

IMPROVEMENT OF QUALITY OF RECLAIMED RUBBER BY MECHANICAL-CHEMICAL SYNTHESSES

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Properties of rubber reclaimed by swelling and mechanical destruction were improved by syntheses realized under the action of mechanical forces. Special recipes of poly(α -methyl styrene-co-butadiene) and natural rubber, without fillers, were used to eliminate the filler's effect. Syntheses were realized by rolling on the first rubber in polymer/monomer (styrene) and polymer/polymer (natural rubber) binary systems. Syntheses using monomer realized at 600C result in polymerisation of styrene, while at 200C in grafting of polystyrene on rubber and styrene oligomers. The obtained compounds preserve their high elasticity and have increased tensile strength. Syntheses using natural rubber give products with higher tensile strength and elongation at break, due to the compoundation of the two polymers and grafting of natural rubber on the synthetic one. The compound synthetic/natural rubber = 3/2 gives, with styrene at 200C, compounds with higher tensile strength and elongation at break, resistant to crude oil and its derivative. DSC curve of the obtained materials shows an increase of glass transition temperature and a widening of its range, while TGA ones a slight increase of temperature at which thermal degradation starts.

Introduction

Polymer destruction using mechanical forces results in formation of a great number of new surfaces, specific area increasing very much. Such surfaces, being very rich in energy, represent convenient places for different chemical reactions [1]. The most important and common are block-copolymerization and grafting.

Taking into account the number of reactants, such syntheses can be divided in binaries, ternaries, etc. Considering the nature of reactants, they can occur in: polymer/monomer, polymer/polymer, polymer/monomer/monomer, polymer/polymer/monomer, etc. systems. However, the most usual are the syntheses in binary systems.

Grafting and co-polymerisation realised under the action of mechanical forces are classified as modern methods for obtaining new polymeric materials.

Modification of reclaimed rubber obtained from poly(α -methyl styrene-co-butadiene), α -SBR, under the action of the shearing forces using a laboratory roller was realized by rolling it on in polymer-monomer (styrene, S) and polymer-polymer (natural rubber, NR) systems. The integral structure α -SBR/NR = 3/2 and S were also used and the result are presented into the present paper.

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Materials and Methods

α -SBR and NR rubbers reclaimed by swelling and mechanical destruction [2] using special receipts without fillers, to eliminate their effect, were used for syntheses under the action of mechanical forces.

α -SBR rubber reclaimed by swelling and mechanical destruction [2] was modified in binary systems, both in polymer/monomer system using styrene and polymer/polymer one using NR. The resulted structure α -SBR/NR = 3/2 and S were also used.

A laboratory roller with temperature and roll-nip adjustment was used. The roller had the following characteristics: cylinders – 400 mm long and 200 mm diameter, friction coefficient – 1/1,24, capacity – 300 g.

α -SBR swollen with 20-40 % S was rolled on at 20 and 60°C for 20÷60 minutes.

Plasticization of the two rubbers was realized on separate rollers at room temperature, for 25 minutes α -SBR and for 15 minutes NR. In order to obtain a convenient viscosity of rubbers, a succession of rollers with different nips was used. Plasticized NR, 10-80%, was introduced on plasticized α -SBR and the two rubbers were rolled on at 20 and 70°C.

The inter-polymeric structure α -SBR/NR = 3/2 was swollen with 10 and 30% S and rolled on at 20°C for 15÷25 minutes.

Syntheses accomplished, conditions used and succession of reactants introduced into the roller are presented in Table 1.

Table 1. Syntheses realized, conditions used and succession of reactants

Reactants, parts per weight		T , °C	Rolling on time, min.	Succession of reactants
α -SBR 100	Styrene 20-40	20; 60	20-60	Swollen α -SBR, simultaneous
α -SBR 100	NR 10-80	20; 70	20-40	Successive
α -SBR/NR = 3/2	Styrene 10; 30	20	15-25	Swollen α -SBR/NR, simultaneous

To realize the stabilization of composition structure, all the reaction products were left at rest for 24 h.

With the goal of the control of the reaction velocities, peroxides and chain transfer agents in proper amounts were also introduced.

The remained styrene and its polymerisation products were extracted with tetrahydrofuran at 25°C and *o*-dichlorobenzene at 135°C and molecular weights of styrene polymers and oligomers were determined from viscosity data.

Sulphur (2%) and vulcanisation accelerators were added and the mixtures were pressed down at 160°C and 10-12 MPa. This operation can be also done during the last stage of the mechanical syntheses. The resulted rubber plates were used to determine the elongation at break as well as tensile and compression strength.

Equilibrium swelling in crude oil and gasoline was determined for the inter-polymeric structure α -SBR/NT = 3/2 as well as for the α -SBR/NR = 3/2 structure modified with 10 and 30% styrene.

Glass transition temperatures and ranges for reclaimed α -SBR and the product obtained by mechanical syntheses were determined by DSC using a V4.OB DuPont 2000 instrument. Temperatures at which thermal degradation starts as well as for some weight losses were determined by TGA using a V5.IA DuPont 2000 equipment.

Results and Discussion

The macroradicals generated by mechanical forces can initiate, into polymer-monomer systems, the polymerisation of monomer and block-copolymers form, can activate the monomer by chain transfer and a mixture of the two polymers results, or can give chain transfer to polymer and graft copolymers obtain. Monomers generating networks can produce interpenetrating networks [3-6], while those giving linear polymers result in semi-interpenetrating networks.

Macroradicals resulted from each polymer are expected to be produced in polymer-polymer systems. Such radicals can recombine giving block-copolymers or can give chain transfer reactions resulting in grafted and mixed structures. When only one polymer gives such radicals, the other one is the support for grafting; shorter macromolecular chains of the first type can also result. Thus, grafted copolymers and/or their mixtures with the first polymer are obtained. If the two polymers have restructuring tendency, grafted cross-linked structures are formed. When only one of the polymers has such a behaviour networks arise by the grafting of fragments belonging to the other polymer. The final structures complicate by block-copolymers cross-linking or by grafting of their fragments and compounds having mixed structure appear. This is why the simultaneous mechanical processing of two or more polymers results in compounds having new properties.

Syntheses realized using shearing forces could be selectively guided through physical and chemical parameters. Considering the physical parameters, at a constant shearing rate an important part is played by temperature.

Reaction velocities can be limited using plasticizers or solvents, role played also by monomers, oligomers or even by one of the polymers.

In α -SBR/S system at 60⁰C a high exothermic effect, typical of polymerisation, is observed. It was found that indeed the polymerisation of styrene takes place and a blend of the two polymers results. About 90% polystyrene reported to the monomer introduced was extracted with tetrahydrofuran and o-dichlorobenzene. The obtained products can be processed easier with sulphur and vulcanisation accelerators. After vulcanisation they preserve the high elasticity but the hardness is a little bit increased, especially when the styrene content exceeds 15%.

A moderate thermal effect is observed when the temperature is decreased to 20⁰C, specific to oligomer formation. Extraction resulted in about 64% oligomers. The obtained viscosity average molecular weight of oligomers was 2×10^3 g/mol. Consequently the amount of bound styrene is about 36%. The vulcanised compounds present a slight increase both of

tensile (8÷12%) and compression (7÷10%) strengths compared to the reclaimed vulcanized rubber. This could demonstrate that grafted structures form, block-copolymers giving higher increase of the above characteristics.

Syntheses in α -SBR/NR systems proved to be more useful from the point of view of mechanical and swelling characteristics of the resulted compounds. In this way a range of tensile strengths and elongations at break as a function of rolling on time were obtained.

Both properties increase with increasing rolling on time and three regions can be distinguished: an almost linear one up to about 40 minutes of processing, an exponential one up to about 80 minutes, and a plateau for a longer time, or even a very slight decrease.

The linear region could be explained by the compounding of the two rubbers and starting of block-copolymerisation by the recombination of the two types of macroradicals, while the exponential one by the increase of molecular weight due to the formation of block-copolymers and structuration phenomena. The structuration once finished, the properties remain constant, which explain the plateau. Continuing the rolling on, degradation takes place, which gives the slight decreasing region.

The most interesting and useful properties were found when the reclaimed α -SBR and NR were used in a ratio of 3/2. The product was obtained by rolling on of the previously plasticized rubbers in the desired ratio for 65÷75 minutes at 70°C. After 24 h of rest DSC curve was registered. The α -SBR/NR = 3/2 product shows an increase of glass transition temperature, T_g , compared to those of the initial reclaimed rubbers: from -56,5°C for α -SBR and -50,9°C for NR to -39,5°C (Table 2). This increase can be explained by the cross-linking reactions taking place between the two polymers. At the same time the transition range is enlarged with about 16°C due to the increasing of molecular weights ranges as a result of rolling on. Liquid-liquid transitions, T_{ll} , at higher temperatures are also observed and the flowing energies were computed. The higher flowing energy obtained for α -SBR/NR = 3/2 interpolymeric structure compared to the two rubbers can be interpreted as evidence that cross-linking took place. TGA curves show an increase of the temperature at which thermal degradation starts, with 6 to 10°C. This can be considered as a supplementary argument that stabilization takes place by cross-linking. Therefore, the obtained compounds can be considered as interpenetrating networks.

Table 2. The main characteristics of reclaimed α -SBR and NR rubbers, α -SBR/NR = 3/2 interpenetrating structure and the last compound rolled on with 10 and 30% styrene

Compound	T_g , °C	T_v range, °C	T_{ll} , °C	T_{ll} range, °C	Starting of thermal decomposition, °C	Liquid-liquid transition energy, J/G
α -SBR	- 56.5	12.0	98	59	164	1.90
NR	- 50.9	9.5	98	61	161	2.39
α -SBR/NR = 3/2	-39.5	26.9	98	50	170	5.27
α -SBR/NR = 3/2 + 10% S	- 53.8	10.0	103	47	180	5.13
α -SBR/NR = 3/2 + 30% S	- 41.0	12.6	110	53	180	5.07

α -SBR/NR = 3/2 interpolymeric structure swollen with 10 and 30% styrene was rolled on at 20⁰C for 80-85 minutes. Extraction with tetrahydrofuran shows that styrene reacted almost completely in the both cases. Vulcanised products have higher tensile strength (with 15-20%) and elongation at break (with 12-16%) compared to the initial ones as well as higher resistance to crude oil and its derivatives. The swelling rate of the compound rolled on with 10 % styrene in crude oil is three times lower than that of the original one, while that of the compound rolled on with 30% styrene is five times lower. The equilibrium swelling in gasoline is 170% for the initial product, 86% for the compound containing 10% styrene and 47% for that containing 30% styrene.

DSC curves of the α -SBR/NR = 3/2 interpolymeric structure and of the compound rolled on with 10 and 30% styrene present also some differences. Thus, the glass transition temperature decreases when the compound contain 10% styrene, becoming lower than of the two reclaimed rubbers (-54⁰C), due to the plasticizing effect of styrene oligomers or polystyrene grafts, while glass transition temperature of the compound containing 30% styrene remain almost unmodified (- 41⁰C). At the same time it is less well defined and more transition appear, which could show that block-copolymerization prevails and more rigid chains are obtained. Liquid-liquid transition temperatures are displaced towards higher temperatures when the amount of styrene increases.

TGA curves show an increase both of the temperatures at which thermal degradation starts as Table 2 shows, and of temperatures for constant weight losses for the two compounds containing styrene.

Temperatures for some constant weight losses for the two reclaimed rubbers, α -SBR/NR = 3/2 interpolymeric structure as well as of its compounds containing 10 and 30% styrene are given in Table 3.

Table 3. Temperatures for specified weight losses for reclaimed α -SBR and NR, α -SBR/NR = 3/2 interpenetrating structure and the last compound rolled on with 10 and 30% styrene

Weight losses, %	α -SBR	NR	α -SBR/NR = 3/2	α -SBR/NR = 3/2 + 10% S	α -SBR/NR = 3/2 + 30% S
5	370	325	305	340	360
10	395	340	350	350	400
15	408	355	370	360	410
20	415	360	380	368	425

The Table shows that the compound containing 10% styrene behaves similar with the reclaimed natural rubber at usual operation temperatures (0-250⁰C), the similitude preserving until about 350⁰C, and it is more stable at temperatures exceeding the last value. Thus, the natural rubber loses 84% from its initial weight at 450⁰C and the compound containing 10% styrene only 65%.

When the amount of styrene is increased at 30% the resulted compound is even more resistant than reclaimed α -SBR, especially at temperatures higher than 400⁰C. Thus, increasing amount of styrene produces increasing of heat resistance and the resulted materials are more heat resistant.

Conclusions

Mechanical syntheses in poly(α -methyl styrene-co-butadiene)/styrene system at 60°C resulted in homopolymerization of styrene and a blend of the two polymers is obtained.

Graft copolymers with relatively short polystyrene grafts are obtained when the syntheses are realized at 20°C, and a moderate increase of tensile strength and elongation at break was registered.

Mechanical syntheses in poly(α -methyl styrene-co-butadiene)/natural rubber system give products with higher tensile strength and elongation at break, the above properties increasing with increasing rolling on time, due to the compoundation, grafting of natural rubber on the synthetic one and cross-linking. Glass transition temperature and range increase as well as the temperature at which the thermal degradation starts.

α -SBR/NR = 3/2 interpenetrating structure subjected to mechanical syntheses with 10 and 30% styrene at 20°C gives products with higher tensile strength and elongation at break, more resistant to crude oil and gasoline, with higher thermal resistance compared to the initial structure and the initial reclaimed rubbers.

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