

# Synthesis and thermal properties of emulsion terpolymers of *N*-p-tolylmaleimide/butadiene–styrene latex/AN/St

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**Abstract** Heat-resistance ABS resin was synthesized by emulsion polymerization of *N*-p-tolylmaleimide (N-PTMI), butadiene–styrene latex (SB), AN and St. Thermal properties of terpolymers with different monomer ratio were characterized by DSC and TG. The molecular mass and molecular mass distribution of terpolymers were determined with GPC. The results shown the heat-resistance of terpolymers, the glass transition temperature and the decomposition temperature were increased with the increasing of N-PTMI feed content. With the increasing of AN feed content, the glass transition temperature of terpolymers decrease while the decomposition temperature increase. The glass transition temperature of terpolymers decrease with SB feed content and the product shows plastic properties when SB feed content is lower than 45 (m/m %).

**Keywords** ABS resin · *N*-p-tolylmaleimide (N-PTMI) · Emulsion copolymerization · Thermal analysis

## Introduction

ABS resin (styrene–butadiene–acrylonitrile) is one of the most successful engineering thermoplastics. It is widely used in the auto motive industry, telecommunications, business machines and consumer markets, mainly because it has excellent properties of the toughness, rigidity, and

machining. Many fields need high-heat resistance ABS such as water heater element, auto-instrument shell and heat home-appliance. But, it is hard to maintain their toughness and rigidity when the temperature is above 100 °C.

Flame retardant ABS, impact resistance ABS, heat resistance ABS, and the other types of ABS were studied by a number of researchers for the requirement of the market and were investigated by means of thermogravimetric analysis [1–7]. Most of them were synthesized by copolymerization or by blending with other polymer such as PC, Nylon, etc. In order to improve the polarity of polybutadiene phase, graft copolymerization is an efficient method. The introducing of maleic anhydride (MAH) onto ABS backbone has been studied in many literatures and it is proved MAH was successfully introduced onto the rubber phase [8–12].

In recent years, *N*-substituted maleimides have been selected as the most valuable monomers to improve the heat resistance of polymers because these monomers contain a rigid planar ring and could enhance the  $T_g$  and the thermal degradation temperature of copolymers effectively [13–17]. But there is no public literature concerning about ABS-co- N-PTMI (*N*-p-tolylmaleimide).

In this article, heat resistance ABS resin was synthesized by emulsion polymerization of N-PTMI, butadiene–Styrene latex (SB), AN and St. The thermal properties and the molecular mass of the terpolymers with different monomer ratio were characterized by GPC, DSC, and TG.

## Experimental

### Materials and processing

*N*-p-tolylmaleimide (N-PTMI) is obtained by one-step dehydration using aniline and maleic acid anhydride [18].

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Styrene (St) and acrylonitrile (AN) were purchased from Guangzhou Chemical Reagent Co. and were used freshly distilled. Sodium dodecyl sulfate (SDS), potassium persulfate ( $K_2S_2O_8$ ), and  $Al_2(SO_4)_3 \cdot 18H_2O$  were all of analytically pure grade and supplied by Guangzhou Chemical Reagent Co. butadiene–styrene (SB) latex was supplied by Shandong Zibo Qilong Chemical Co. Ltd. and the glass transition temperature ( $T_g$ ) which was measured as  $-46\text{ }^\circ\text{C}$ .

### Emulsion polymerization

SDS was used as emulsifier, and  $K_2S_2O_8$  as initiator. The St, AN, N-PTMI,  $K_2S_2O_8$ , SDS, and distilled deionized water (DIW) were charged into a four-necked flask according to Table 1. The reaction vessel was heated using water bath and the mixture was stirred using mechanical stirrer. When the reaction temperature reached  $80\text{ }^\circ\text{C}$ , the SB was charged into the flask in 5 min using a dropping funnel. The reaction temperature was held at  $80\text{ }^\circ\text{C}$  for additional 2 h. At the end of the reaction, the terpolymers was precipitated with 2%  $Al_2(SO_4)_3 \cdot 18H_2O$  solution, washed with DIW then dried in vacuum oven at  $80\text{ }^\circ\text{C}$  for 24 h. The conversion of the monomers was above 95%. The recipes of emulsion polymerization are shown in Table 1.

### Methods

The GPC chromatograms were acquired on a Waters model 1515 pump system equipped with a model 2414 differential refract meter using THF as the eluent operating at  $1.00\text{ mL min}^{-1}$  at  $40\text{ }^\circ\text{C}$ . Three Styragel HR columns from Japan covering a molecular mass range of  $2 \times 10^3$ – $10^6$  Da were used and calibrated using five polystyrene narrow standards from BF Goodrich (Richfield, Ohio, USA).

The IR spectra were recorded on a Fourier transformation infrared (FTIR) spectrometer (IR Prestige-20, Shimadzu, Japan). The powder samples were used for IR analysis.

DSC was measured on a differential scanning calorimeter (DSC 200PC Netzsch, Germany) with a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  from  $30$  to  $250\text{ }^\circ\text{C}$  and nitrogen was used as the purge gas at a  $50\text{ mL min}^{-1}$  flow rate. About 10 mg of sample was used in aluminum pans in each analysis. The

analysis of the thermogravimetry behavior of the samples were performed on a thermogravimetry instrument, model STA 409PC (Netzsch, Germany), with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from  $30$  to  $650\text{ }^\circ\text{C}$ . Air was used as the purge gas at a  $100\text{ mL min}^{-1}$  flow rate. About 6 mg of samples was used in each test.

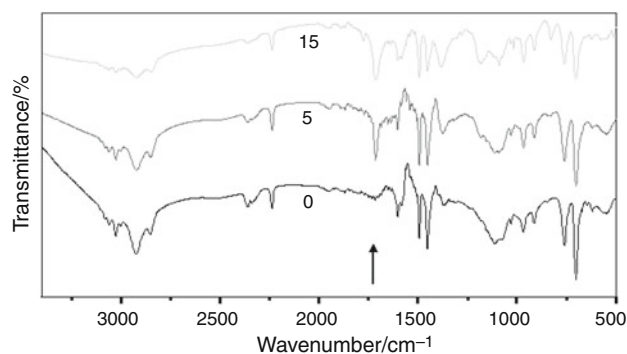
## Results and discussion

### Infrared analysis

The IR spectra of terpolymers with 0, 5, 15 (m/m %) feed content of N-PTMI were shown in Fig. 1. As can be seen from Fig. 1, the characteristics absorption peak of group  $-CN$  in AN is  $2240\text{ cm}^{-1}$ , the absorption peaks of the phenyl group are  $1450$ ,  $757$ , and  $700\text{ cm}^{-1}$ , and the carbonyl group of N-PTMI is at  $1710\text{ cm}^{-1}$ . The area of absorption bands at  $1710\text{ cm}^{-1}$  was increased with the increasing of N-PTMI feed content in the terpolymers. This result suggests that the content of N-PTMI in terpolymers increase with the increasing of N-PTMI feed content. The chemical structure of the terpolymer was shown as Scheme 1.

### Molecular mass and distribution

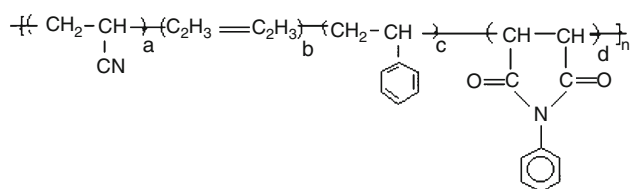
The feed content of SB and AN in the recipe were maintained 25 (m/m %), respectively, increasing N-PTMI feed content, decreasing St feed content. The molecular mass of the terpolymers was given in Fig. 2. As shown in Fig. 2,



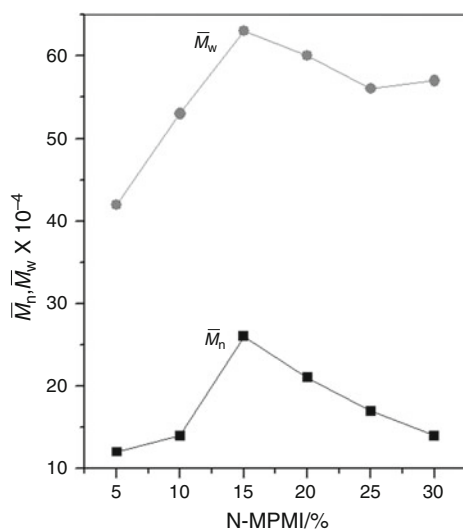
**Fig. 1** FTIR spectra of the terpolymers at different N-PTMI feed content

**Table 1** Recipes of N-PTMI/St/SB/AN terpolymers system

| N-PTMI/m/m % | 0  | 5  | 10 | 15 | 20 | 25 | 30 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
|--------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| St           | 50 | 45 | 40 | 35 | 30 | 25 | 20 | 60 | 55 | 50 | 45 | 40 | 35 | 30 |
| SB           | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| AN           | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 0  | 5  | 10 | 15 | 20 | 25 | 30 |



**Scheme 1** Chemical structure of terpolymer



**Fig. 2** Molecular mass of the terpolymers at different N-PTMI feed content

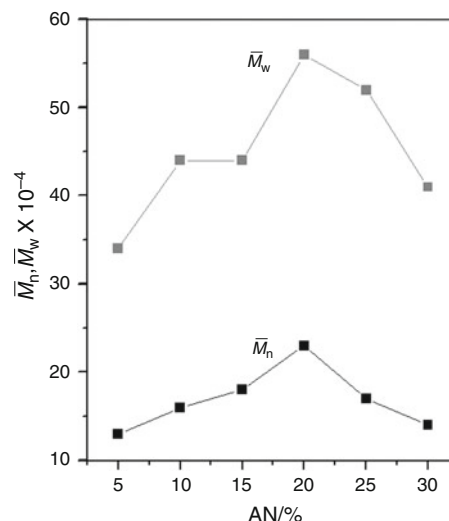
the maximum of  $\bar{M}_w$ ,  $\bar{M}_n$  appeared at the feed content of the N-PTMI was 15 (m/m %) and the distribution coefficient was between 2.42 and 3.79.

The feed content of SB in the recipe was maintained 25 (m/m %) and N-PTMI was maintained 15 (m/m %), increasing AN feed content, decreasing St feed content. The molecular mass of the terpolymers was given in Fig. 3. As seeing from Fig. 3, the maximum of  $\bar{M}_w$ ,  $\bar{M}_n$  appeared at the content of the AN was 20 (m/m %) and the distribution coefficient was between 2.43 and 3.05. When reaction temperature, initiator concentration, emulsifier concentration and other factor were maintained, polymer chain length and average molecular mass were only the function of free radical reaction rate. In this condition, free radical growth rate  $v_p$  was only relate to monomer ratio [20], the maximum value of  $\bar{M}_w$ ,  $\bar{M}_n$  appeared in the right monomer ratio.

## Thermal analysis

### Thermal analysis of terpolymers at different N-PTMI feed content

Thermal degradation temperature ( $T_d$ ) and glass transition temperature ( $T_g$ ) data of terpolymers at different N-PTMI



**Fig. 3** Molecular mass of the terpolymers at different AN feed content

feed content are summarized in Table 2. Figure 4 shows the relationship of  $T_g$  of terpolymers with N-PTMI feed content. Figures 5 and 6 show DSC and TG results of the terpolymers at different N-PTMI feed content when the SB and AN mass fractions was 25 (m/m %), respectively.

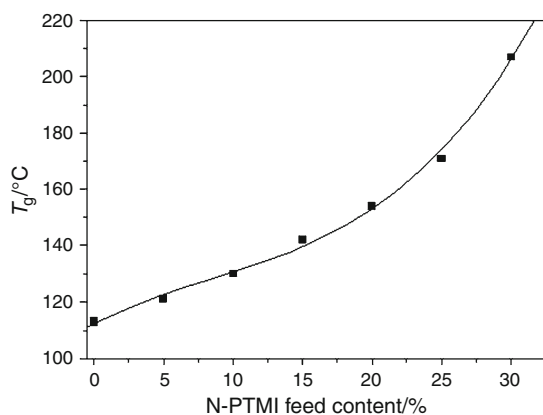
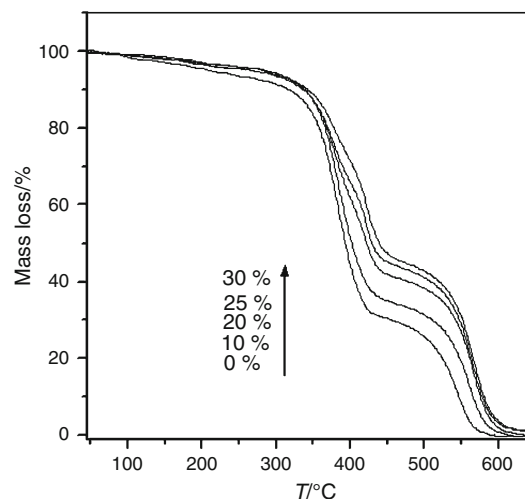
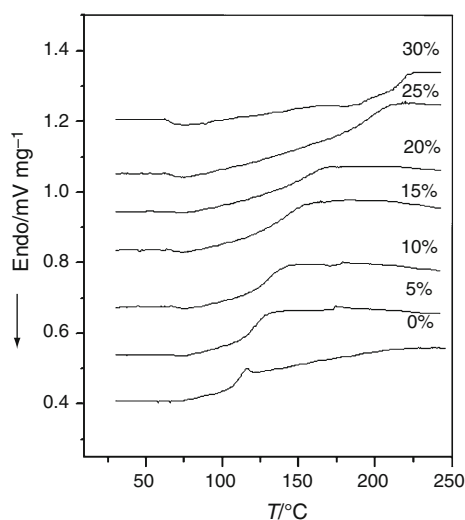
From Table 2 and Figs. 4 and 5,  $T_g$  of the terpolymers were increased with the increasing of N-PTMI feed content. Compared to 0 (mass%) of N-PTMI feed content,  $T_g$  of terpolymer with 30 (m/m %) N-PTMI feed content was 207 °C, increased by 94 °C. This is because of steric hindrance of the N-PTMI is bigger than St and can effectively hinder molecule rotation and the chain mobility decreases, and the stiffness increases. As shown in the Table 2 and the TG curves of the terpolymers in Fig. 6,  $T_{di}$ ,  $T_{d10}$ ,  $T_{d20}$ ,  $T_{d30}$ ,  $T_{d40}$ , and  $T_{d50}$  ( $T_{di}$  is the initial decomposition temperature for the first step of decomposition.  $T_{d10}$ ,  $T_{d20}$ ,  $T_{d30}$ ,  $T_{d40}$ , and  $T_{d50}$  are the temperatures at which a mass loss of 10, 20, 30, 40, and 50% occurred) for the terpolymers were increased with the increasing of N-PTMI feed content. Compared to 0 (mass%) of N-PTMI,  $T_{di}$  and  $T_{d50}$  of terpolymer with 30 (m/m %) N-PTMI feed content are 379, 443 °C, respectively, and increased by 31 and 45 °C, respectively. These results suggested that N-PTMI can markedly enhance the thermal properties of ABS resin.

### Thermal analysis for different AN feed content

Thermal degradation temperature ( $T_d$ ) and glass transition temperature ( $T_g$ ) data of terpolymers at different AN feed content are presented in Table 3. Figure 7 show TG curves of the terpolymers, which maintaining SB 25 (m/m %) and N-PTMI 15 (m/m %) mass fraction, respectively, increasing AN feed content, decreasing St feed content as the recipe in Table 1.

**Table 2**  $T_d$ ,  $T_g$  of the terpolymers at different N-PTMI content

| NM-PMI feed content/% | $T_{di}/^{\circ}\text{C}$ | $T_{d10}/^{\circ}\text{C}$ | $T_{d20}/^{\circ}\text{C}$ | $T_{d30}/^{\circ}\text{C}$ | $T_{d40}/^{\circ}\text{C}$ | $T_{d50}/^{\circ}\text{C}$ | $T_g/^{\circ}\text{C}$ |
|-----------------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|------------------------|
| 0                     | 348                       | 328                        | 358                        | 371                        | 381                        | 398                        | 113                    |
| 5                     | 348                       | 290                        | 360                        | 375                        | 390                        | 404                        | 121                    |
| 10                    | 352                       | 344                        | 368                        | 381                        | 391                        | 404                        | 130                    |
| 15                    | 345                       | 323                        | 359                        | 373                        | 386                        | 407                        | 142                    |
| 20                    | 345                       | 343                        | 370                        | 386                        | 406                        | 424                        | 154                    |
| 25                    | 359                       | 345                        | 372                        | 392                        | 416                        | 433                        | 171                    |
| 30                    | 379                       | 348                        | 381                        | 406                        | 423                        | 443                        | 207                    |

**Fig. 4** Relationship of  $T_g$  with N-PTMI feed content**Fig. 6** TG curves of terpolymers at different N-PTMI feed content**Fig. 5** DSC curves of terpolymers at different N-PTMI feed content

From Table 3 and the curves of terpolymers in Fig. 7,  $T_{di}$ ,  $T_{d10}$ ,  $T_{d20}$ ,  $T_{d30}$ ,  $T_{d40}$ , and  $T_{d50}$  of the terpolymers were increased while AN feed content increased in the terpolymers. Compared to 0 (m/m %) AN feed content,  $T_{d50}$  of 30 (m/m %) AN feed content was 424 °C and increased by

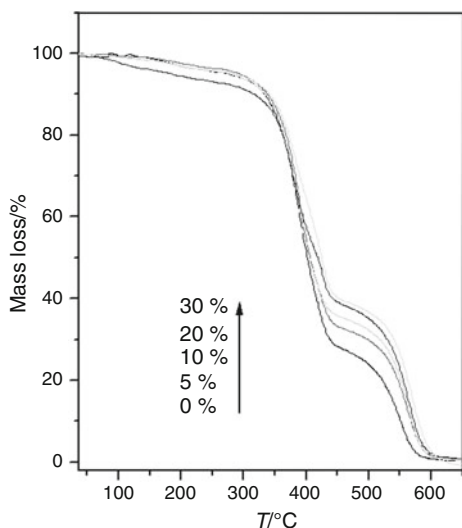
24 °C. With the increasing of AN feed content,  $-\text{C}\equiv\text{N}$  group became more in the molecule chain, leading to ring reaction between border upon two nitrile groups. So  $T_d$  of the terpolymers was increased.  $T_g$  of the terpolymers, as can be seen from Table 3, was decreased as the AN feed content goes up. This is because of AN is a polar molecule but the bulk is smaller than St. Side group of the main chain was mainly benzene ring and nitrile group was a few, distance of the AN went beyond the scope of nitrile group polarity function. Incorporation of AN enhanced flexibility of the main chain, so  $T_g$  was decreased [18, 19].

#### Thermal analysis for different SB content

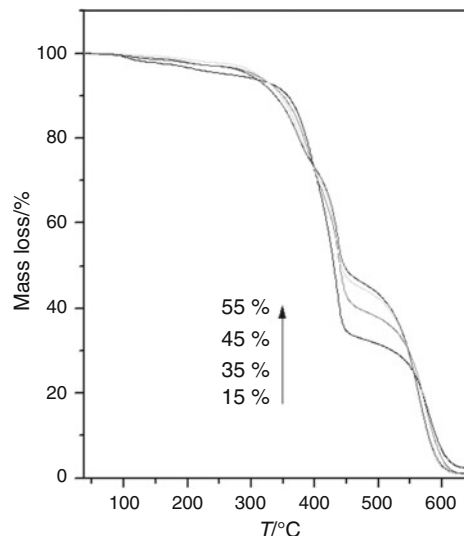
For investigate the effect of SB on the thermal properties, terpolymers which maintaining monomer mass ratio as N-PTMI:St:AN = 20:30:25, increasing SB feed content were synthesized according to the experimental part. Thermal degradation temperature ( $T_d$ ) and glass transition temperature ( $T_g$ ) of terpolymers at different SB feed content are presented in Table 4. The DSC for these samples

**Table 3**  $T_d$ ,  $T_g$  of the terpolymers at different feed AN content

| AN Feed content/% | $T_{di}/^{\circ}\text{C}$ | $T_{d10}/^{\circ}\text{C}$ | $T_{d20}/^{\circ}\text{C}$ | $T_{d30}/^{\circ}\text{C}$ | $T_{d40}/^{\circ}\text{C}$ | $T_{d50}/^{\circ}\text{C}$ | $T_g/^{\circ}\text{C}$ |
|-------------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|------------------------|
| 0                 | 351                       | 330                        | 361                        | 376                        | 388                        | 400                        | 172                    |
| 5                 | 354                       | 340                        | 368                        | 368                        | 393                        | 405                        | 172                    |
| 10                | 353                       | 340                        | 367                        | 367                        | 392                        | 406                        | 170                    |
| 15                | 353                       | 332                        | 364                        | 364                        | 388                        | 404                        | 151                    |
| 20                | 349                       | 334                        | 366                        | 366                        | 398                        | 422                        | 145                    |
| 25                | 345                       | 323                        | 359                        | 359                        | 386                        | 407                        | 142                    |
| 30                | 353                       | 344                        | 373                        | 391                        | 409                        | 424                        | 154                    |



**Fig. 7** TG curves of terpolymers at different AN feed content



**Fig. 8** TG curves of terpolymers at different SB feed content

**Table 4**  $T_d$ ,  $T_g$  of the terpolymers at different SB feed content

| SB/m/m % | $T_{di}/^{\circ}\text{C}$ | $T_{d10}/^{\circ}\text{C}$ | $T_{d20}/^{\circ}\text{C}$ | $T_{d30}/^{\circ}\text{C}$ | $T_{d40}/^{\circ}\text{C}$ | $T_{d50}/^{\circ}\text{C}$ | $T_g/^{\circ}\text{C}$ |
|----------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|------------------------|
| 0        | 376                       | 368                        | 384                        | 393                        | 399                        | 406                        | 154                    |
| 15       | 382                       | 355                        | 381                        | 399                        | 413                        | 423                        | 141                    |
| 25       | 345                       | 343                        | 370                        | 386                        | 406                        | 424                        | 134(-2)                |
| 35       | 384                       | 346                        | 377                        | 400                        | 421                        | 432                        | 54(-19)                |
| 45       | 385                       | 340                        | 371                        | 401                        | 423                        | 436                        | 54(-20)                |
| 55       | 383                       | 334                        | 370                        | 407                        | 426                        | 443                        | 59(-35)                |
| 100      | 410                       | 389                        | 413                        | 425                        | 432                        | 439                        | -46                    |

of different SB feed content were carried out between -90 to 200 °C and the results shown that when SB feed content is lower than 25 (m/m %) the DSC curves only show one single  $T_g$  transition. When SB feed content is over 35 (m/m %) the DSC curves show two glass transition which suggest the terpolymer has two phase. As can be seen from Table 4,  $T_g$  of terpolymers decrease with the increasing of

SB feed content. But the terpolymers appeared entirely rubber phase properties when SB feed content was above 45 (m/m %). As shown in Table 4 and Fig. 8,  $T_d$  of 100% mass SB was the highest, so  $T_{di}$ ,  $T_{d10}$ ,  $T_{d20}$ ,  $T_{d30}$ ,  $T_{d40}$ , and  $T_{d50}$  of the terpolymers were increased with the increasing of SB content.  $T_{d50}$  of 55 (m/m %) SB increased by 37 °C compared with 0 (m/m %) SB feed content.

## Conclusions

Terpolymers of N-PTMI/SB/St/AN were synthesized by emulsion copolymerization. The total monomer conversion of N-PTMI, St and AN is over 95%. The IR spectrum shows the content of N-PTMI in terpolymers increase with increasing N-PTMI feed content.

The thermal properties of the N-TPMI modified ABS resin improved greatly.  $T_g$  and  $T_d$  of the terpolymers increase with increasing N-PTMI feed content. N-PTMI can markedly enhance the thermal properties of ABS resin.

The incorporation of AN enhanced  $T_d$  of the terpolymers but  $T_g$  of the terpolymers decrease. SB feed content should be lower than 45 (m/m %), otherwise the product will shows rubber property.

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