

Study of Influence of Copolymer Vinyl Chloride and Vinyl Acetate on the Properties of Butadiene Nitrile Rubber

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Abstract Influence of a copolymer of vinyl chloride and vinyl acetate to the properties of butadiene nitrile rubber has been studied. It is shown that the growth of the molecular weight of BNR by mixing latex rubber and copolymer in a ratio 80:20, 75:25, 65:35 leads to obtaining micro heterogeneous systems. Copolymer initially acts as an interstructural amplifier and then depending on their ratio plays the role of the dispersed phase in the plasticization. By the method of rheological analysis it was found out that increase of molecular weight was observed in the interval time (0-90 min), characteristic viscosity increases with the ratio of 75:25 copolymer from 0.6 to 1.4. A sol-gel analysis showed that with increase in the concentration of the copolymer in BNR the number of chains grid (1/Ms) in the rubber decreases. It was found out that consumption of cross linked molecules (1/Mn) for the cross-linking is reduced, it becomes constant at a ratio of 100:65:25. Comparison of the kinetics of thermometallic oxide vulcanization of BNR with the accelerator disulphide chloride benzene (DSCB) increases the yield concentration of the effective cross-links (n %c) in the molecule BNR. Experiment showed that in the presence of the accelerator DSCB and zinc oxide the structuring mainly goes by the double bond.

Keywords Butadiene Nitrile Rubber, Vinyl Chloride, Vinyl Acetate, Viscosity, Rheology, Vulcanization, Spectroscopy

1. Introduction

It is known[1-10], that the vinyl compounds containing active and polar groups interact strongly with the hydrocarbon molecular part of polymer. The structuring of elastomers is observed in the presence of compounds containing two or more active halogen atom and acetate, thus it is possible to obtain sufficiently strong elastomeric materials having a high resistance to the heat ageing, abrasion and dynamic endurance[11-17]. The study of occurring at the same chemical reaction makes it possible to facilitate significantly the development of cross-linking system for manufacturing materials with predetermined properties.

In the literature[1, 11-22] the large number of various substances are described which promotes acceleration of the chemical reaction in butadiene nitrile elastomers, for example, with polyvinyl chloride (VC). With filling polyvinyl chloride butadiene nitrile rubber (BNR) enhances ozone resistance of elastomer and helps to create a solid structure and to form ozone protective film on its surface.

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The systematic researches of the effect of unsaturated elastomers filled with copolymer vinyl chloride with vinyl acetate (VA) to the output parameters of the grid, the changes of the molecular structure, rheological properties and also the content of the double bonds in the polyblend (mixture of elastomer with vinyl chloride and vinyl acetate) was not carried out. It is presented to study the effect of interaction of copolymer of vinyl chloride with vinyl acetate on the elastic, structural parameters of the grid and rheological properties of butadiene nitrile elastomer.

2. Experimental

The butadiene nitrile rubber filled with copolymer of vinyl chloride with the vinyl acetate is used as an object of research. Filled BNR is obtained during joint coagulation of butadiene nitrile latex (with the content of the bound acrylonitrile 37-40 %) with latex of polyvinylchloride (PVC) and poly vinyl acetate (PVA) in the ratio of 80:20, 75:25,

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65:35. According to the research results carried out by IR method -spectroscopy in a butadiene part of polymer upon polymerization of the isometric composition of double bonds in the filled system was: 1,2-isomer of 16 %, 1,4-isomer of 18,7 % and trans 1,4 isomer. Macromolecules of SKN-40 rubber consists of statically allocated parts of butadiene, acrylonitrile and filled with vinyl chloride copolymer with the vinyl acetate. Features after the structuring BNR influence to their microstructure, molecular weight, molecular mass distribution (MMR) and gel content. Therefore, before processing researches in filled BNR, number-average and weight-average molecular weight and polydispersity (M_n -69 thousand; M_w -226 thousand; $M_w/M_n=4.1$) has been defined by gel permeation chromatography (GPC) beforehand.

BNR filled with PVC copolymer and (PVA) is expanded in the ratio 75:25, after 15-20 minutes of plasticization the obtained mixture is produced compression of the sample at 143K in the range 0-90 minutes during 20 minutes. For studying kinetic of structuring the 3 mass. part system of disulphonic acid chloride benzene (DSHB) + 5 mass. part ZnO on 100 mass. part of rubber has been used. The characteristic viscosity of BNR filled with copolymer was determined in toluene at 293K by known procedures on Ubbelohde type of viscosimeter. The calculation was carried out on Marx Hauvink's equation $[\eta] = K M^\alpha$ at value of the constant $K=4,9 \cdot 10^4$ and $\alpha = 0,64$ for toluene[23]. Studying elastic formation properties were carried out according to GOST 10722-74. Entrance of concentration of cross-linkage (n/c); number of the cross-linked molecules ($1/Mn\tau$) was determined by a sol-gel analysis. The calculation of parameters of a spatial grid of cross-linked elastomer was determined by Flory-Rainieri formula[24]. The change of the molecular structure, filled BNR was determined by IR method of infrared spectroscopy (IRS) in the range of 700-3000 cm^{-1} . For this filled BNR was dissolved in toluene during 24hrs. The rubber film was obtained by applying a solution onto a substrate and a constant evaporation of solvent. The boxes of KBr were used as a substrate during the measurement of spectrum in the range of 600-2000 cm and the boxes of LiF and NaCl in the range of 2000-3000 cm . The substrate with a film was fixed the holder and placed in the sample compartment in the spectrophotometer. Identification of the spectra was carried out in accordance with correlation tables[25-27].

3. Results and Discussion

Put forward[7] the colloidal-chemical concept of anomalous growth of viscosity BNR during filling of copolymer vinyl chloride with the vinyl acetate in works is reduced the fact to the following: Fillers (copolymers) are limited compatible with the polymers in the field of the concentration, corresponding to molecular solubility. Copolymers (vinyl chloride and vinyl acetate) of the correct reinforcement of rubber increase free volume of polymer,

and more, the dense packing of its molecular structure. The increase of a ratio of concentration of copolymer in a polymeric matrix leads to the formation of micro heterogeneous system. Copolymer (filler) first plays a role of the inter structural amplifier, and then the role of fulfilling the disperse phase at plasticization depending on their ratio.

Based on this situation and granting various ratios of filler (copolymer) in BNR, it is necessary to expect:

- Extremum existence on curve viscosity - a filler ratio only in limited area of temperature test;
- Dependence of effect of structural changes on transverse strain τ ;
- Dependence of viscosity of the filled rubber on time and temperature of storage of a sample.

Carried-out experimental researches in properties of the butadiene nitrile rubbers (BNR-40) filled with copolymer vinyl chloride and vinyl acetate, confirmed the mentioned assumptions. On figure 1, 2, 3 shown the dependence of elastic characteristics of BNR, filled with copolymer vinyl chloride and vinyl acetate.

One can see that the copolymer chosen in various ratios of copolymer causes change of properties of BNR in plasticity (figure 1), hardness (figure 2) and Mooney viscosity (figure 3). Comparatively observable small growth of plasticity (figure 1) and a decrease of hardness (figure 2) at copolymer ratios 80:20 and 75:25 in BNR lead to change these characteristics on regularities, usual for BNR. According to[1] for mechanical solubility (plastification) to rise in the rate of the gel above 70% leads to the destruction of chains, which leads to the destruction of the chains that partly different effects on molecular weight and mechanical - mechanical processes during the dissolution of the copolymers.

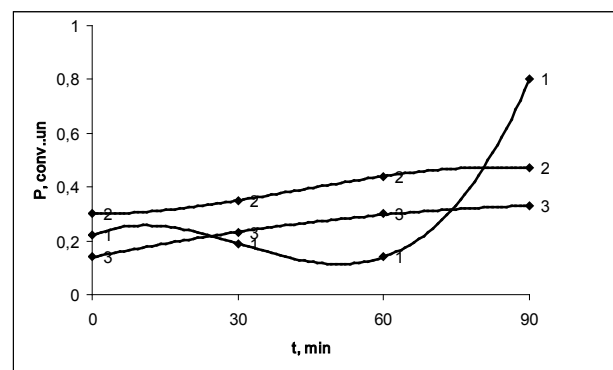


Figure 1. The dependence of plasticity of BNR filled with various ratios of the copolymer of vinyl chloride and vinyl acetate by heating during 90 min; 1- 80:20, 2- 75:25, 3- 65:35

Mooney viscosity practically doesn't change at ratios of copolymer 80:20 and 65:35 at the duration of structuring within 90 minutes. The structuring BNR with copolymer in ratio of 75:25 was characterized by a higher change of Mooney viscosity after heating.

Studying of the laboratory samples filled with copolymer based on BNR showed that depending on the content of copolymer and duration of time of characteristic viscosity

monotonously increases in samples and becomes constant and isn't observed increasing of viscosity in samples 1-3 has smaller structuring level.

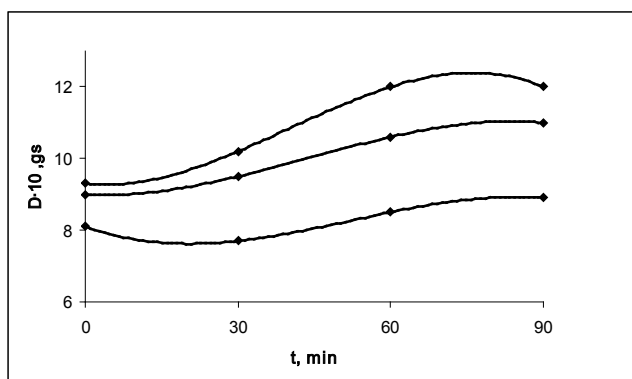


Figure 2. The dependence of hardness of BNR filled with various ratios of the copolymer of vinyl chloride and vinyl acetate by heating during 90 min; 1- 80:20, 2- 75:25, 3- 65:35

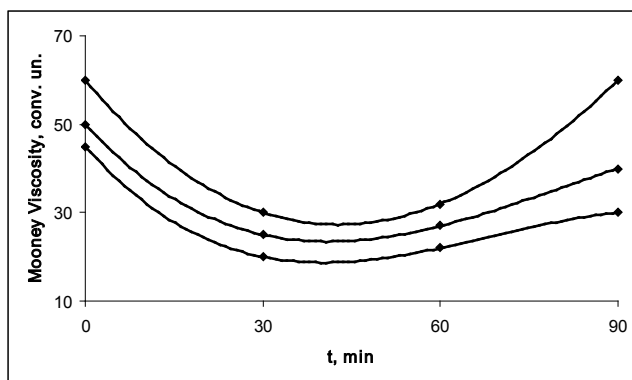


Figure 3. The dependence of viscosity of BNR filled with various ratios of the copolymer of vinyl chloride and vinyl acetate by heating during 90 min; 1- 80:20, 2- 75:25, 3- 65:35

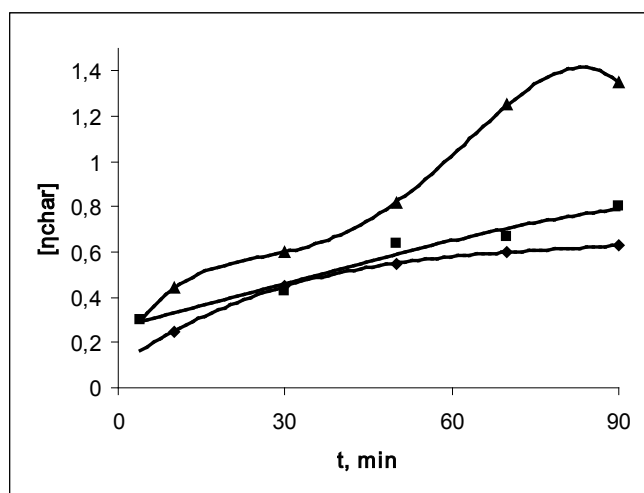


Figure 4. Dependence of the characteristic viscosity of BNR filled with copolymers of vinyl chloride and vinyl acetate after heating at 423K during 90 min; 1- 65:35, 2- 75:25, 3- 80:20

The growth of molecular weight is observed at duration of structuring at the time interval 0-90min. The characteristic viscosity increases at samples 2 (75:25) with 0.6 to 1.4. With increase of time the characteristic viscosity (2) becomes constant at 70 minutes, and further reduction of molecular weight is observed at all samples at 120 minutes. BNR is associated with a destruction of main circuit of polymer.

Viscosity increase in the range of values (0-90min) can be bonded with formation of spatial structures due to reaction of intermolecular cross-linking (figure 4).

On figure 5 IR-spectra of SKN-40 rubber filled with copolymer vinyl chloride with vinyl acetate 75:25) is presented. The SKN-40 system + copolymer (PVC+PVA) are characterized by polarity, therefore the process of combination SKN-40 with copolymer is mainly defined by polar groups $\text{C}\equiv\text{N}$, $\text{C}-\text{Cl}$ and their reactivity at mechanic - chemical and thermal influences.

On this basis, the main consideration was given to studying of intensity of the bands of the stretching vibration of the nitrile group, located in areas 2235cm^{-1} (figure 5) and being characterized by exceptional stability, both in frequency and form. The intensity of a nitrile band naturally decreases with longer heating from 0 to 90 minutes. For the characteristic of intensity of a nitrile bands were chosen the relative values representing the relation of intensity (or the optical plane) bands 2235cm^{-1} to intensity of bands 2925 and 2850cm^{-1} , corresponding to dissymmetric and symmetric stretching vibrations of communications $\text{C}-\text{H}$ of CH_2 group. (Figure 5 the bands are not specified).

The most significant changes was observed in the IR spectrum of the sample in the final state, it should be noted decrease in intensity of the band 675cm^{-1} , observed in the form of a doublet with a band 688cm^{-1} in a range of an initial sample and corresponding to stretching vibrations of $\text{C}-\text{Cl}$ communication should be noted.

The band at 1730cm^{-1} , being observed in IR spectra of the sample in both original, and final states, corresponds to $\text{C}=\text{COC}(\text{C})=\text{O}$ group[25-27]. It is known that, with introduction of fillers into polymer the chemical interaction at the interface of two phases is possible between polymer and fillers[1, 28].

The filling of elastomers is that during insertion into the elastomer (in different ratios) the significant change in the parameters of the grid of elastomer occurs.

By sol-gel analysis was found out that with increase in the ratio of the copolymers in BNR monotonically increase share of sol-gel fraction (28-35%), the average number molecular weight (M_n , by Charlz is 3240-4600 and the number of chain mesh is 8-14) (table 1).

Represented in Table 1 results show that in the process of structuring the of BNR in the presence of the copolymer at various ratio, spending number of cross-linked molecules to form in macromolecule of BNR number of cross-links decreases and becomes constant at ratio of copolymer 100:65:35.

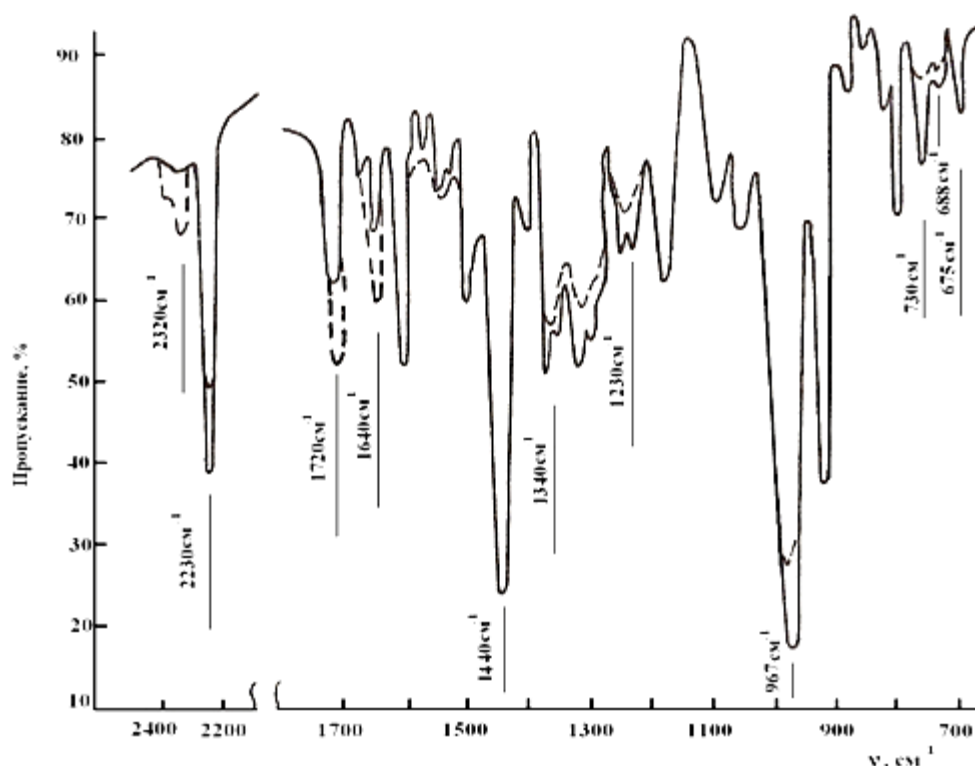


Figure 5. IR spectra of BNR filled with copolymer of vinyl chloride and vinyl acetate (75:25). After heating for 90 min at 423K

— No fillers

---In the presence of a copolymer of vinyl chloride and vinyl acetate

Table 1. The basic structural parameters of the grid for elastomer SCN-40 filled with copolymer vinyl chloride with vinyl acetate

Copolymer ratio, %	Percentage sol -fraction, %	Number-average molecular weight, M_n	Number of chain mesh $1/M_c \cdot 10^5$, mol/cm ³	Number of cross-linked molecule, $1/M_c \cdot 10^5$, mol/cm ³
100:80:20	28	3240	8	1,8
100:75:25	36	4400	14	1,1
100:65:35	35	4600	11	1,1

BNR significantly differs with greater tendency to cross-linking than other diene rubbers. So it is vulcanized during heating even without the addition of indirect material, and in the presence of disulfide chloride benzene (DCHB) valuable technical vulcanizates can be obtained with participation of zinc oxide.

The system filled of 100 mass. part BNR (100:75:25) + 4 mass. part DSCB+5 mass.part ZnO was used for vulcanization of filled BNR. The vulcanization was taken in a hydraulic press at 423K. The duration of vulcanization is 90 minutes.

From the data of table 2 shows that increasing the maximum yield of effective cross-links n_c DSCB and metal oxides compared to the thermal vulcanization to the calculation suggest that the presence of reinforcing DSCB and ZnO vulcanization is mainly on the double bond and the formation of new active sites of metal oxides is suppressed or products their transformation.

Table 2. Limiting energy of activation and level of cross-linking at vulcanization of filled BNR (100:75:25)

Cross-linking agents, mass.p per 100 mass.p. rubber	E, ccal/mol			$n_c \cdot 10^{-19}$, cm ⁻³		
	intervals of time, min			intervals of time, min		
	30	60	90	30	60	90
thermal vulcanization	13,6	18,7	21,7	1,4	2,4	4,1
4 DSCB+ 5 ZnO	19,8	24,1	29,3	3,9	5,6	7,8

Comparison of the structural features of the parameters of the grid with their staple rheology, plastic and vulcanizing properties suggests that when combining BNR is a copolymer of VC and VA copolymers with increasing content of the destructive processes are observed. The best bed-elastic properties when the content of the copolymer has in the redistribution of 75:25. With increasing heating time, the rise of cross-links and the number of cross-linked molecules remains constant.

4. Conclusions

The present work shows that by mixing of latex BNR and filled vinyl chloride and vinyl acetate in a ratio of 80:20, 75:25, 65:35 leads to formation microheterogeneous systems, acting as a dispersed phase in mechanical dissolution (plastification).

It is shown that the shear stress of solubility vinyl chloride

copolymers and vinyl acetate in the rubber, observed the rise in the rate of the gel (70%) of the elastomer system, which leads to the destruction of the chains of BNR. Decreasing of the molecular weight of the polymer mass at a shear stress on the rollers influence differently to the rheological properties such as plasticity (figure 1), hardness (figure 2) and of Mooney viscosity (figure 3).

With duration of the structuring in mode 423K·90', in a filled elastomer system observed an increase in molecular weight. Characteristic viscosity is increased in samples 2 (75:25) from 0.6 to 1.4. With increasing time, the molecular weight of the samples filled copolymers at 70 min is constant, but then, with increasing time of the process of structuring observed decreasing of molecular weight in all samples.

Filled copolymers of vinyl chloride and vinyl acetate with BNR mainly determined by polar groups-C≡N, C-Cl and their reactivity at mechanical, chemical and thermal influences.

Comparison kinetics of thermometal oxide vulcanization of BNR with participation of amplifier disulphide chloride benzyl (DSCB) show the increasing of cross links yield (n') in the molecule of BNR. By method of sol-gel analysis determined that in the presence of reinforcing DSCB and zinc oxide are primarily structured by a double bond and the formation of new active centres are suppressed by metal oxides or the products of their transformation.

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