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EFFECT OF METAL IONS ON THE THERMAL DEGRADATION OF CHLORO PHOSPHORYLATED NBR

Abel M. Maharramov[1], Abdulsaid A. Azizov[1], Ofeliya O. Balayeva[1]*, Rasim M. Alosmanov[1], Mustafa B. Muradov[2], Irada A. Buniatzade[1]

[1]Department of Chemistry, Baku State University, Baku, Azerbaijan
[2]Department of Physics, Baku State University, Baku, Azerbaijan

Abstract. The thermal analysis of nitrile butadiene rubber (NBR), functionalized nitrile butadiene rubber (FNBR) and transition metal ions containing functionalized nitrile butadiene rubber (Me-FNBR) were carried out under argon flow (50 mL/min) at three different heating rates of 3;5;10ºC/min. The starting temperature was 26 °C and the final temperature was 900°C and 950°C for initial and modified polymers, respectively. Effect of functional groups, metal ions and organic solvents on the thermal degradation of polymers has been discussed in detail.

Keywords: *functional groups, Polymer sorbent, Thermal degradation, TG, DTA*

Corresponding Author: *Ofeliya O. Balayeva, Department of Chemistry, Baku State University, Z. Khalilov str., 23, AZ1148 Baku, Azerbaijan, Tel.: +994558345043, e-mail: ofeliya1989@inbox.ru oobalayeva@gmail.com*

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1. Introduction

Thermal analysis is an important branch of materials science is carried out under an inert gas (e.g. nitrogen and argon) or in the air. Thermal behavior of some phosphorus- and phosphorus/ nitrogen-containing functional polymers synthesized by either hydrolysis or aminolysis and alcoholysis reaction of PChBR was investigated in our provious work (Alosmanov *et al.*, 2017). It was indicated that thermal degradation of the polymers depends on the nature of the functional groups attached to polymer backbone (Alosmanov *et al.*, 2017).

Derivatized poly (styrene-co-divinylbenzene) resins have been prepared from the commercial crosslinked polystyrene by the aromatic electrophilic substitution reaction using $PCl_3/AlCl_3$ or $PCl_5/AlCl_3$, followed by base-promoted hydrolysis (Santa Maria *et al.*, 2008). The modified copolymers have presented higher thermal stability than unmodified one, showing that the introduction of phosphinic or phosphonic acid groups modifies their kinetic pathways (Santa Maria *et al.*, 2008).

There are many investigations about the thermal characterizations of functional polymers (Janowska *et al.*, 2010; Yang *et al.*, 2014; Zhang *et al.*, 2012). In this paper, we present a thermal study of nitrile butadiene rubber (NBR), functionalized nitrile butadiene rubber (FNBR) and transition metal ions containing functionalized nitrile butadiene rubber (Me-FNBR). Effect of heating rate, functional groups of polymers, metal ions and organic solvents on the thermal degradation of polymers has been discussed in detail.

2. Experimental

All chemicals (PCl_3, NaOH, $Pb(NO_3)_2$; $ZnSO_4 \times 7H_2O$; $CdCl_2 \times 2.5H_2O$; $CuSO_4 \times 5H_2O$) were of analytical grade. NBR-26 was purchased from Voronezh Synthetic Rubber Manufactory (Russia). Differential thermal analysis and thermogravimetric analysis were recorded by NETZSCH leading TA using STA449 F3 Jupiter program. Inductively coupled plasma-optical emission spectrometry (ICP-OES) Optima 2100 DV (Perkin Elmer) have been used for the determination of metal ions in the solution.

2.1. Synthesis of F^1NBR and F^2NBR

FNBR containing -$PO(OH)_2$ and -$OPO(OH)_2$ functional groups were synthesized by the oxidative chlorophosphorylation reaction of NBR-23 with PCl_3 and oxygen (Balayeva *et al.*, 2016; Alosmanov *et al.*, 2011). $CHCl_3$ and CCl_4 solvents were used to prepare the F^1NBR and F^2NBR, respectively. The reaction temperature was increased to 45 ºC. F^1NBR and F^2NBR were synthesized from the homogenius and heterogenious medium, respectively.

F^1NBR and F^2NBR functional acid group polymer sorbents has been synthesized using different solvents like $CHCl_3$ and CCl_4, respectively.

2.2. Sorption of Na^+, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} ions by F^2NBR

30 ml 10^{-3} M of water solutions of $Pb(NO_3)_2$; $ZnSO_4 \times 7H_2O$; $CdCl_2 \times 2.5H_2O$; $CuSO_4 \times 5H_2O$; $NiSO_4 \times 7H_2O$ has been prepared for the sorption. 0.1 g of polymer sorbent was added to each solution. The prepared samples were filtered after 24h and air dried for the further thermal analysis. Each filtrate has been analyzed by the ICP Optima using the WinLab32 software.

3. Results and discussion

3.1. Study of the sorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions by FNBR

ICP-OES has been used for the determination of metals in solution. The results obtained during the experiment indicate that the F^1NBR and F^2NBR can be used for separation of Cd^{+2}, Zn^{+2}, Pb^{+2} and Cu^{+2} ions from the solution. According to the table, we can demonstrate the sorption of metal ions as below:

$$Cd^{+2} > Zn^{+2} > Pb^{+2} > Cu^{+2}$$

Table 1. Sorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions by FNBR.

Salts	Quantity of Me^{2+} ions in solution		
	Before the sorption C_i (mmol/l)	After the sorption (Me-F^1NBR) C (mmol/l)	After the sorption (Me-F^2NBR) C (mmol/l)
$ZnSO_4 \times 7H_2O$	0,0504	0.0027	0.0069
$CdCl_2 \times 2.5H_2O$	0.1634	0.0072	0.0141
$CuSO_4 \times 5H_2O$	0.0084	-	-
$Pb(NO_3)$	0.0359	0.0005	0.0005

3.2. Thermogravimetric analysis of NBR, F^1NBR, F^2NBR, Na-F^1NBR, Cd- F^1NBR,Zn- F^1NBR

From Fig. 1 it can be seen that, there are not chemical changes in the material during the initial period of the thermal analysis of NBR. It is obvious that, in this process the phase change (the softening of the material) has been found. From the thermal analysis of the NBR the TG and DTG curves show that, by increasing temperature the following processes occur in the materials.

1. The phase change (melting or softening) at about 150-200 °C;
2. Significant change in the mass;
3. Further fragmentation of the material.

The temperature corresponding to the chemical stability is ~30-150ºC. According to the TG curve (Fig. 1) the initial polymer (NBR) was exposed to a one-step thermal destruction and 93.76% lost of the mass at 560ºC.

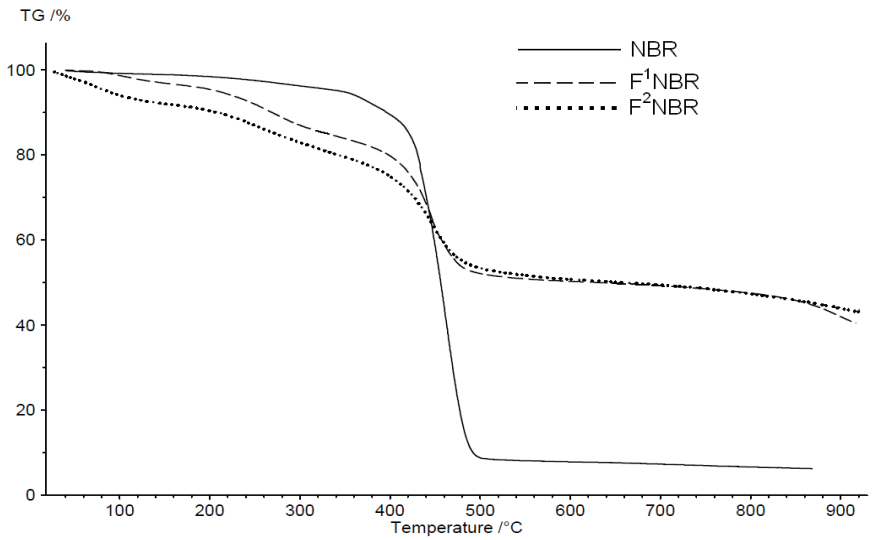

Figure 1. TG curves of the NBR-26, F^1NBR and F^2NBR at 10ºC /min heating rate.

Due to the fact that, the structure and properties of the polymer has changed dramatically after the modification, the thermal stability of the polymer increases (Fig.1). According to the TG and DTG curves, thermal destruction of F^1NBR and F^2NBR occurs in three stages. The mass loss of F^2NBR was 7.88% at 155ºC and 20.76% at 350ºC. There is a sharp decline above 350 ºC indicates the weight loss of the polymer. The mass loss was 50.07% at 630 ºC. The total mass loss was 57.03% at 870ºC and 59.77% at 930ºC for F^1NBR and F^2NBR respectively. From the results of the thermal analysis, it seems that after modification the chemical and thermal properties of the polymer have been changed sharply. In the first step of thermal destruction the evaporation of water has been occurred. The second-stage destruction occurred mainly in the functional groups. We could explain the second step destruction by the dehydration process within the- $PO(OH)_2$ functional groups of the polymer formed after the modification (Alosmanov *et al.,* 2017). Eventually, the third step destruction observed in DTG curve is explained by the polymer chain degradation. Compared with initial modification (FNBR), there is a sharp contrast has occurred in Na-FNBR complex according to TG and DTG curves (Fig. 2). The two-step destruction in the Na-FNBR complex can be explained by the fact that after the sorption the Na+ ions are

completely replaced by hydrogen in the OH groups, which are present in the polymer -$PO(OH)_2$ functional groups. Thus, the dehydration in the second step is not observed here. The DTG curve of the complex Na-FNBR indicated a double step decomposition between 220 ºC and 650ºC with a rapid weight loss.

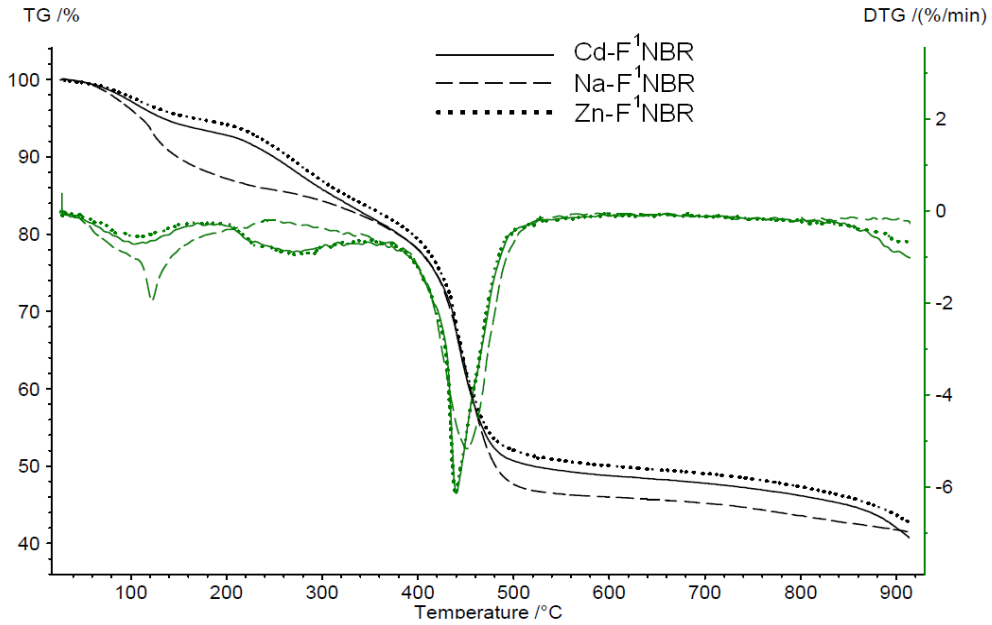

Figure 2. TG and DTG curves of the Na-F^1NBR (A), Cd- F^1NBR (B), Zn- F^1NBR (C) at 10 ºC /min heating rate

According to the TG and DTG curves, three-step thermal destruction occurs in Cd-F^1NBR and Zn-F^1NBR. There three-step destruction could be explained that, after the sorption, Cd^{2+} and Zn^{2+} ions are not completely replaced by hydrogen in the OH groups, which are present in the polymer -$PO(OH)_2$ functional groups. The total mass loss of Cd-F^1NBR and Zn-F^1NBR was 60.03% and 57.79% at 930ºC, respectively.

4. Conclusion

F^1NBR and F^2NBR functional acid group polymer sorbents has been synthesized using two different solvents like $CHCl_3$ and CCl_4, respectively. Due to the fact that, the structure and properties of the polymer has changed dramatically after the modification, the thermal stability of the polymer increases. According to the TG and DTG curves the initial polymer (NBR-26) indicates a one-step, Na-FNBR two-step and F^1NBR, F^2NBR, Cd-F^1NBR and Zn-F^1NBR three-step thermal destruction.

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