTERISTICS

Sulphur content (phr)	1	2	3	4
tc10 (s)	51	70	73	82
tc90 (s)	505	512	470	550
M_L (dN m)	14.7	18	16.7	18.2
M_H (dN m)	30.3	38.1	41.4	44.1
DT (M_H-M_L) (dN m)	15.6	20.1	24.7	25.9

Effect of sulphur content on dynamic mechanical properties of vulcanized TPI: The tan δ-temperature curves,

shown in Fig. 2, indicated that when the sulphur content changed from 0-3 phr (Fig. 2(a-d)), the samples exhibited similar dynamic mechanical analysis curves containing two peaks. One peak was below -40 ºC, which was related to the glass transition due to the segmental motions in TPI's amorphous phase. The other peak, which was composed of multiple peaks occurring at above 40 ºC, was explained by the melting of the crystallize regions in TPI vulcanizates. The reason of the existence of multiple peak was that crystallizing at ambient temperature from the molten state would lead to a large number of crystal defects. Each crystal defect had its own melting point. However, when the sulphur content reached 4 phr (Fig. 2(e)), the dynamic mechanical analysis curve changed obviously compared to that of Fig. 2(a-d). There was only one peak, which was related to the glass transition. The crystal melting peak could not be seen from the dynamic mechanical analysis curve, which indicated that the degree of crystallinity of sample was very low at this sulphur content. In fact, the dynamic mechanical analysis curve was similar to that of conventional rubber, such as NR, SBR *etc.*[15]. From the above analysis, the amount of sulphur between 3 and 4 phr presented an elastic critical turning point. Furthermore, from Fig. 2(e), it could be found that the values of tan δ at 60 ºC (characterization point of rolling resistance) and 80 ºC (characterization point of dynamic heat build up) were smaller than some other rubber, such as NR, SBR *etc.*[1]. These properties were essential to produce high speed energy-saving tires. The reason was that the regularity of molecular chains of TPI was better than NR or SBR, thus the internal friction of TPI would be lower.



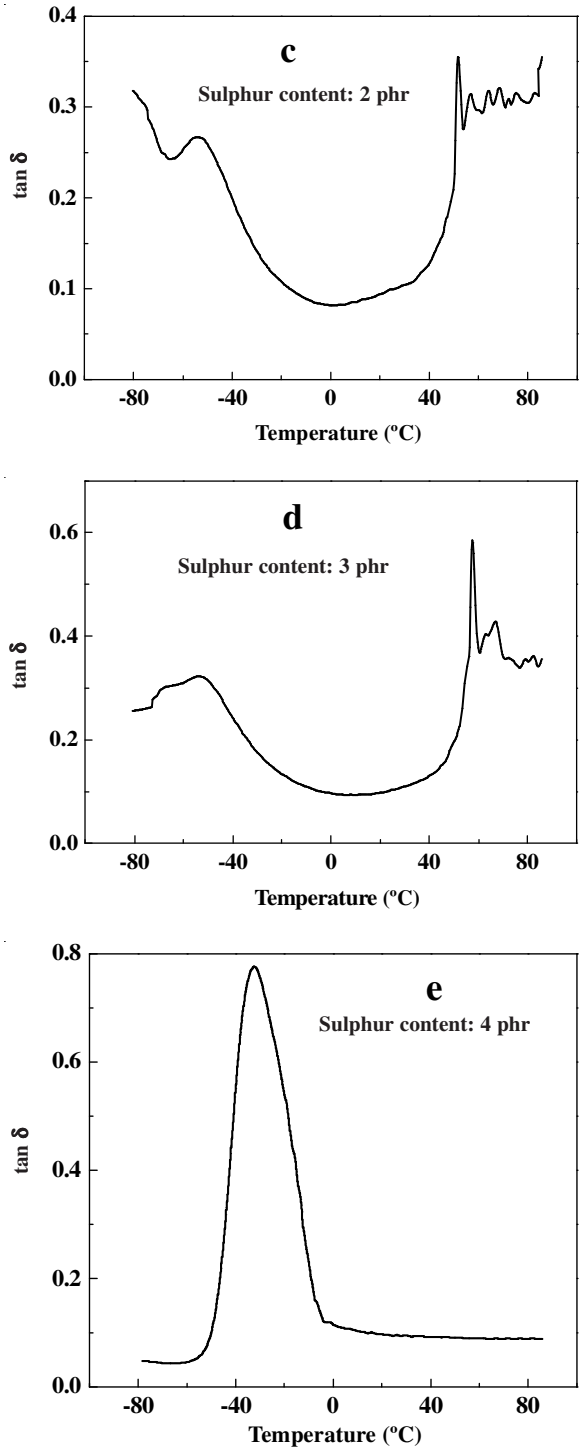


Fig. 2. Effect of sulphur content on the TPI dynamic properties

Effect of sulphur content on mechanical properties of vulcanized TPI: As can be seen from Table-3, when the sulphur content increased from 1 to 4 phr, the tensile strength, the 100 % modulus, the 300 % modulus, the drum abrasion resistance (DIN) and the shore A hardness of TPI vulcanizates decreased gradually, while resilience increased. In addition, the tear strength and elongation at break first increased and then decreased. Theoretically, the increase of crosslinks could reduce the mobility of molecular chains, hence increased the strength, modulus and hardness of vulcanizates. But TPI was

TABLE-3
EFFECT OF SULPHUR CONTENT ON THE TPI MECHANICAL PROPERTIES

Sulphur content (phr)	1	2	3	4
Tensile strength (MPa)	23.5	21.4	20.1	10.8
Tear strength (KN m^{-1})	60.3	61.7	58.7	17.3
Modulus at 100 (%) (MPa)	11.3	10.0	8.9	3.3
Modulus at 300 (%) (MPa)	23.0	20.7	17.5	–
Elongation at break (%)	360	425	423	237
DIN (cm^3)	0.0812	0.1162	0.1598	0.2586
Shore A hardness	96.2	95	94.5	71.5
Resilience (23 ºC) (%)	21.5	26.5	27	30.5

a crystalline polymer, which exhibited the characteristics of rigid resin. The increase of sulphur content decreased the degree of crystallinity of TPI, which leaded to decrease of the modulus and strength of TPI vulcanizates. When the sulphur content was 4 phr, the tensile strength, the tear strength, the DIN and the shore A hardness decreased obviously while resilience increased. This phenomenon can be explained as follows: the crosslink density of TPI at sulphur content of 4 phr was so high that TPI could not crystallize and thus material properties had a qualitative change from plastomer to elastomer.

Effect of sulphur content on shape memory properties of vulcanized TPI: The thermal response temperature and strain recovery ratio were main factors which decide the applicable scope of shape memory materials. As can be seen from Table-4, with the sulphur content increased from 1-3 phr, the thermal response temperature decreased from 55.9 to 40 ºC and the strain recovery ratio increased from 97.2 to 98.4 %. This was because when the sulphur content increased, the crosslink degree increased, thus the crystal region and the perfection degree of grain decreased, which leaded to the decrease of thermal response temperature. Moreover, the higher crosslink degree also suppressed molecular relative slippage, thus the permanent deformation decreased. In addition, when the sulphur content was 4 phr, the shape memory property disappeared and the TPI vulcanizates showed the typical rubber-like material. This was because the crystals of TPI vulcanizates restricted the mobility of the molecular chains and hence fixed the strain temporarily when the sulphur content was at a lower level. When the sulphur content reached 4 phr, fewer crystals could formed, hence less strain was fixed due to the elastic recovery of the network.

TABLE-4
EFFECT OF SULPHUR CONTENT ON THE TPI SHAPE MEMORY PROPERTIES

Sulphur content (phr)	1	2	3	4
Shape memory function	Yes	Yes	Yes	No
Thermal response tem. (ºC)	55.9	45.9	40.0	–
Strain recovery ratio (%)	97.2	97.9	98.4	–

Difference of TPI crystalline microscopy: The pure TPI had an obvious crystallization phenomenon with spherulite crystalline form and the polymorphs were perfect. When the sulphur content changed from 1 to 3 phr, the spherulite size became smaller and the perfection degree of the grain declined. When the sulphur content reached 4 phr, the crystallization phenomena could not be observed obviously. The reason was that, with the increase of sulphur content, the crosslink density increased, which led to the decrease of the regularity and flexibility of molecular chains resulting in the decline of the degree of crystallinity and the perfection degree of grain. When the sulphur content reached 4 phr, the crystallization of sample became impossible due to the shackle of crosslinks.

Conclusion

When the sulphur content increased from 0 to 3 phr, the degree of crystallinity decreased from 36.3 to 12.1 %, while the crystal size became smaller and the perfection degree of grain declined, which indicated that the vulcanization had an obvious influence on the crystal. When the amount of sulphur was up to 4 phr, the crystalline melting peak could not be observed obviously. In addition, with the increase of sulphur content, Tm_1 and Tm_2 were decreased gradually. When the sulphur content changed from 3 to 4 phr, the dynamic properties changed obviously. The lower values of tan δ at 60 and 80 ºC were found compared to conventional rubber when the sulphur content reached 4 phr. These properties were essential to produce high speed energy-saving tyres. With the increase of sulphur content, the tensile strength, modulus, DIN and shore A hardness decreased, while resiliency increased. When the sulphur content was below 4 phr, TPI vulcanizates had the shape memory property. With the increase of sulphur content, thermal response temperature decreased, strain recovery ratio increased. When the sulphur content was up to 4 phr, shape memory property disappeared.

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