STUDYING THE DESTRUCTION OF VARIOUS FLUOROPOLYMERS CAUSED BY γ - IRRADIATION AND MeV PROTONS

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While fluoropolymers are normally used as anti-adherent coating, they are intensely investigated for potential use in various radiation dosimeter applications as well as space technology. In order to understand the discrepancy between high chemical and thermal stability and low radiation stability of various fluoropolymers, we are bombarding them with 1 MeV protons to fluences up to 2×10^{15} protons/cm^2 as well as subjected some of them to γ-irradiation by dose of 10 kGy. During bombardment we are monitoring the emission of chemical species with a residual gas analyzer (RGA). γ - irradiated samples were tested by Radio thermoluminescence (RTL) method. The results we present here are a good indicator that material damage happens much earlier than 2×10^{15} protons/cm$^-$ and that further work should be addressed at much smaller exposures. RTL also can be used at small doses of irradiation (10-30 kGy). The thermomechanical curve (TMC) of radiation-free polyvinyledenefluoride (PVDF) is characteristic for topologically di-block amorphous polymer of quasi-crossing structure. in the temperature range of from 173 K up to 228 K polymer is vitrified. The vitrification temperature of PVDF is 228 K. All molecular-relaxation and quantitative characteristics of PVDF were determined before and after its irradiation by protons. Protons caused significant changes in PVDF. From di-block amorphous it transformed in to amorphous-crystalline structure. An appreciable influence of dose at proton irradiation of polymer was revealed both on topological level and on molecular-relaxation one.

Introduction

The discrepancy between the high chemical and thermal stability of polytetrafluoroethylene (PTFE) and other fluoropolymer variants and their very low radiation stability remains a subject of discussion. PTFE has been described as a "very radiation-unstable synthetic polymer material". The radiation stability of PTFE is two orders lower than that of polyethylene (PE) [1]. In contrast, short chain linear perfluoroalkanes (the low-molecular analogues of PTFE) have greater radiation stability than their hydrocarbon analogues. In PTFE the radiation-chemical yield of paramagnetic particles is very low (G=0.25), more than one order lower than for polyethylene (G=5.8). The value of the radiation-chemical yield for the PTFE destruction calculated from literature data indicates < 0.1 chain cleavage for 100 eV of absorbed energy. On the basis of such yields for chain destruction, this polymer is considered to be a radiation-chemical stable polymer. The radiation-chemical stability of PTFE is one order greater than that of polyethylene and two orders greater than those for cellulose and polysulfones. Thus, together with excellent thermal and chemical stability, PTFE also has radiation-chemical stability.

The basic radical formation process upon exposure to radiation of PTFE is cleavage of C-C bonds [2-4]. Additionally, our analysis indicates that cleavage of C-F bonds is possibly just as important as that of C-C bonds. We used residual gas analysis to monitor the gaseous species emitted from the various polymer samples during the MeV proton bombardment. Comparative results among these polymers are presented here. When RTL method has been used to study low-molecular, polymolecular, crystalline and amorphous organic matters, its most common feature is that the luminescence is tightly

connected with the processes of molecular relaxation or mobility. This fact enables widely to use RTL to study polymers structure, homogeneity of polymer mixtures, copolymers. It should be noted that there is individual, characteristic only for certain polymer, dependence of RTL from temperature - so called "curve of luminescence". At rather low doses (10-30 kGy) the curves' form - the number of maximums, their position, half widths - remains without changing. These curves may be used for identification of unknown polymer compositions.

Experimental work

For this study we used PTFE, PVDF, polytrifluorochloride (PTFC) and perfluoroalkylvinyl ether (PFA) films of 100 μm in thickness and 20×20 mm^2. The films were bombarded with 1 MeV protons from the Pelletron accelerator at the Alabama A&M University at fluences of 5×10^{14}, 1×10^{15}, and 2×10^{15} protons/cm^2. The current was kept below 300 nA to avoid macroscale sample heating during bombardment. Residual gas analyses (RGA, Stanford Research Systems, Model 200) were conducted in real time during the bombardment. RTL studies were carried out in PTFE as well as in copolymer of tetrafluoroethylene with ethylene (CTE) γ-irradiated with the dose 10 kGy.

Cap of symbols and abbreviations used in the table

α_1, α_2 – factors of the linear thermal expansion in glassy state and in high - elasticity state; Tg - temperature of glassy transition of the amorphous block; T_{m1}, T_{m2}, T_{m3} – temperatures of the fusion beginning of low - melting , intermediate and high - melting crystalline modification; T_f - temperature of molecular

flow; V_f - free geometrical volume; M_{an}, M_{aw} - average numerical and average weight molecular mass in amorphous block; M_{cr1}, M_{cr2}, M_{cr3} – molecular mass in low - melting, intermediate and high fusible crystalline modification; M_n, M_w – the average weight molecular mass of blocks; φ_a, φ_{cr1}, φ_{cr2}, φ_{cr3} - weight factors of the amorphous block, low-melting, intermediate and high fusible crystalline modification.

Results and discussions

Exposure of the selected fluoropolymer films to the proton beam shows that there is a large number of gaseous species emitted from the samples during ion bombardment. The most notable species were selected from the RGA spectra taken at the beginning (denominated as "initial") and during the last minute of the exposure (denominated as "final") to the proton beam. Ratios of final over initial partial pressures for each of the selected gaseous species were calculated for all four fluoropolymers and the fluences they were exposed to. A very important observation is the emission of H_2, H_2O, HF, and HCl, as well as N_2 and O_2, since these are not constituent parts of any of the polymeric chains used in this work. Rather, some seem to form dynamically during the ion bombardment process (HF and HCl) with elements both native and foreign to the original polymers, while others (H_2, H_2O, N_2, O_2) were present in the samples since before the exposure to the beam, as atmospheric constituents diffused in the porous, open macrostructure of the commercial-grade polymers used. First, the gaseous species started being formed inside the whole region of exposed material as soon as the beam was applied (the "initial" RGA scan took about 30 seconds during which an equivalent fluence of $10^{1.5}$ protons/cm^2 was accumulated), and the "reservoir" for producing them got drained already around the time we reached 10^{15} protons/cm^2 in exposure, since the partial pressure ratios for the lighter species decreased as we reached twice that fluence. An opposite behavior of the heavier species does not necessarily contradict this hypothesis, but rather coming to support it in the light of the second observation, that the emission of the produced gaseous species is a diffusion driven process that is taking place from the entire region of material exposed to the proton beam, and therefore is size and mass dependent. Notable, too, is the ratio for HF that after exposure to $10^{1.5}$ protons/cm^2 was close to 1400 and decreased to almost 10 after 2×10^{15} protons/cm^2. Also, while H had to come from sources external to the structure of PTFE (atmospheric humidity), F was produced from the cleavage of C-F bonds during exposure. Considering that most of the other species were produced by cleavage of C-C bonds to form various lengths of C_aF_b, we can observe that cleavage of C-F bonds seems to be the preferred avenue of destruction. The PFA has degraded much faster than PTFE as the lighter gases are only residual compared to their levels in PTFE, while the heavier gases are in full process of emission, probably helped also by macroscale material decomposition following intense degradation under the proton beam, at the same time as in the PTFE the same gases are just starting to come out of the

material. From this point of view, PVDF seems to be a more stable material (at least under 1 MeV proton bombardment) that both previous materials since HF (with H from both native and external humidity sources) ratio climbs slowly as it approaches 2×10^{15} protons/cm^2 and very few other C-H-F radicals are observed yet at this moment. Also, the common contaminants (H_2, H_2O, N_2, O_2) are following a similar behavior as in the case of PTFE and PFA (that is their concentration decreases as the fluence increases). Further studies of this polymer to higher fluences are considered necessary at this point. Finally, a very brief exposure (had to stop experiment due to strong material outgassing / decomposition) to protons of PTFC (up to 5×10^{14} protons/cm^2) shows that this fluoropolymer presents the least structural integrity to radiation. We noticed only residual amounts of the lighter gaseous species (Cl-based radicals and HCl are additional, specific to this material), while there is a tremendous increase in the ratios of heavier gases, up to three orders of magnitude.

The thermomechanical curve (TMC) of initial PVDF is characteristic for topologically di-block amorphous polymer of quasi-crossing structure. In the temperature range of from 173 K up to 228 K polymer is in glassy state. The vitrification temperature of PVDF is 228 K. TMC analysis allows to determine the values of the average numerical (M_n) and the average weight (M_w) molecular mass. The weight portion of macromolecular fragments inbound amorphous and cluster blocks, are 0.75 : 0.25, respectively. All molecular-relaxation and quantitative characteristics of PVDF are given in Table. Proton–bombardment causes significant changes in PVDF. From di-block amorphous it transformed in to amorphous-crystalline structure. Instead of cluster cross-centers (like in initial PVDF) crystalline blocks of three modification with different melting temperature, weight portion have originated, and molecular characteristics of glassy chains. Four-block topological structure has remained even at higher protons' doses. The only difference is in the structure of low-melting crystalline modification. At minimal dose it has quasi-crossing character, when the cross-centers are the crystallits of intermediate modification.

An appreciable influence of dose at proton irradiation of polymer has been revealed both on topological level and on molecular-relaxation one (see Table).

RTL investigations have shown that in the case of γ - irradiated PTFE there are 2 peaks at temperatures 147 K and 206 K. RTL curve of γ - irradiated CTE has 4 peaks at 116 K, 155 K, 194 K and 395 K.

Conclusions

Bond breaking (i. e. gaseous emission) begins as soon as beam is applied, pointing to a bombarding ion-driven process, rather than purely thermal (sample heating). PTFE appears to be more resistant than PFA for similar exposures. PVDF seems to be the most resistant of all four materials investigated, while PTFC seems to be the least resistant, at least to 1 MeV protons. Time dependence of the amount of gas species is related to the degree of damage to

material, mass and physical dimensions of gas species (i. e. diffusion process). Most samples are porous, filled with air and water, and outgassing during exposure to protons. Also, most of the H contaminant forms HF and, respectively, HCl with elements native to the materials investigated, and large amounts of HF and HCl are released during the process.

An analysis of the results allows to conclude:

(i) Proton irradiation of PVDF does not change quasi-crossing character of its amorphous block, but leads to sharp decreasing in it of intermodal chains weight portion, as well as to extreme changes in molecular mobility, mass, and poly-dispersion.

(ii) Protons' energy impact on PVDF causes the destruction of cluster cross-centers. In so doing three crystalline modification with different temperature and rate of melting, molecular masses, and weight portion have appeared.

(iii) The increasing of proton energy has brought to extreme changes in numerical molecular mass averaged over blocks. It is an evidence of the same changes in crystalline blocks of every separate macromolecules. The same extreme changes has been revealed in the molecular flow temperature. Average-weight molecular mass significantly decreases with the irradiation dose, i.e. macromolecular destruction. Double-sided TMC of PVDF films of 100 μm and 500 μm in thickness allowed to determine the minimal thickness of proton penetration into the polymer (100 μm) upon which molecular-topological structure does not change.

Acknowledgements

References

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Table

Effect of bombardment by MeV protons on molecular – topological structure of PVDF

PVDF characteristic	Mev				
	0	2	2	1	1
	Fluence (protons/cm^2)				
	0	1×10^{15}	2×10^{15}	1×10^{15}	2×10^{15}
Amorphous block					
T_a, K	228	209	216	220	218
$\alpha_1 \cdot 10^5$, K^{-1}	15.4	16.0	13.9	17.2	17.1
$\alpha_2 \cdot 10^5$, K^{-1}	62.5	46.5	85.5	83.3	88.9
V_f	0.321	0.179	0.430	0.403	0.465
$M_{an} \cdot 10^{-3}$	24.3	147.0	29.1	32.7	28.2
$M_{aw} \cdot 10^{-3}$	35.9	248.9	47.1	53.0	41.1
φ_a	0.75	0.21	0.04	0.06	0.05
Low – melting crystalline modification					
T_{m1}, K	--	428	351	370	357
$M_{cr1} \cdot 10^{-3}$	--	95.3	79.4	77.9	31.6
φ_{cr1}	0.00	0.13	0.12	0.15	0.04
Intermediate crystalline modification					
T_{m2}, K	--	441	375	382	381
$M_{cr2} \cdot 10^{-3}$	--	446.7	199.5	198.1	112.2
φ_{cr2}	0.00	0.47	0.34	0.37	0.26
High – melting crystalline modification					
T_{m3}, K	--	483	412	414	413
$M_{cr3} \cdot 10^{-3}$	--	398.1	35.5	37.9	31.5
φ_{cr3}	0.00	0.19	0.50	0.42	0.65
T_f, °C	--	524	447	438	436
Cluster modification					
T_{cl}, K	53	--	--	--	--
$M_{n(cl)} \cdot 10^{-3}$	272.8	--	--	--	--
$M_{w(cl)} \cdot 10^{-3}$	1347.8	--	--	--	--
T_f, °C	388	--	--	--	--
φ_{cl}	0.25	0.00	0.00	0.00	0.00
Averaged molecular mass					
$M_n \cdot 10^{-3}$	31.5	231.4	55.4	59.8	38.5
$M_w \cdot 10^{-3}$	363.9	353.5	97.0	103.5	53.0