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# THERMAL BEHAVIOUR OF PVC/POLY(MMA-CO-DVB) POLYMER SYSTEMS AND MEMBRANES BASED ON PVC/POLY(MMA-CO-DVB) SYSTEMS

*I. Alexandrova, K. Gjurova and G. Iordanov*

Prof. Dr. As. Zlatarov University, Bourgas, Bulgaria

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## Abstract

The thermal stabilities of PVC/poly(MMA-co-DVB) polymer systems and membranes prepared by the paste method were investigated. The thermoanalytical curves were used to determine the main thermal stage of the decompositions. It was found that the thermal properties of the polymer systems were affected by the divinylbenzene content. A membrane based on the PVC/poly(MMA-co-DVB) system with 5 mass% DVB displays thermal stability up to 210°C.

**Keywords**: membrane, PVC/poly(MMA-co-DVB) polymer systems, thermal analysis, thermal behaviour, thermal stability

## Introduction

In recent years, the interest in polymer – polymer blends has rapidly grown. The structure and the properties of such systems depend on the mode of their preparation.

In a previous paper [1], we reported the preparation of poly(vinyl chloride)/poly(methyl methacrylate) and poly(vinyl chloride)/poly(methyl methacrylate-co-divinylbenzene), PVC/PMMA and PVC/poly(MMA-co-DVB) systems by the radical polymerization and copolymerization of methyl methacrylate and divinylbenzene in polyvinyl chloride. The polymer systems obtained are highly promising materials for the preparation of ion-exchange membranes.

In this respect, it is important to know the thermal stabilities of the polymer systems obtained. Most of the relevant reports [2–7] related to the thermal and oxidative degradation of poly(methyl methacrylate) and some copolymers of MMA. Findings on the thermal properties of PVC/poly(MMA-co-DVB) systems have not been published.

In this paper, the thermal behaviour of PVC/poly(MMA-co-DVB) polymer systems and carboxylic membranes based on PVC/poly(MMA-co-DVB) systems is reported.

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## Experimental

### *Materials*

The poly(vinyl chloride) (PVC) was a product of Polychim. Devnia, Bulgaria (Devilit E-70 with $M_n=9\cdot10^4$ g mol$^{-1}$).

Methyl methacrylate (MMA) and divinylbenzene (DVB) were commercial products. The DVB was supplied by Koch-Light Laboratories Ltd and contained 54% of isomers of DVB.

Benzoyl peroxide (BPO) of reagent grade was used as initiator of the polymerization.

### *Preparation of polymer composition and membranes*

The PVC/PMMA and PVC/poly(MMA-co-DVB) polymer systems were prepared by the paste method. A monomer mixture consisting mainly of MMA or MMA and DVB was mixed with a fine powder of PVC to prepare a paste. The DVB content in the monomer mixture was varied from 2 to 10 mass/%. The concentration of BPO in the monomers was 2 mass%. This composite was placed between two cellophane films and heated at 373 K for 10 h to copolymerize the monomers. The powdery PVC was converted into a film gel.

Carboxylic membranes were prepared from PVC/poly(MMA-co-DVB) polymer systems with 5 mass% DVB by acid hydrolysis. This was carried out with glacial acetic acid at 353 K for 3 h. The membranes were used in H-form.

The PMMA and MMA-co-DVB copolymer were prepared by radical polymerization of MMA or copolymerization of MMA and DVB under the same polymerization conditions as for the polymer systems.

### *Method*

The thermal studies were carried out with an OD-102 derivatograph (MOM, Budapest). The DTA, DTG and TG curves were obtained under the following conditions: temperature range 20–600°C; heating rate 6 deg min$^{-1}$; sample mass 50±0.5 mg; in a medium of nitrogen (17 l h$^{-1}$). The activation energy of thermal degradation ($E_a$) and pre-exponential factor ($Z$) were calculated as in [8] and [9].

## Results and discussion

The thermal stabilities of the PVC/PMMA and PVC/poly(MMA-co-DVB) polymer systems and ion-exchange membranes prepared by the paste method were investigated. The results of the thermal analyses of the polymer composition and the corresponding homopolymers are presented in Fig. 1 and Table 1.

It can be seen from Fig. 1 that there is a small endothermic peak at 275°C in the DTA curves for PVC (curve 3) and at 370°C for the PVC/PMMA system (curve 2). When cross-linked PMMA was introduced into PVC, two endothermic peaks were

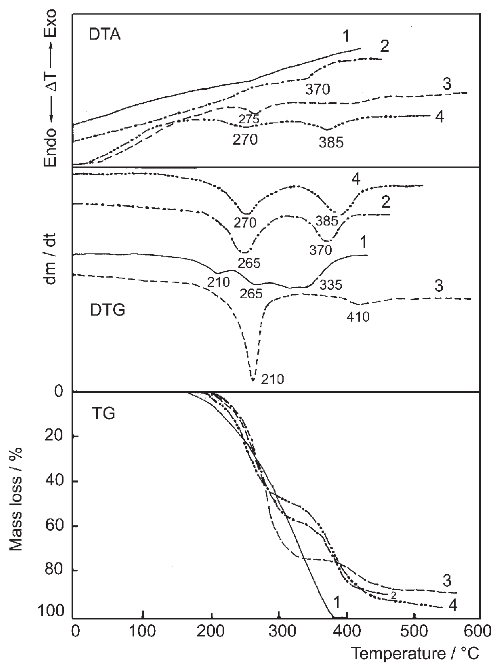

**Fig. 1** DTA, DTG and TG curves of 1 – PMMA; 2 – PVC/PMMA; 3 – PVC and 4 – PVC/poly(MMA-co-DVB) polymer systems

clearly detected in the thermal curve (curve 4) in the temperature range studied, at 270 and at 385°C. As compared with the PVC/PMMA system, there is an increase of 15°C, i.e. with DVB, the second peak is shifted to a temperature higher by 15°C. The TG and DTG curves exhibit two-stage degradation behaviour. The first stage of decomposition occurs up to 320°C. The maximum rate of decomposition (d*m*/d*t*) is observed at 265°C for the PVC/PMMA system (curve 2) and at 270°C for the PVC/poly(MMA-co-DVB) system (curve 4). At the same temperature (270°C), the PVC decomposition rate is expressed. The PVC loses 74% of its mass in the temperature region 200–320°C (TG, curve 3). The mass losses for the PVC/PMMA system (TG, curve 2) and the PVC/poly(MMA-co-DVB) (curve 4) system are 60 and 52%, respectively, i.e. 19 and 29% lower as compared with that for PVC. For PMMA (curve 1) the sample mass decreases by 60% up to 320°C. It was found that the mass loss for the MMA-DVB copolymer (5 mass% DVB) in this temperature region is 70%. This indicates that the decomposition of PVC occurred together with degradation of the MMA-DVB copolymer in the polymer system.

The second stage of decomposition starts at 325°C. The region of the maximum rate of decomposition is from 325 up to 425°C with, an endothermic peak at 385°C for the PVC/poly(MMA-co-DVB) polymer system (curve 1). In this stage, the decomposition of PVC continues, but the degradation of the poly(MMA-co-DVB) co-

**Table 1** Thermoanalytical results (TG/DTG curves) for all studied polymer systems

| Sample | Range 1/°C | | | Range 2/°C | | | Total mass loss up to 500°C/% |
|---|---|---|---|---|---|---|---|
| | a | b | c | a | b | c | |
| PVC/PMMA | 180–325 | 265 | 60 | 325–405 | 370 | 28 | 90 (410°C) |
| PVC/poly(MMA-co-DVB) with | | | | | | | |
| 2 mass% DVB | 185–325 | 270 | 52 | 325–410 | 385 | 38 | 95 |
| 5 mass% DVB | 190–330 | 270 | 52 | 330–440 | 385 | 40 | 95 |
| 10 mass% DVB | 195–325 | 265 | 42 | 325–410 | 385 | 46 | 91 |
| 15 mass% DVB | 170–325 | 263 | 42 | 325–415 | 380 | 48 | 94 |
| PVC | 200–320 | 270 | 74 | 320–462 | 410 | 16 | 95 |
| PMMA | 150–240 | 210 | 20 | 240–380 | 265 | | |
| | | | | | 335 | 80 | 100 (360°) |
| MMA-co-DVB copolymer with | | | | | | | |
| 5 mass% DVB | 180–385 | 320 | | | | | 100 (385°) |
| Carboxylic membrane | 215–325 | 250 | 36 | 325–420 | 370 | 68 | 94 (420°) |

a – Temperature range; b – Temperature of DTG maximum; c – Mass loss

polymer in PVC plays a dominant role. This decomposition stage is accompanied by a practically total mass loss for PMMA and the MMA-DVB copolymer up to 385°C.

The effects of DVB on the thermal stabilities of the polymer systems were also studied. The results obtained are presented in Figs 2 and 3 and Table 1.

It can be seen from Fig. 2, that two basic steps of decomposition are observed when the DVB content is varied from 2 to 15 mass%. It was found that the starting temperature of PVC decomposition and also the temperature of the maximum PVC decomposition rate decrease with increasing DVB content. Higher rates of decomposition were observed in the second stage when 10 or 15 mass% DVB was used. In these cases, the mass losses were 19 and 27% higher than those for the first stage of decomposition. This may be due to the fact that a more cross-linked MMA-DVB copolymer is formed in PVC and a less regular structure results.

Figure 3 reveals that an increase of the DVB content up to 15 mass% leads to increasing characteristic temperature $T_{50}$ (50% decomposition) in comparison with that for the PVC/PMMA system. This is not the case for $T_0$ (beginning) and $T_{10}$ (10% decomposition). The values of $T_0$ increase slightly up to 10 mass% DVB, while those of $T_{10}$ remain unchanged in this region of DVB content.

From the mass changes in the characteristic temperature range, the activation energy of thermal degradation ($E_a$) and pre-exponential factor ($Z$) were calculated for the temperature range 185–320°C. It was found that $E_a$ decreases from 108.6 to 81.9 kJ mol$^{-1}$ ($Z$ from $11.5\cdot10^7$ to $0.27\cdot10^5$) as the DVB concentration is increased up to 15 mass% DVB. The $E_a$ values are considerably higher than those for PMMA ($E_a$=30.2 kJ mol$^{-1}$; $Z$=0.29) and the MMA-DVB copolymer ($E_a$=63.7 kJ mol$^{-1}$;

$Z$=8.65·10$^2$). For the PVC/poly(MMA-co-DVB) system with 2 or 5 mass% DVB the values for $E_a$ are also higher than those for PVC ($E_a$=97.4 kJ mol$^{-1}$; $Z$=8.1·10$^6$) and the PVC/PMMA system ($E_a$=104.9 kJ mol$^{-1}$; $Z$=51.5·10$^6$). This correlates with the results from the TG curves. It indicates that the intermolecular interaction has an important role. MMA copolymerizes with DVB and the poly(MMA-co-DVB) copolymer formed in PVC may be grafted on PVC and may be entwined with the PVC chain [1].

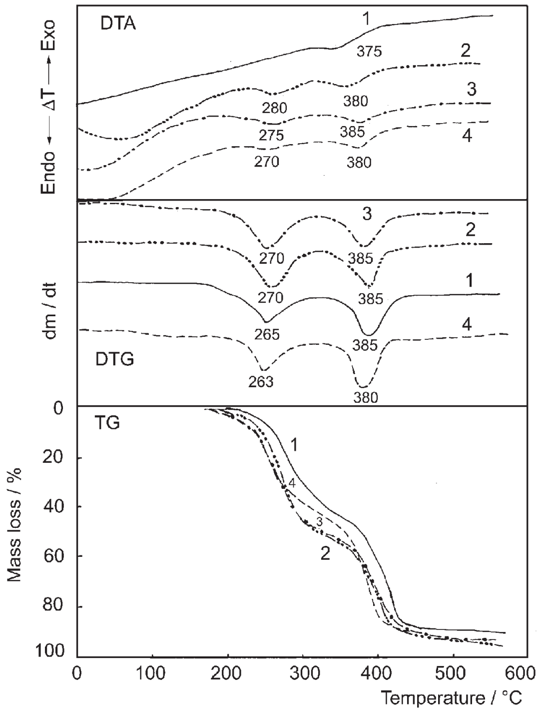

**Fig. 2** Thermal curves of PVC/poly(MMA-co-DVB) polymer systems at different DVB contents (mass%): 1 – 10%; 2 – 2%; 3 – 5% and 4 – 15%

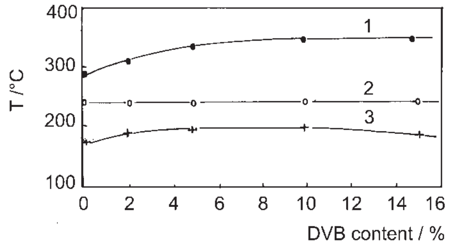

**Fig. 3** Dependence of some thermal characteristics on the DVB content: 1 – $T_{50}$; 2 – $T_{10}$ and 3 – $T_0$

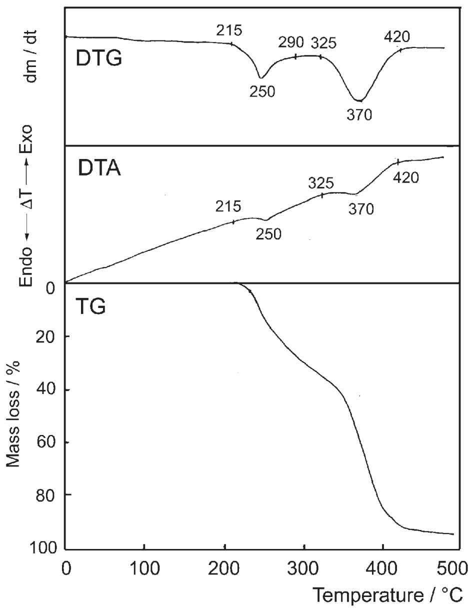

**Fig. 4** DTA, DTG and TG curves of the carboxylic membrane

The results obtained on the thermal stability of the membrane prepared from the PVC/poly(MMA-co-DVB) system with 5 mass% DVB are presented in Fig. 4.

It can be seen that the DTA, DTG and TG curves reveal two stages of decomposition. The first endothermic effect occurs between 215 and 325°C ($T_{max}$=250°C). The mass loss at the end of this stage is 30%. The second endothermic effect in the temperature range 325–420°C is connected with a 68% mass loss. The activation energy of degradation was 223.8 kJ mol$^{-1}$ and $Z$=1.5·10$^8$ for the temperature region 210–300°C, while for the region 320–420°C it was 181.8 kJ mol$^{-1}$. It was found that the membrane is thermally stable up to 210°C.

## Conclusions

The thermal behaviour of PVC/poly(MMA-co-DVB) polymer systems and membrane based on PVC/poly(MMA-co-DVB) system with 5 m.% DVB on dynamic heating in nitrogen was studied. It was found that the thermal stability of polmer systems affected by DVB contents. The decomposition took place in two basic stages: the first one up to 320°C and the second one from 325 to 425°C, when DVB was varied from 2 to 15 m.%. The membrane showed thermal stability up to 210°C.

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