THERMAL STABILITY OF ELASTOMERS

L. Ślusarski

INSTITUTE OF POLYMERS, TECHNICAL UNIVERSITY OF ŁÓDŹ, POLAND

Thermal transitions of elastomers are classified and problems concerning their stability are discussed. It is concluded that in the case of general-purpose elastomers no simple correlation exists between the energy of the bonds in the skeleton of a chain and their thermal stability. This also holds for the parameters of the physical structure of the chains. A high tendency to cross-linking, a high concentration of cross-links and their chemical structure give rise to a more perceptible effect.

The temperature range in which elastomers exhibit their specific properties is of the order of $4 \cdot 10^2$ K. During heating of an elastomer, many physical transformations and chemical reactions can be observed (Table 1). In principle a loss of elasticity may be due to a transition into a glassy state, crystallization, cross-linking, degradation, depolymerization, or destruction; here only the four last reactions are taken into consideration. In practice, unlike other kinds of polymers, two or even three different rubbers are often mixed together. A rubber mix as a rule contains solid-phase particles in the form of fillers, carbon black or mineral, and low molecular weight additives, i.e. softeners, cross-linking substances, accelerators, activators, pigments and others. It is no wonder that the thermal stability of such a complicated system is neither well defined nor investigated. In this paper a dependence between the structure and thermal stability of elastomers is discussed.

Methods of investigations

Heat effects and mass losses resulting from the reactions of elastomers may in principle be investigated by classical methods of thermal analysis, i.e. DSC, DTA, TG and DTG. However, reactions occurring with a relatively low heat effect, in the range of several mJ/mg, could involve deep changes in the structure and properties of elastomers. Hence, a sensitive apparatus should be employed or high mass samples should be used. The second solution of the problem is rather inadvisable, for it increases the probability of side-reactions. It happens that the heat effects of some reactions, e.g. cross-linking and degradation, to some extent compensate each other,

Table 1 Main thermal transitions of elastomers

Temp. rise	Transition or reaction	Heat effect
	Glassy transition	—
	Crystallization	exo
	Melting	endo
	Viscous flow	endo
	Modification	exo
	Cross-linking	exo
	Degradation	endo
	Depolymerization	endo
	Destruction	endo

and in such a case the usefulness of DSC and DTA is restricted. Similar difficulties are connected with the application of TG, for deterioration of elasticity may occur without any change or with as low as a few per cent of the sample weight. If unextracted vulcanizate is investigated in air atmosphere, i.e. under conditions that are important from a practical point of view, the results are influenced by the volatilization of low molecular weight components and by oxidation reactions. The 5 and 50 per cent losses of sample weight are often determined and treated as the basis for comparison of the thermal stability of polymers. However, for elastomers this criterion may be deceptive and should be used very carefully. The thermal properties of an elastomer could be evaluated better if DTA or DSC, TG and DTG methods are applied simultaneously. Nevertheless, in many cases only investigations carried out by complementary methods, e.g. gas chromatography, mass spectrometry, elemental and functional group analysis, sol-gel analysis, swelling measurements and others, allow interpretation of a thermal spectrum. As an example, in Fig. 1 the thermal curves of uncross-linked, acteone-extracted cis-1,4-polybutadiene are shown. The following five regions of thermal transition could be recognized (Table 2).

Table 2

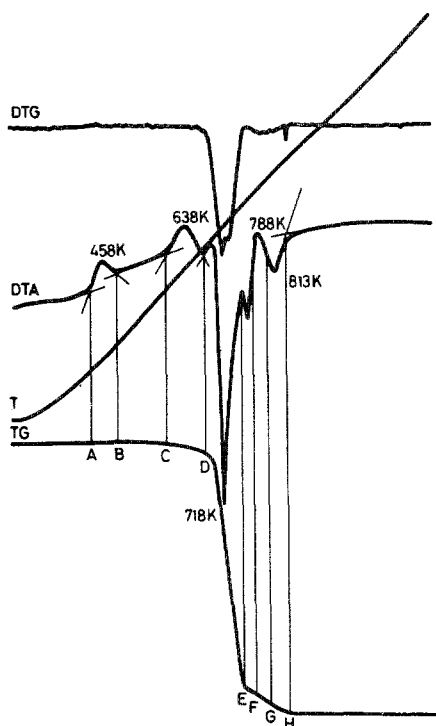| Region	Heat effect	Kind of transition
AB	exo	peroxide group formation, weak cross-linking
CD	exo	strong cross-linking, with symptoms of degradation and destruction
DE } EF }	endo	thermal destruction
FG	exo	cyclization, recombination of radicals, oxidation of a solid residue
GH	endo	desorption of destruction and combustion products

Fig. 1 Thermal curves of uncross-linked, acteone-extracted cis-1,4-polybutadiene

Thermal curves of other elastomers, though similar in general form to those shown in Fig. 1, usually give evidence of specific features. Especially noteworthy are the transitions occurring in the regions AB, CD and DE. They are of a fingerprint character and may be used for analytical purposes. In principle on the basis of thermal analysis and complementary investigations the point "D" could be acknowledged as the top limit of thermal stability of an elastomer. Nevertheless, throughout the region AD deep changes in elastomer structure and properties are usually observed. As a result of the intense decomposition of a sample in the region DE, a considerable amount of volatile substances is generated, which is of special importance from the point of view of the ability of elastomers to undergo ignition and combustion. If thermal analysis is carried out in an inert atmosphere, the exothermic peaks AB, CD and also FG diminish or even disappear [1]. The changes depend on the nature of the elastomer and on the concentration of functional groups in its macromolecules.

At the same time, point D shifts toward higher temperature and the rate of sample decomposition in the region DE is lowered. The thermal spectrum of an elastomer is also influenced by the sample weight and heating rate; only results obtained under exactly the same conditions are mutually comparable.

3

Dependence between structure and thermal stability of elastomers

1. Uncross-linked elastomers

Several features of an elastomer backbone should be taken into consideration. The data characterizing different but commonly used elastomers are collected in Table 3. To improve the thermostability of polymers, high-energy chemical bonds are usually built into their macromolecules. In the typical carbochain elastomers, the energy of single C–C bonds varies between about 244 and 324 kJ/mol. In the skeleton of a macromolecule "weak links" could occur, introduced, for example, in the form of foreign monomer units, residues of an initiator, configurational and other defects [4, 5]. The allylic bonds between monomer units in polydienes could be treated as "weak links".

The energy of such bonds is lowered by 50 to 67 kJ/mol, as a result of a coupling effect, in comparison to sp^3–sp^3 carbon–carbon bonds in polyolefins. They therefore split off first, which favours the depropagation reaction. The thermal stability of elastomers was investigated by derivatography (in air), DSC (in nitrogen) and complementary methods; the results are given in Table 4. From the data of Tables 3 and 4 it follows that no simple correlation exists between the bond energy and the thermal stability of elastomers. Rather surprisingly, a low concentration of unsaturated monomer units, and therefore also of allylic bonds in isobutylene-isoprene copolymer, increases their thermal stability somewhat, in comparison to that of isobutylene homopolymers. The presence of such a species increases the yield of branching and gel formation in comparison to the degradation of chains [6].

The molecular weight of an elastomer has a positive, though not very pronounced effect on its thermal stability, as measured by T_{max} and E_A. On the other hand, the coefficient of degradation P increases with the molecular weight. The probability that a chain will break as a consequence of thermal fluctuations is the greater,

Table 3 Parameters of elastomer structure

Elastomer	Monomer units, weight %	$\bar{M}_v$	$e_{coh},$ MJ/m^3	$\left(\dfrac{\bar{r}^2}{\bar{r}_0^2}\right)^{1/2}$	$E_b,$ kJ/mol
Cis-1,4-polybutadiene, SKD II	94 cis-1,4	397.800	288.6	1.70	252
Cis-1,4-polyisoprene, Cariflex IR 307	92 cis-1,4	416.000	274.9	1.70	252
Butadiene–styrene rubber, Ker 1500	23.5 styrene	437.400	335.6	1.84	252, 254
Butadiene–akrylon rubber, SK N 26	26 akrylon	245.000	432.1	2.05	252
Polyisobutylene, liquid	100 head to tail	28.300	251.5	2.20	283.9
Polyisobutylene, Oppanol B 100		984.000	251.5	2.20	283.9
Polyisobutylene, Oppanol B 200		2726.000	251.5	2.20	283.9
Butyl rubber, ESSO Butyl 325	2.5 isoprene	297.000	251.5	2.19	252, 283.9

$\bar{M}_v$ = viscosity average molecular weight, e_{coh} = cohesive energy density [acc. to 2], $\bar{r}$, $\bar{r}_0$ = mean distance between ends of a chain, unperturbed and freely jointed [acc. to 3], E_b = energy of C–C bond, the weakest one in the skeleton of a chain [acc. to 2].

the higher the number of bonds in its skeleton. It seems that some role is played by the tension resulting from the thermal contraction of entangled chains. The thermal stability of elastomers is not or only slightly influenced by the flexibility of their chains and intermolecular interactions (Tables 3 and 4). Both of these parameters are of great importance in the case of other groups of polymers, e.g. those of ladder type, strongly cross-linked chemically or through hydrogen-bonds [7]. The mechanism of thermal degradation and destruction of elastomers has some specific features. Cleavage of a main chain generates two macroradicals which in principle may undergo primary recombination. However, the probability of such an event in the case of unfilled elastomers is rather low, owing to the high mobility of macro-radicals. A cage effect does not in general play an important role, therefore, unless the macroradical mobility is restricted, e.g. as a result of adsorption on a surface of active filler or cross-linking. This conclusion is testified to by the lack of a correlation between the parameters $(\bar{r}^2/\bar{r}_0^2)^{1/2}$, e_{coh} and E_b (Table 3) and T_{max}, E_A and P (Table 4). On the other hand, a very distinct dependence appears between the thermal stability and cross-linking ability of an elastomer. Of the elastomers investigated, cis-1,4-polybutadiene and butadiene—styrene rubber are especially thermostable. Their specific feature is cross-linking occurring through the thermally initiated polymerization of butadiene monomer units. A macroradical generated in the matrix of such an elastomer is immediately trapped and stabilized.

Table 4 Thermal stability of elastomer

Elastomer	T_{max}, K	E_A, kJ/mol		Coefficient	
		air	N_2	degrad. P	cross-link. $1/Q$
Cis-1,4-polybutadiene, SKD II	638	286.8	344.6	—	0.57
Cis-1,4-polyisoprene, Carifax IR 307	533	95.7	123.0	3.62	—
Butadiene—styrene rubber, Ker 1500	633	265.0	327.0	—	0.12
Butadiene—akrylon rubber, SK N 26	628	163.4	—	—	1.56
Polyisobutylene, liquid	503	73.3	—	1.13	—
Polyisobutylene, Oppanol B 100	533	84.6	154.1	2.01	—
Polyisobutylene, Oppanol B 200	533	96.2	—	2.69	—
Butyl rubber, ESSO Butyl 325	548	105.1	221.1	2.19	—

T_{max} = temperature of peak maximum in DTA curve in air atmosphere in CD region, $P = \bar{M}_{v,0}/\bar{M}_v$, ratio of viscosity av. molec. weight, before and after degradation, $1/Q$ = reciprocal value of equilibrium swelling.

2. Vulcanizates

Vulcanization is a process mainly involving the cross-linking of an elastomer. This reaction is usually accompanied by the modification, isomerization and cyclization of its chains. The structures of the cross-links may be quite different, depending on

3*

the kind of cross-linking substances used. In practice, we first have to consider net-works containing C—C or sulphidic cross-links. In the latter case the number of sulphur atoms per cross-link may range from 1 to 6. Some sulphur is usually bonded intra-molecularly in the form of thiol or sulphidic groups or residues of accelerators [8, 9]. The concentration of cross-links is low; on average it is 1 per 100 monomer units. There are some discrepancies concerning the energy of polysulphidic cross-links, but there is no doubt that they are more labile than other kinds of cross-links and bonds in the skeleton of carbochain elastomers. Even among monosulphidic cross-links, for example, marked differences of thermal stability can be detected [10]. Generally speaking cross-linking increases the thermal stability of an elastomer, but this effect depends strongly on the nature of the cross-links. For instance, in the case of poly-sulphidic cross-links, as a result of their thermal dissociation and further transforma-tions, degradation too may be initiated as additional cross-linking could occur. Because of the relatively low concentration of cross-links, their thermal transformation can hardly (if at all) be detected by DSC or DTA methods; rather the effects of post-reactions are observed. Nevertheless, it is fairly well established that the thermal stability of elastomers depends not only on the cross-link density, but also on their chemical structure [11—14]. This dependence is observed even in the case of special fluoroelastomers [15].

3. Effect of oxygen

Most types of general-purpose elastomers, e.g. homopolymers and copolymers of dienes, are reactive toward oxygen. In the first step, mainly hydroperoxides are formed, probably as a result of singlet oxygen ($^1O_2$, $^1\Delta_g$) attack on methylene groups of diene monomer units [14]. This reaction manifests itself as an exothermic peak in the AB region in the DTA or DSC curve (Fig. 1). Thermal decomposition of unstable peroxide groups initiates the degradation or cross-linking of an elastomers. Both reac-tions could occur simultaneously. In the case of homo- and copolymers of butadiene cross-linking prevails initially, while polyisoprene undergoes scission from the begin-ning. Further oxidation of polydienes leads to deep changes in the structure of their macromolecules and the evolution of low molecular destruction products [17, 18].

Saturated elastomers or those containing only a small amount of diene monomer units, e.g. butyl rubbers or ethylene—propylene—diene terpolymers, are not attacked so easily through oxygen and therefore do not exhibit an exothermic transition in the AB region [3, 6]. Some kinds of cross-links, e.g. sulphidic cross-links, are very reactive toward oxygen. In the first step, sulphoxides and thiosulphinates of the structure $R'S(O)R''$ and $R'SS(O)R''$ are probably formed, where R' and R'' denote residues of elastomer chains. These species are subsequently transformed to sulphenic or thiosulphoxylic acids, which can basically play the role of antioxidants catalyzing the decomposition of hydroperoxides [10, 11]. However, their efficiency is rather low because of the formation of stable complexes with sulphoxides and antagonistic effects toward conventional antioxidants [11]. For this reason it is somewhat difficult to protect against oxidation in the case of elastomers containing a high level of chemi-

cally bonded sulphur. Nevertheless, the exothermic reaction in the AB region, connected with the formation of hydroperoxides in many cases, could be suppressed by the addition of antioxidants. Especially active are derivates of aromatic diamines, e.g. disubstituted p-phenylenediamine [19]. They act as quenchers toward singlet oxygen and as free radical scavengers. In the CD region macroradicals are formed as a result of the thermal splitting of chains or cross-links. Both initiate exothermic oxidative reactions. Because of the mechanism of initiation and the high temperature at which these events occur, in this region conventional, low molecular weight antioxidants exhibit low activity. Macromolecular antioxidants or chains grafted onto an elastomer should therefore be used.

Elastomer destruction in the region DF is endothermic, even in an air atmosphere. The products of destruction are undoubtedly partially oxidized, but the concentration of oxygen in the reaction zone is controlled by its diffusion and is evidently insufficient under the conditions of analysis [20]. The mechanism and kinetics of low molecular weight hydrocarbon evolution are of importance from the point of view of the flammability of an elastomer.

References

1 A. K. Sircar and T. G. Lamond, Rubber Chem. Technol., 45 (1972) 329.
2 D. W. van Krevelen, Properties of Polymers, Elsevier, Amsterdam, 1976.
3 Enciclopedia of Polymers, Soviet. Enciclop., Moscow, 1972, vol. 1, p. 618.
4 C. C. Cameron and G. P. Kerr, Europ. Polym. J., 4 (1968) 709.
5 N. Grassie and R. Mc. Guhan, Europ. Polym. J., 7 (1971) 1091, 1357.
6 L. Ślusarski and G. Janowska, J. Thermal Anal., 19 (1980) 435.
7 L. Reich and S. Stivala, Elements of Polymer Degradation, McGraw-Hill Book Co., New York, 1971, p. 299—301.
8 T. D. Skinner, Rubber Chem. Technol., 45 (1972) 182.
9 F. K. Lautenschlaeger, Rubber Chem. Technol., 52 (1979) 213.
10 G. P. Mc Sweeney and N. J. Morrison, Rubber Chem. Technol., 56 (1983) 337.
11 D. Barnard, M. E. Cain, J. I. Cunneen and T. H. Houseman, Rubber Chem. Technol., 45 (1972) 381.
12 J. R. Shelton, Rubber Chem. Technol., 47 (1974) 949.
13 J. R. Shelton and E. R. Harrington, Rubber Chem. Technol., 49 (1976) 147.
14 L. Ślusarski and G. Janowska, J. Thermal Anal., 29 (1984) 95.
15 U. Flisi, G. Giunchi and S. Geri, Kautschuk Gummi, 29 (1976) 118.
16 J. Carlsson and D. M. Wiles, Rubber Chem. Technol., 47 (1974) 991.
17 Z. Jedliński and A. Jarich, Roczniki Chemii, 40 (1966) 1639; ibidem 41 (1967) 1311; ibidem 41 (1967) 1931.
18 J. L. Morand, Rubber Chem. Technol., 50 (1977) 373.
19 W. R. May, L. Bsharah and D. B. Merrifiels, Ind. Engn. Chem. Prod. Res. Develop., 7 (1968) 57.
20 K. Ono, A. Kaeriyama and K. Murakami, Rubber Chem. Technol., 50 (1977) 43.

Zusammenfassung — Thermische Umwandlungen von Elastomeren werden klassifiziert und mit der Stabilität von Elastomeren zusammenhängende Probleme diskutiert. Es wird gefolgert, daß bei Elastomeren für allgemeine Verwendungszwecke keine einfache Korrelation zwischen der Energie

der Bindungen im Kettengerüst und der thermischen Stabilität besteht. Das gilt auch für die Parameter der physikalischen Struktur der Ketten. Der Effekt einer starken Neigung zur Vernetzung, der Netzwerkdichte und der chemischen Konstitution der Netzwerkbrücken ist dagegen augenscheinlicher.

Резюме — Представлена классификация термических переходов эластомеров и обсуждены проблемы их устойчивости. Сделано заключение, что в случае эластомеров общего назначения не существует прямой корреляции между энергией связей в остове цепи и термоустойчивостью. Такой же вывод справедлив и для параметров физической структуры цепей. Высокая тенденция к образованию поперечных связей, большая концентрация таких связей и их химическая структура, оказывают более заметное влияние.