

THERMAL CHARACTERIZATION OF NITRILE BUTADIENE RUBBER (NBR)/PVC BLENDS

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Nitrile butadiene rubber (NBR) and NBR/PVC blends were produced using 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) or not as antioxidant. Controlled ozone degradation was performed in several samples. Thermal, compositional and morphological analysis was performed by means of differential scanning calorimetry, thermogravimetry, chemical analysis and scanning electron microscopy. Thermogravimetry analysis shows four mass loss processes related to plastizicer, complex rubber degradation and metallic oxides and other additives. In NBR (NBR/PVC blends) the onset temperature of the first degradation process varies between 227–231°C (259–262°C) and the apparent activation energy between 26 and 36 kJ mol⁻¹ (36–57 kJ mol⁻¹), the NBR/PVC samples non degraded presents the higher thermal stability.

Keywords: degradation, NBR, NBR/PVC, TG

Introduction

Polymer blends are considered as mixtures of macromolecular species. Blending of two or more polymers for property improvement and economic advantage has gained considerable importance. A large number of polymer blends has been proposed for commercial purpose [1–3]. Usually, the amount of minor component must exceed at least 4–5 mass%. Rubber blends based on natural rubber as well as PVC blends are extensively used in several potential applications [4, 5]. During last years several works were performed on butadiene rubber (BR) with poly(vinyl chloride) PVC blends, analyzing different aspects like the interfacial reaction and the cross-linking behavior [6], the thermally induced decomposition [7] or the characteristics of several ternary blends [8].

This work focuses on the thermal characterization of polymer blends that consist in a mixture of nitrile butadiene rubber (NBR)–PVC (17 mass%). The mixtures were produced in laboratory conditions. Different additives were added to the base material as adhesives, plasticizers, antioxidant. Furthermore, blends were subjected to controlled degradation.

Experimental

Materials and methods

NBR and NBR/PVC blends formulation and production is described in [9]. The manufacture of this com-

posite material was performed in five steps: *i*) rubber plasticization in a roller mixer (15 min), *ii*) incorporation of additives (SiO₂) and plasticizer (DOP) (90 min), *iii*) activator incorporation (ZnO) (20 min), *iv*) incorporation of the vulcanization agent (S), primary and secondary vulcanization process accelerants, mercaptobenzothiazols (MBTS) and diphenyl guanidine (DPG) and the optional addition of a chemical agent to prevent degradation (30 min) and finally, *v*) the final blended sample was performed by controlled hot pressing, at 2 MPa and 170°C during 15 min. The main difference is the addition or not of 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (2.2%) as antioxidant agent during step *iv*). It is well known that antioxidants affect to the thermal stability of natural rubber [10]. When the process was finished, the samples extraction of the press was performed using the normative UNE 53 509. Ulterior controlled degradation was performed in an OREC-0500 chamber using the normative ISO 1431/1 1989.

Thermal treatments were performed by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). DSC analysis was conducted using a Mettler TA4000 thermoanalyzer coupled with a low temperature DSC30 calorimeter to determine the glass transition temperature. TG was performed in a TG/SDTA851 Mettler Toledo equipment at different heating rates to obtain the activation energy of the first (low temperature) degradation process. Temperature range is from –150 to 200°C, typical values of the glass transition temperature of NBR varies be-

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tween -70 and -50 , and 85°C for PVC [9, 11]. The microstructure of samples was characterized by scanning electron microscopy (SEM) in a Zeiss DSM 960 device. Samples were sputtered previously with a K550 Emitech equipment. Resolution was 4.5 nm , acceleration voltage was 15 kV , and working distance was between 15 and 25 mm . Chemical analysis was performed to check the C, H, N, S content and to control the final PVC percentage.

Results and discussion

The glass transition temperature; T_g , of the samples was analyzed using heat flow DSC. The experiments were performed under synthetic air atmosphere (flow rate 30 mL min^{-1}). Figure 1 shows DSC scans of several samples and Table 1 the T_g values. The wide temperature range and shape of the glass transition are difficult in accurate temperature measurement. Nevertheless, it is possible to establish that the degraded samples present lower values. Likewise, the NBR/PVC blends have also lower T_g , strong result because PVC and NR is a miscible system [12].

The thermal degradation was studied in order to evaluate the thermal stability and kinetic parameters such as activation energy [13]. The TG scans of the

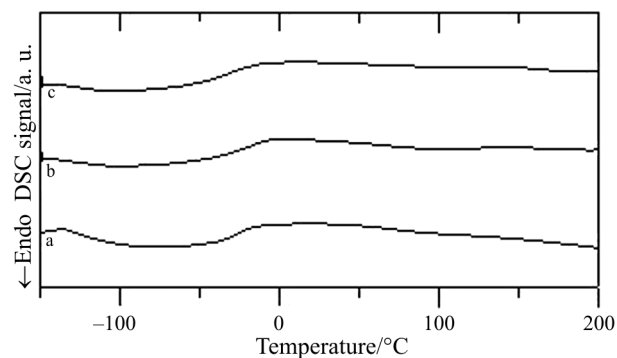


Fig. 1 DSC scans of: a – NBR, b – NBR/PVC+antioxidant and c – degraded NBR/PVC+antioxidant

Table 1 Characteristic temperatures and apparent activation energies obtained from DSC and TG scans

Sample	Antioxidant	$T_g/^\circ\text{C}$ (DSC)	$E_a/$ kJ mol^{-1}	$T_0/^\circ\text{C}$ (TG)
NBR	N	-41	31	227
	Y	-62	36	230
degraded NBR	N	-18	26	224
	Y	-31	28	231
NBR/PVC	N	-52	55	261
	Y	-57	57	262
degraded NBR/PVC	N	-34	36	259
	Y	-46	48	262

different samples indicate, in all samples, mass losses related basically with the complex degradation of rubber and the different additives used. Figure 2 shows the mass loss during heat treatment in air atmosphere of degraded NBR. In all NBR samples the overall mass loss can be divided into four stages, as well shown by the derivative of the thermogravimetry curve, labeled as DTG. The first mass loss that occurs at about 230°C and it is attributed to the DOP plasticizer and other low temperature volatile components [14]. The second and third are associated to complex rubber decomposition influenced by the different additives. During the second degradation, oxidation, cross-linkage and chain scission may occur at the same time, and the main reaction may be oxidation and cross-linkage. In this case, mass loss is slower [15]. During the third process, the main reaction is oxidative degradation and obvious the main mass loss occurs. Complementary information about the four processes is given in the DTA curve, the last process presents the higher ΔT . Figure 3 corresponds to TG scans of degraded NBR/PVC blend. In this samples, the first process begins at higher temperature (about 260°C) and the main loss of the second process is lower. Furthermore, the last process can probably be associated to inorganic metallic oxides and begins at higher temperatures.

The combination of high onset temperature and activation energy of the first degradation process is a good reference of the thermal stability of the material, Table 1. The onset temperature is measured in samples heated at 10 K min^{-1} and activation energies calculated from peak temperature of experiments at different heating rates: 2.5 , 5 , 10 , 20 and 30 K min^{-1} . The apparent activation energies associated with the first

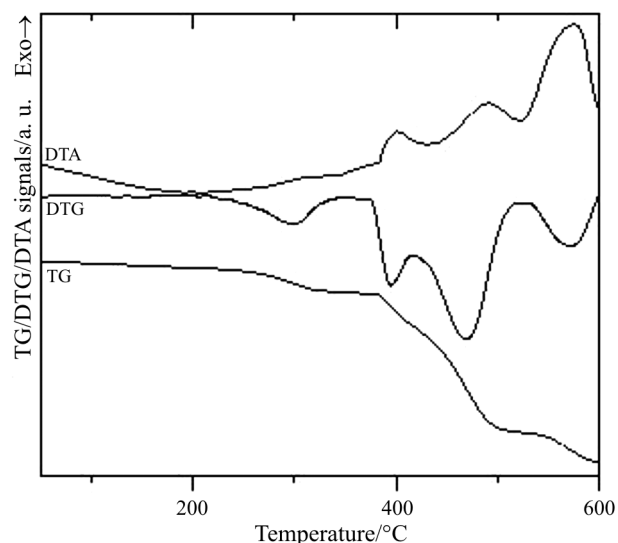


Fig. 2 TG scan at 10 K min^{-1} of degraded NBR as well as their DTG and DTA

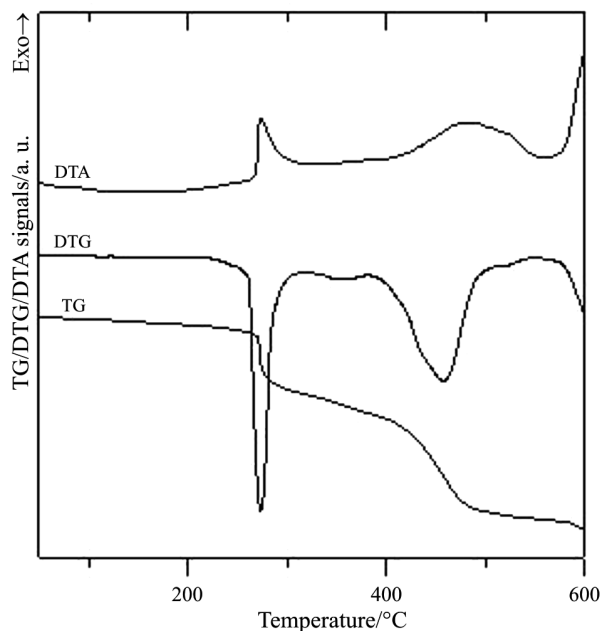


Fig. 3 TG scan at 10 K min^{-1} of degraded NBR/PVC as well as their DTG and DTA curve

degradation processes were determined using the Kissinger method [16]. From DSC and TG scans, we can state that NBR/PVC samples present higher thermal stability than NBR samples. Furthermore, the antioxidant selection modifies the thermal behavior and working interval temperature of the mixtures defined as the interval between the glass transition and initial decomposition temperature. Likewise, parameters as heating rate or atmosphere influence the degradation processes [17].

As shown in previous works [18, 19], the addition of PVC or polymer compounds containing Cl produce a significant increase of the thermo-oxidative stability of NBR front to ozone or other oxidative atmospheres. The main causes can be related to: *i*) the PVC have not double bonds susceptible to the ozone attack. PVC addition reduces the butadiene concentration in the blend and the possibility of the O_3 reaction, *ii*) the electronegativity of Cl atoms provokes a steric effect and an electrostatic repulsion protecting the butadiene groups from ozone. The ozone is electrophilic and their reactivity decreases in the presence of atoms receptors of electrons. Furthermore, the higher volume of the Cl atoms produces an effective protection even when for low PVC concentrations.

SEM micrographs show minor changes due to induced degradation or antioxidant addition. As an example, Fig. 4 shows the micrographs corresponding to degraded NBR (up) and NBR/PVC (down) blends without antioxidant. Ulterior study of the mechanical properties is needed to determine the influence of PVC addition in the elastic rubber behavior.

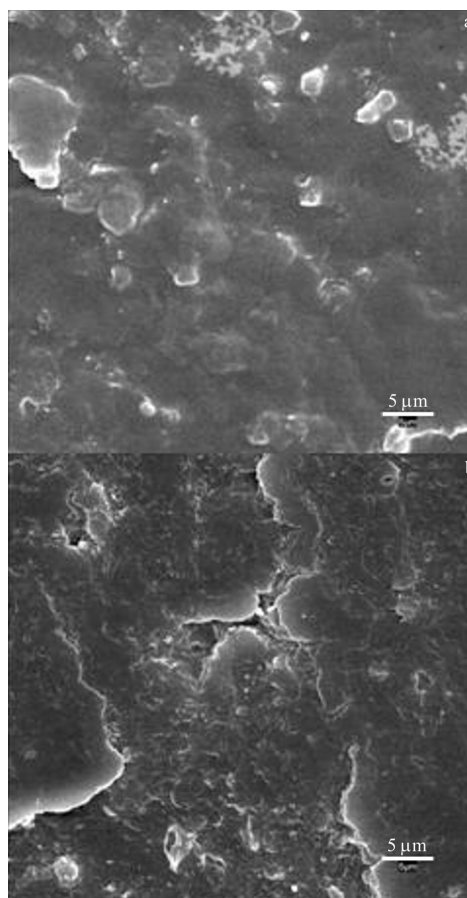


Fig. 4 SEM micrographs corresponding to degraded: a – NBR and b – NBR/PVC

Table 2 Chemical analysis: C, H, N and S average mass content (%) in the NBR and NBR/PVC blends

Samples	N	C	H	S	rest
NBR	5.33	61.97	7.70	0.93	24.06
NBR/PVC	3.74	54.99	6.91	0.97	33.06

Chemical analysis is similar in all NBR or NBR/PVC samples. In Table 2, the average values are given. The difference in the rest column can be associated to the Cl of the PVC. The calculus allows us to state that the Cl is present in 16.4 ± 0.7 mass%, close value to the 17% of the formulation.

Conclusions

Thermogravimetry analysis shows mass losses related basically with the complex degradation of rubber and the different additives used. The first mass loss is mainly attributed to the DOP plasticizer. During the second complex rubber degradation, oxidation, cross-linkage and chain scission probably occur at the same time, and the main reaction may be oxidation and

cross-linkage. In the third process, the main reaction is oxidative degradation, and obvious the main mass loss occurs. The last process is associated to inorganic metallic oxides. From DSC and TG scans the NBR/PVC samples present higher thermal stability than NBR samples because onset temperature and activation energies of the first degradation process are higher. This higher stability is related to Cl electronegativity and size as well as to the no presence of double bonds in PVC. Furthermore, blends with the antioxidant TMQ presents higher thermal stability.

Acknowledgements

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