Study of Butadiene Rubber Mastication and Mixing with Carbon Black

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ABSTRACT: A thermomechanical method was applied to study the topological and molecular structure of SKD butadiene rubber masticated and mixed with carbon black. Triblock structure (two amorphous blocks and one a pseudocrystalline structure) of a studied raw rubber and rubber compound networks were found. A ratio of these morphology structures changes during mastication. After mastication, a low-temperature block has two glass transition temperatures that shows its more complex structure than that in raw rubber. This shows deep transformations taking place during the mastication process. Despite applying high shear forces and heating during mixing with carbon black in a filled BR compound, we present three structures characteristic for BR. However, introduction of carbon black changes the topological structure of polybutadiene. A part of both amorphous blocks grows. A part of a crystalline structure lowers from 88% after 2.5 min of mixing to 54% after 20 min of compounding. The molecular weight distribution of the chains between the junctions of the network and parts of low-temperature and high-temperature amorphous blocks, and pseudocrystalline structures in architecture of the rubber network were also calculated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 729–737, 1999

Key words: butadiene rubber; mastication; rubber compounding; carbon black; topological structure; molecular structure; thermomechanical analysis; rubber network

INTRODUCTION

The processability and exploitation properties of rubbers are largely governed by their molecular architecture, and slight changes of it often makes differences between characteristics of nominally "identical" materials. In rubber technology a key factor is to obtain optimal creation of a controlled spatial architecture of the rubber network. This very complex structure[1] depends not only on a rubber recipe content, but also on manufacturing technology used. One part of this architecture is formed during compounding, storage, and shaping, another during vulcanization. Many aspects of this problem investigated for almost 100 years were summarized in literature surveys,[2–7] but not all is clear up to now. It suggests further investigation of an influence of the recipe content and technological parameters on the molecular-weight distribution and the topological structure of rubbers being changed during processing. Some phenomena taking place during mastication of butyl rubber were studied in our previous

article.[8] There it was found that introduction of sulfur changes the molecular and topological structures of IIR. Now, a method of thermomechanical analysis of solid polymers is used to study changes in the molecular and topological structures of cis-1, 4-polybutadiene type SKD during mastication and mixing with active filler, which essentially increases shearing forces as a reason of macroradical generation.

METHODOLOGY

This method is based on the evaluation of two properties of macromolecules in a thermal field being variable against time.[9,10] The first property is that segmental relaxation starts at the glass transition temperature, T_g, and it ends when the molecular flow starts at the temperature T_f. The higher the molecular weight of a polymer homolog, the higher is the starting temperature of the molecular flow.

The second property is that when segmental relaxation ends, it gives to the system, being under appropriate loading, a jump of deformation ΔH, directly proportional to the weight fraction of the involved molecules. Based on this, the intermediate zone of the thermomechanical curve (TMC) of an arbitrary polymer can be shown as the fencing of deformation jumps.

EXPERIMENTAL

Material and Testing Conditions

For this study, a compound containing 100 phr of cis-1,4-polybutadiene SKD type (from Russia) and 50 phr of carbon black grade N330 was used. This compound was prepared in a laboratory mixing mill with the friction ratio 1 : 1.04. In the beginning of compounding, the mixing rolls were heated to over 60°C. The compounding procedure was as follows: (1) preliminary mastication of rubber; (2) addition of carbon black and, next; (3) homogenization of such a compound.

Samples for TMA were taken 2.5, 5, 7.5, 10, 15, and 20 min after the start of the homogenization time. Raw rubber taken for comparison was milled at the same conditions. Next, a sample of 1.2-mm thick was put into a thermostatic chamber of the testing device. The sample was frozen without pressing under a scanning rate of 2–10°C/min to a temperature of −120°C and, next, was stored for 10–15 min to stabilize the temperature. To obtain a TMC, the sonde with a load of 0.2 g was moved down to contact the surface of a sample; further, the sample was defrosted with a rate of 5°C/min. The deformation of the sample was measured when heated.

RESULTS AND DISCUSSION

To separate processes occurring in tested rubber during mixing on an open mill in the presence of carbon black and without it, all experiments were arranged in two steps. First, the molecular and topological structures of BR and its changes as the result of 5, 10, 15, and 20 min of milling were evaluated. Next, studying of the carbon black influence on changing in the structure of butadiene rubber during compounding was performed.

Mastication

TMC for cis-1,4-polybutadiene not containing the cis-1,2 isomer is shown in Figure 1. The character of the curves for rubber before (1) and after milling (2) shows a complex topological structure of the tested polymer and mechanochemical transformations during its mastication. For unmasticated rubber, the curve (1) shows a zone of the glassy state—the straight line AB. In point B (T'_g), this zone is passing to the linear high elastic expansion—the straight line BC. True thermomechanical deformation of the polymer is starting at a temperature in point C, characterizing the end of segmental relaxation in the polymer homologies with the lowest molecular weight, which passes next into "sol" and reduces the modulus of a physical network of rubber. As the temperature grows, rubber homologies with higher and higher molecular weight little by little reach a critical value of $\Delta T = T_f - T_m^b$. This reduces the modulus and thermomechanical deformation H_i. The process of including successive homologies is running until the higher molecular weight homolog will pass into "sol," obtaining a possibility of molecular flow. In a linear polymer at this time the molecular flow of stock starts. In a crosslinked polymer thermomechanical deformation is ending due to stabilization of the modulus, and the polymer reaches a plateau of high elasticity—the straight line DK.

At a temperature corresponding to point K, a process of a thermal expansion of the network of strong physical junctions creating a physically

Figure 1 Typical thermomechanical curves for raw SKD butadiene rubber (1) and milled for 5 min (2); (a) a low-temperature amorphous block, (b) a high-temperature amorphous block; (c) a zone of melting of a pseudocrystalline block. T'_g—the glass transition temperature of a low-temperature amorphous block of SKD; $T^{*'}_g$—the glass transition temperature of the first low-temperature amorphous block of SKD milled 5 min; T^{**}_g—the glass transition temperature of the second low-temperature amorphous block of SKD milled 5 min; T''_g—the glass transition temperature of a high-temperature amorphous block of SKD; T^b_m—temperature of the beginning of melting process; T^e_m—temperature of the terminating of melting process; T_f—temperature of the molecular flow, H_{cr}—deformation jump caused by melting of a crystalline structure.

networked structure of a low-temperature block of BR ends. Here, the thermal expansion of the polymer is starting to be visible, which is accompanied by melting a crystalline structure. An accumulation rate of this deformation, as a rule, is higher then that in a high elasticity zone—the straight line DK. This fact was shown earlier in studying amorphous and crystalline sulfur and polyethylene.[9,11] The resulting deformation being cumulated in the melting process of a crystalline structure of a polymer, H_{cr}, is directly proportional to a weight share of this fraction.[9]

Process of transformation of a crystalline structure into amorphous, being completed at a temperature in point M, is passing into the zone of a glassy state of the high-temperature block—the straight line OO'—if the temperature gets higher. Next, like other polymers, an increase in a temperature close to $T^{(1)''}_g$ results in a transitional zone between the glassy and high-elastic states,

when a straight line of the thermal expansion of this fraction is observed until reaching a temperature in point P. From this moment, like the temperature for point B, accumulation of thermomechanical deformation starts due to successive degradation of the network of physical junctions during segmental relaxation of polymer homologies of a high-temperature block. This process runs until it reaches a temperature T_f in point O'', over which the molecular flow—the curve $O''T^{(1)}$ starts.

A topological structure of SKD butadiene rubber evaluated in this way in a temperature interval from -150 to $+150°C$ is a typical structure for block polymers. This structure shows a "diphilic" nature of macromolecules of BR, resulting from the presence of two types of structures differing in both polarity and related interactions between the chains. This is the reason for the appearance of the diblock structure. A physically crosslinked structure of a low-temperature block has polymeric crystallites as branching junctions.

Mastication resulted in a change in a general topology structure of SKD rubber (Fig. 1, curve 2). Instead, a single low-temperature block in the same temperature interval of two physically crosslinked low-temperature blocks differing by 20°C in the glass transition temperatures (T^*_g and T^{**}_g) are found. Further extension of mastication time principally does not change a topological structure of rubber. Triblock structure (two low-temperature and one high-temperature blocks) is preserved.

The mastication process results in the degradation of a crystalline structure of a polymer. Dependencies of the glass transition temperature of the high-temperature block, T_g, temperature of the beginning of polymer's flow, T_f, and crystallinity degree, φ_{cr}, of SKD vs. milling time have extreme character (Fig. 2). An equal period until maximum probably is not random. It could be explained if it is accepted that during the beginning of the milling some fluctuations in structural limitations are reduced, and a system is transformed into the more uniform state. Here, it obtains a potential possibility to increase some in the crystallinity degree, T_g and T_f. This state is reached after 5 min of rubber milling. Further milling, due to deeper mechanochemical transformations in BR, results in lowering of its possibility to crystallize, giving a decrease of T_g and T_f. Here, a part of a crystalline structure after 5 min of milling is equal $50 \pm 5\%$. After 20 min of mastication it is reduced to 23%. However, taking into account that this parameter is evaluated with

Figure 2   Glass transition temperature T_g (1), molecular flow temperature, T_f (2), and crystallinity degree φ_{cr} (3) of SKD butadiene rubber vs. milling time.

the accuracy of $\pm 10\%$, it could be also said that, in fact, the reduction of a crystalline structure is lower.

Parameters of molecular-weight distribution of a crystalline polymer ($\bar{M}_n$, $\bar{M}_w$, and $K = \bar{M}_n / \bar{M}_w$) are essentially changed because of milling (Table I). The growth of crystallinity degree observed after the initial 5 min of milling could be explained as a result from transformation of a part of an amorphous polymer (passing chains) into a crystalline structure. This gives an increase in molecular weight of this phase. The growth of

Table I   Properties of a Crystalline Structure of *cis*-1,4-Butadiene Rubber SKD Type

Milling Time (min)	T_m^b, °C	T_m^e, °C	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K
0	−30	−19	545,500	1,127,200	2.10
5	−32	−16	681,700	1,534,400	2.25
10	−33	−16	687,100	1,270,700	1.85
15	−31	−16	892,500	1,496,700	1.68
20	−36	−22	211,300	1,020,500	4.83

T_m^b—temperature of the beginning of melting process; T_m^e—temperature of the terminating of melting process; $\bar{M}_{n(n)}$—the number-average molecular weight between the junctions of a polymer network; $\bar{M}_{n(w)}$—the weight-average molecular weight between the junctions of a polymer network; $K = \bar{M}_{n(n)} / \bar{M}_{n(w)}$—the polydispersity coefficient of chains between the junctions.

$\bar{M}_n$ up to 15 min of milling is observed here despite the beginning of a lowering of the crystalline structure content. Here, transformation of a low molecular-weight fraction of crystallites into an amorphous phase occurs. This results not only in a growth of $\bar{M}_n$, but also in the reduction of the polydispersity coefficient K.

Longer milling, i.e., for 20 min, gives a considerable lowering of the $\bar{M}_n$ value and more than twice the growth of the K value. This evidences the growth of macromolecules branching. It is possible to accept that rapid activation of mechanochemical processes up to this moment of time essentially reduces $\bar{M}_n$ and gives a growth of branching macromolecules creating a crystalline structure of a polymer.

Extension of milling time hardly changes the temperature, either at the beginning or the termination of the melting process (Table I). They are equal -33 ± 3°C and -19 ± 3°C, respectively.

In Table II is shown that in an amorphous phase of the SKD rubber some structural changes are also observed. The number-average molecular weight of chains between the junctions (chains passing from one crystallite to another) in the physically networked structure of a low-temperature block go down during milling and stabilizes only after 10 min of the mastication. Transferring

Table II   Properties of an Amorphous Phase of SKD Butadiene Rubber

Milling Time (min)	T'_g, °C	$\bar{M}'_{n(n)}$	$\bar{M}'_{n(w)}$	K'	φ'	T''_g, °C	$\bar{M}''_{n(n)}$	$\bar{M}''_{n(w)}$	K''	φ''
0	−99	21,900	30,100	1.37	0.52	—	—	—	—	0.0
5	−104	12,600	17,000	1.35	0.22	−85	16,400	21,500	1.32	0.22
10	−104	4,400	5,800	1.32	0.19	−86	10,900	14,300	1.31	0.30
15	−105	4,000	5,300	1.33	0.24	−88	17,600	24,500	1.39	0.43
20	−104	6,400	8,100	1.41	0.30	−87	14,800	20,200	1.36	0.47

φ—a weight share of the low-temperature (′) and the high-temperature (″) block.

of macromolecule fragments from the state of a potential possibility to crystallize into the amorphous phase and vice versa activates redistribution of chains in the low-temperature block.

At 5 min of milling the low-temperature block is divided into two autonomous blocks characterized by the glass transition temperatures of −104 and −87°C ($T_g^{*\prime}$ and $T_g^{**\prime}$), respectively [Fig. 1(2)]. This topological structure of an amorphous phase of BR is also preserved during further milling. However, the ratio of these two amorphous blocks changes during the extension of milling time. Also, molecular-weight characteristics of chains between junctions in blocks and polydispersity coefficients are different. The change in K values evidences the different regularity of the polymer networks in both blocks resulting from the mastication process.

Mixing with Carbon Black

Introduction of carbon black into rubber during compounding changes the processes discussed above. This is due to a higher viscosity of the batch, giving an increase in shear forces, which are the reason of generation of macro radicals. Simultaneously, the presence of a highly developed carbon black surface and the presence of different active groups on it, participating in chemical reactions, influences the mobility of macromolecule segments. Due to this introduction of carbon black, changes in the topological structure of rubber during the initial 2.5 min of mixing. $\bar{M}_{n(n)}$ of an amorphous phase of SKD is changed from 21,900 (Table II) into 300 (Table III). Here, the process of recrystallization is suppressed in full (Fig. 3). On the other hand, in the rubber–carbon black compound conditions are created to arrange a pseudocrystalline structure, which starts to melt at a temperature of about 100°C, giving the start of the molecular flow of rubber at 140–150°C. This type of structure is called a pseudocrystalline, because transformation of it into a regime of the molecular flow is preceded by its melting, and followed by an essential increase in the thermal expansion (segment OT in Fig. 3). Here, a rate of accumulation of deformation has a value close to that for the melting process of a crystalline polymer.[9] Due to this, a part of this structure, like for a crystalline polymer, was evaluated by the ratio of expansions during melting (H''' in Fig. 3) and resulted in deformation of all processes in the high elasticity zone of TMC.

Typical TMC for a rubber–carbon black compound (Fig. 3) differs from that for the raw SKD

Table III   Molecular Weight and Thermomechanical Characteristics of an Amorphous Phase of the Rubber Compounds Filled with Carbon Black

Milling Time (min)	T_g, °C	$\bar{M}_{n(n)}$	$\bar{M}_{n(w)}$	K	φ
Low-Temperature Block					
2.5	−67	300	410	1.39	0.021
5	−67	460	610	1.32	0.020
7.5	−66	780	1,060	1.35	0.023
10	−63	2,850	3,980	1.38	0.021
15	−67	1,670	2,280	1.37	0.054
20	−67	5,710	7,800	1.37	0.055
High-Temperature Block					
2.5	11	50,200	70,200	1.47	0.10
5	6	65,700	96,300	1.47	0.11
7.5	−3	278,300	404,600	1.45	0.12
10	−7	273,400	402,400	1.47	0.14
15	−6	146,100	240,400	1.65	0.24
20	−17	115,500	171,100	1.48	0.41

Figure 3 Typical TMC for rubber–carbon black compound; T_g—the glass transition temperature of the low-temperature block (′) and the high-temperature block (″), T_m^b—temperature of the beginning of the melting process, T_m^e—temperature of the terminating of the melting process, T_f—temperature of the molecular flow, H—deformation directly proportional to the share of the low-temperature block (′), the high-temperature block (″), and the crystalline structure (‴).

rubber (Fig. 1). A melting zone of the crystalline phase of the polymer is absent at a temperature of about −30°C. However, a pseudocrystalline structure characterized by a melting temperature of 110–120°C is found. This level of temperature evidences the essentially higher density of contact interferences between adjacent macromolecules, and macromolecules and a surface of carbon black particles of this compound in the pseudocrystalline part than that for the crystalline part of SKD alone.

During mixing of the rubber compound, there are many different processes. The batch is subjected to mechanical action, resulting in degradation of macromolecules and networking because of transferring the chain, which changes molecular and topological structure of the polymer. An amorphous phase of rubber has a diblock structure (Fig. 3), characterized by the glass transition temperatures being changed during mixing time in an interval from −63 to −67°C for a low-temperature block and from −17 to 11°C for a high-temperature block (Table III). A physically crosslinked structure of the rubber compound is probably created by the "diphilic" nature of studied BR, and strong interactions between its macromolecules and a surface of active carbon black.

The "diphilic" nature of polybutadiene macromolecules is accepted as a result of the isomer content. These isomer forms, being characterized by different cohesion energy, probably differ in interaction ability with a surface of carbon black particles. On the other hand, excluding that fragments of rubber macromolecules participate in forming topological structures of a rubber compound is impossible. Due to this, for a low-temperature block in the zone of a plateau of high elasticity (*CD* straight line in Fig. 3) networked zones are created by fragments of macromolecules of a high-temperature block being in a glassy state. Their relaxation transformation into a high elastic state starts at T_g''. Networking fragments of a high-temperature block are pseudocrystalline supermolecular structures ($C'D'$ straight line). Melting of these networked structures results from its degradation, which starts at the temperature in point D'. At the temperature in point O, the rubber–carbon black compound is subjected to the molecular flow of fragments of the BR macromolecules. This state of the system is reached at 140–150°C.

Mobility of macromolecules in the low-temperature amorphous block is independent of the mastication time, which results in the constant glass transition temperature (Table III). The average molecular weight of chains between junctions grows (Fig. 4), but the coefficient of the polydispersity is stable. The share of this block is only 2% at the beginning of mixing, and it grows to 5.5%

Figure 4 Dependence of the number-average molecular weight between the junctions in a low-temperature block of raw rubber (1) and the rubber–carbon black compound (2) on milling time.

Figure 5 Dependence of the number-average molecular weight between the junctions in a high-temperature block of raw rubber (1) and the rubber compound (2) on milling time.

Figure 6 Molecular weight distribution between the junctions in the low-temperature block of rubber compound vs. milling time: 1–2.5 min, 2–5 min, 3–7.5 min, 4–20 min.

as mixing time extends to 20 min. Another picture is found for the high-temperature amorphous block (Fig. 5). Here, mobility of the macromolecules increase (the glass transition temperature lowers) as mixing time extends.

Stability of the polydispersity coefficient, being a measure of macromolecules' transformation, evidences the uniform distribution of active sites along rubber chains in both blocks, where sites interact with carbon black particles. This stability in both physically crosslinked blocks should result from a unimodal molecular-weight distribution of chains between the junctions. This is an indirect confirmation of lack of a change in isomer distribution between low-temperature and high-temperature blocks during milling. Simultaneously, interaction of active carbon black with fragments of chains in a low-temperature block is changed as well. Comparing T_g values from Tables II and III to evaluate which effect predominates is possible. In the studied case an interaction of rubber and carbon black predominates. This conclusion for a low-temperature block is confirmed by a unimodal symmetric shape of MWD of the chains between the junctions (Fig. 6).

The main structural and molecular changes during mastication occur in a high-temperature block (Table III) and in a pseudocrystalline structure (Table IV). In the first one, the highest average molecular weight is found after 7.5–10 min. Later it is reduced. Also, the coefficient of polydispersity is stable here. The part of this block in

the rubber compound is higher (10%) than that for a low-temperature block, especially in the beginning of the mixing, and it grows very fast to 41% as the mixing time extends to 20 min. Most of the rubber compound is as the pseudocrystalline structure (Table IV). In the beginning of the mixing it is predominantly (88%), and after 20 min of mixing it is reduced to 54%. The rate of this reduction depends on the stage of mixing. Between 2.5 and 10 min of mixing it is small, and later it grows rapidly. After 7.5 min of mixing a pseudocrystalline structure is maximally decompacted because of the weakening of intermolecular interactions. Here, the temperature of the beginning of the melting is the lowest (107°C), and the temperature interval ΔT between the beginning of melting T_m^b and the start of the molecular flow T_f reaches a maximal value equal to 44°C.

The degree of regularity in a structure of arbitrarily chosen supermolecular arrangement (crys-

Table IV Molecular Weight and Thermomechanical Characteristics of a Pseudocrystalline Structure of Tested Rubber–Carbon Black Compounds

Milling Time (min)	T_m^b, °C	T_f, °C	φ''
2.5	117	148	0.88
5	115	154	0.87
7.5	107	151	0.85
10	125	156	0.84
15	123	152	0.71
20	123	143	0.54

Figure 7 Dependence of ΔT in the rubber pseudocrystalline structure on milling time, $\Delta T = T_f - T_m^b$, where: T_f—temperature of the starting of the molecular flow and T_m^b—temperature of the beginning of melting.

talline or pseudocrystalline) could be evaluated not only by absolute value of temperature of the beginning of its degradation, but also by $\Delta T = T_f - T_m^b$. According to this factor, a structure of the pseudocrystalline block is not uniform during successive stages of mixing. The degree of this nonuniformity depends on mixing time (Fig. 7). As far as we know, predicting *a priori* which measurement of this network uniformity is more applicable to obtain the required complex of properties of rubber is impossible. For this purpose using different testing methods, including thermomechanical analysis, is necessary. The last gives a multiaspect information on the structure of the rubber compound.

Mixing longer than 7.5 min is accompanied by lowering of T_g'' due to migration of more polar fragments of rubber macromolecules from a high-temperature block. Simultaneously, in a pseudocrystalline structure T_m^b grows and ΔT value lowers. Here, as it was during the first 5 min of mixing, energetic uniformity of the rubber structure is grown (Fig. 7). Nevertheless, lack of an influence of mixing time on molecular uniformity of networks in the blocks of the compound does not show absence of its influence on the energetic state of the components of their structures. Here, it is found that mobility of fragments of chains in the amorphous blocks is more and more similar as mixing time is extended. The difference in the glass transition temperatures between blocks is

reduced as mixing extends. It is reached mainly due to the growth of mobility of macromolecules in a high-temperature block.

Comparing data from Figure 2 and Table IV, it is shown that because of the interaction with carbon black, the mobility of the macromolecules in a crystalline structure is considerably reduced. This results in an essential growth of the melting temperatures (about 140°C). Temperature of the molecular flow is changed differently. During the first 15 min of mixing the temperature of the molecular flow of BR is about 10°C higher than that for the rubber–carbon black compound.

The result of mechanochemical transformations and isomer redistribution of fragments of macromolecules between the high-temperature amorphous block and the pseudocrystalline structure during mixing is the widening of a shape of MWD of this block (Fig. 8). Here, the shape of the MWD is more asymmetric than that for a low-temperature block (Fig. 6).

It is concluded that mixing of the rubber–carbon black compound for more than 10 min results in the degradation of macromolecules in all structures of rubber. The influence of carbon black on this process is evident. This is given from the discussion shown above and Figures 4 and 5, where it is shown that a critical moment of topological structure formation for the rubber compound is between 7.5 and 10 min of mixing. A maximum on the function of molecular weight vs. mixing time probably is a result of the two processes: the first was related to the well-known scission mechanism of macromolecules, making possible the mechanochemical transformations

Figure 8 Molecular-weight distribution between the junctions in the high-temperature block of rubber compound vs. milling time: 1–2.5 min, 2–5 min, 3–7.5 min, 4–20 min.

during mastication of rubber. It reduces molecular weight, especially the longest chains, and generates macro radicals. Second, this process consists of both branching of macromolecules because of macroradical recombination and networking because of interferences of macroradicals with the surface of carbon black. It gives a growth of the molecular weight of rubber. Competition of these processes in the change of the molecular weight gives a maximum in the resulting function. This fact could also be a cause of disturbance of the symmetry of MWD, with a low-molecular "tail" appearing on it. (Fig. 8).

CONCLUSIONS

1. It was stated that raw *cis*-1,4-polybutadiene has two amorphous blocks and one a pseudocrystalline structure. A ratio of these morphology structures changes during mastication. After mastication, a low-temperature block has two glass transition temperatures that show its more complex structure than that in the raw rubber.
2. Despite applying high shear forces and heating during mixing with carbon black in a filled BR compound, three structures characteristic for BR are present. However, introduction of carbon black changes the topological structure of polybutadiene. A part of both amorphous blocks grows. A part of a crystalline structure lowers from 88% after 2.5 min of mixing to 54% after 20 min of compounding.

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