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PhD Thesis Summary

**SPECTROSCOPIC INVESTIGATION OF SOME COMMON
POLYMERS UNDER THE ACTION OF SOME DEGRADANT
PHYSICAL AGENTS**

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Keywords: high-density polyethylene, polystyrene, polypropylene, Raman spectroscopy, FT-IR spectroscopy, NMR spectroscopy, ESR spectroscopy, gamma irradiation, UV irradiation, X irradiation.

INTRODUCTION

Nowadays, the polymer materials are important in all the fields and activities, being present more and more in every day life. The factors which generate the degradation of polymer materials are physical factors like heat, light, and other radiations of high energy (X rays), mechanical treatments, ultrasounds, chemical factors like gas, solvents oxygen and ozone or other chemical agents. These factors can produce different reactions depolymerization, the scission of macromolecular chain, oxidation etc. The obtained products may contain also new groups which can modify the stability or toxicity of the molecular compound. The process of degradation is undesirable in remaking and exploitation of macromolecular substances. These facts make the topic of this thesis to be of present interest. There were selected some polymers like high-density polyethylene, polystyrene and polypropylene, polymers with multiple use in medical field, industry and everyday life. The selected studying methods are the electron spin resonance (ESR), FT-IR and Raman spectroscopy, nuclear magnetic resonance (NMR). The selection of these methods had been imposed by the necessity of characterization of the samples from point of view of physical and chemical behaviour at microscopic level and for emphasizing of eventual structural changes at molecular level induced by these interactions.

During the applications, these polymers are under the effects of solicitant conditions e.g. X, UV and gamma rays, thermal treatments, which can produce changes on macroscopic and microscopic scale. The aim of this thesis was the investigation of these actions for establishing the optim condition of their utilization.

Preliminar studies were accomplished in this thesis in order to establish the category of the most important degrading agents with possible effects upon the properties of these materials. The thesis is organized as follows, the introduction, a theoretic part regarding the polymeric materials in general, the characterization of studied systems, methods of investigation and the apparatus used, a part of experiments regarding the results of studied systems, conclusions and bibliography.

The introduction presents a syntetic description of polymers and of theirs main charateristics. The description is backed up by figures and footnotes to references of bibliography. This chapter consists in a theoretic introduction in the research of polymers

degradation and a short classification of these polymers.

The characterization of the investigated systems was described in the second chapter. The observed polymers were presented and all the information regarding their physical and chemical properties and also their practical applications.

The methods of investigation and the apparatus used were shortly described in the third chapter. The apparatus used consists in FT-IR, Raman, NMR and ESR spectrometers.

The results of experiments chapter is structured in many sub chapters which deals with three researched polymers, the high-density polyethylene, the polystyrene and the polypropylene.

This work ends with conclusions wich result from this study and the references.

THE EXPERIMENTAL RESULTS

Due to their special physical and mechanical properties, synthetic polymers take an important place in all the domains of activity, being present more and more in every day life. Taking into consideration the diversity of medical and pharmaceutical fields, the synthetic polymeric biomaterials (simple or compound) is an actual topic with a special dynamics. The systems studied in this thesis are HDPE, PP are PS.

1. High-density polyethylene (HPDE)

Polyethylene is often used in the field of medicine due to its physical, chemical and mechanic properties. Its structure is as follows (Figure 1).

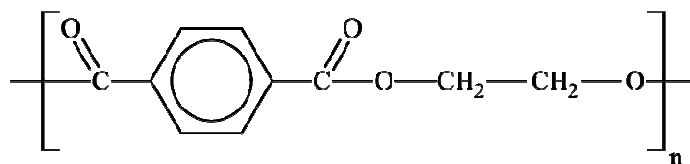


Figure 1 Molecular structure of high-density polyethylene.

Molecular structure of High-density polyethylene has linear fashion rather than branching out to form long chains and it is prepared from polymerization of ethylene under a medium and low pressure, using molybdenum oxide and chrome trioxide as catalytic components. Also it can be prepared through Ziegler-Natta polymerization using titanium compound catalytic and conducting the reaction to the atmospheric pressure. HDPE has the mass density from 0,94 to 0,96 g/cm³, a white aspect, it is also harder and more opaque .

1.1. The radioactive degradation

The degree of radioactive degradation depends of the wavelength of the irradiation, of the rradiation,of the intensity and the dose of the rradiation, of the conditions of the irradiations and the structure of irradiated polymer. It is very important that any risk of radioactive contaminations to be eliminated in the medical field. We observed in this research

that the sample of polyethylene was investigated from the point of view of microscopic modifications after it had been X and UV gamma irradiated, with different doses.

a) ESR investigation

Generally the irradiation with gamma and X radiations may produce atomic or molecular, ionizations, breaking of chemical chains or modifications local conformation [1]. Through ESR spectroscopy I studied the changes of the microscopic structure of the polyethylene. It is possible that after this irradiation this sample to produce free radicals or to appear some atomic species with a different spin states [2]. The forming of free radicals in the high-density polyethylene which had been gamma irradiated is important for further research [3-13]. I compared the possible effects of changes on molecular scale after irradiation. The witness sample presents a large RES signal without a hyperfine coupling (fig.2) [14].

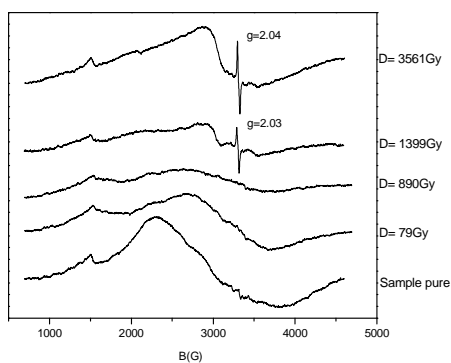


Figure 2. The ESR spectra of HPDE gamma irradiated at different doses.

Starting with irradiation doses of 1399 Gy, the recorded spectra presents an additionally a narrow signal at the value of $B = 3300$ G magnetic field and $g = 2,03$. So this means beginning to $D = 1399$ Gy there are unpaired electrons associated to formation of free radicals or other energetic configurations [15]. So we can assume that there is an effect of ionization or even a breaking chain [2]. The small amplitude of the signal doesn't allow the detection of a hyperfine coupling. It is possible that an electron under gamma radiation action to be set free from a chemical chain and to become an unpaired electron. If the dose of radiation is increased, this signal still exists, it appears at the same value of magnetic field and its intensity is bigger. After the exposure stops, the system is relaxed (Figure 3). We can

associate this effect with a process of recombination, in fact, the capture of the electron [13-14].

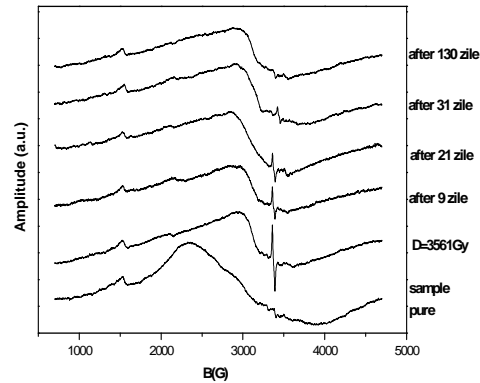


Figure 3. The ESR spectra for HPDE relaxed.

In the case of irradiated sample with UV rays, ESR spectra were recorded immediately after the irradiation stopped. After 1 hour of irradiation the signal is light and it has a relative small intensity (Figure 4), so we can assume that the first electrons appear unpaired [16]. If the time of irradiation is longer the signal still persist, and also the intensity increases. It is possible that an electron to be released from a chemical chain under the pressure of UV irradiation [8].

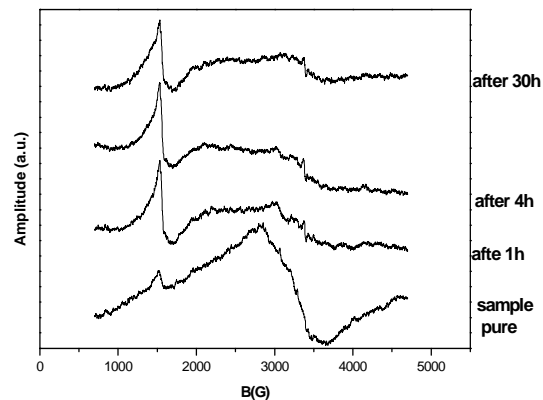


Figure 4. The ESR spectra of HDPE UV irradiated.

b) NMR investigation

Generally, the effect of aggressive agents (gamma and X irradiations) leads to changes like, the damage of the organization (damage of the crystal or amorph state), the breaking of polymeric chains [17-20]. I analyzed the comparatively the ^{13}C spectra and ^1H NMR spectra for irradiated sample and the sample which was not irradiated. From the ^{13}C CPMAS spectra of the prove of the polyethylene which was not irradiated we can identify an maximal absorption value, tall and narrow at 32 ppm and a larger maximal absorption value at 31 ppm [21-23] (Figure 5). These values are associated to methyl group of crystallographic and amorph component.

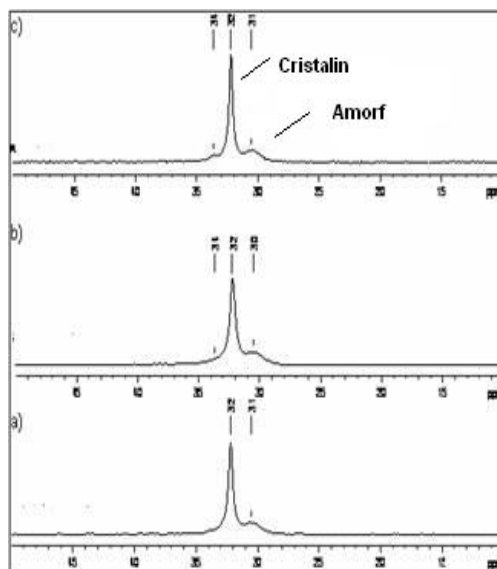


Figure 5. CP MAS ^{13}C NMR spectra of a) pure; b) gamma irradiated and c) X-ray irradiated high density polyethylene.

After the irradiation with gamma radiation we can observe a slightly modification of the spectra related to the appearance of one more peak at 34 ppm. This peak can be associated with a crosslink effect of the group carbon-carbon (C-C) [22-24]. In the case of irradiation with X rays, we can observe the appearance of a maximal absorption peak at 34 ppm related the crystalline phase carbon-carbon (C-C). The relative intensity of this registered maximal absorption value of the irradiation with X rays is bigger than the registered peak of gamma

radiation of the same sample. We took into consideration the fact that the dose of irradiation was 25 times smaller than in the case of X irradiation sample, so we can conclude that this type of radiation produces a much bigger damage than in the case of polyethylene radiation with gamma rays [21]. So it is obvious that X rays irradiation and also gamma encouraged the rearrangement of polymeric chains.

c). Raman and IR investigation

I used Raman and IR methods to emphasize the possible changes on molecular scale induced by irradiation [25-27]. As regards Raman spectrum, the most intense bands are 1060 cm^{-1} and 1125 cm^{-1} C-C stretching band, 1295 cm^{-1} CH twisting band, 1428 cm^{-1} -CH₂ bending band, 2842 cm^{-1} and 2878 cm^{-1} -C-H stretching band [28] (Figure 6).

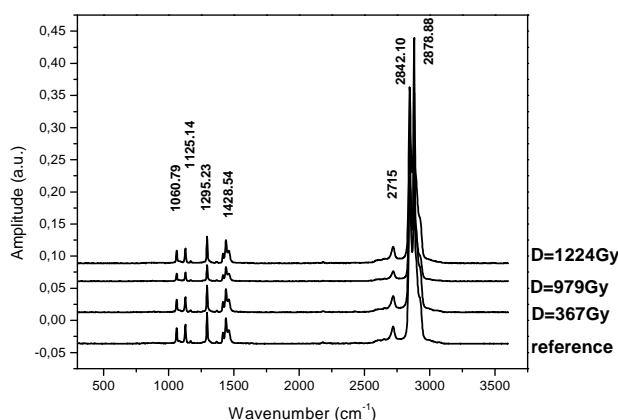


Figure 6. The Raman spectra of the HDPE with different doses of irradiation.

The vibration bands appear at the same wavenumbers for the gamma irradiated sample and the unirradiated one, so we can conclude that we don't have modifications related to the chemical structure of the molecule. The strong absorption bands can be easily distinguished in the IR spectra of the polyethylene situated at 2846 cm^{-1} according to the vibrations of stretching C-H, 1474 cm^{-1} according to the vibrations of bending chains C-H, 1461 cm^{-1} according to the vibrations of waving groups CH₃ and band situated at $733\text{-}720\text{ cm}^{-1}$ due to long vibrations of the chains with 4 or more groups CH₂ [29-31]. The doublet situated between $730\text{-}719\text{ cm}^{-1}$

corresponds to crystallinity region of polymers (Figure 7).

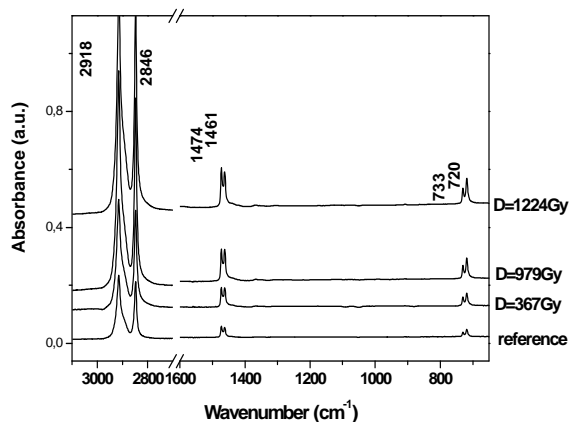


Figure 7. IR spectra of the HDPE with different doses of irradiation.

After gamma irradiation the vibrations bands of the high-density polyethylene appear at the some wave numbers. Altogether with the increase of the dose, these vibrations bands develop their amplitude. The increase of these vibration bands is determined by the increase of the number of chemical chains involved in this kind of vibrations. More chemical chains can vibrate when the molecules are free to move. A possible effect of γ irradiation is the scission of the chains which leads to the increase of local dynamics of polymeric chain.

1.2. Thermal degradation

As a result of overheating, the polymers suffer different physical and chemical modifications followed by the elimination of gaseous products, liquids, colour changing. The chemical reactions of polymers which occur due to overheat ca be split in two groups, reactions which appear altogether with the breaking of the main molecular chain, reactions which appear without the breaking of the main molecular chain [32-33]. We paid attention to the changes of microscopic structure of the polyethylene in accordance with different thermal treatments (240 °C melting process, cycles of heating and cooling at the temperature of 134

$^{\circ}\text{C}$ degrees, for 45 minutes, and the immersion in the liquid nitrogen at the temperature of -196°C , for 5 minutes). When the polymer is heating, the energy of thermal movement in some places of the system becomes equal with the energy of chemical chain and finally the chemical chain breaks down. The bond C-C is one of these chains stable at thermal action. The presence of H atoms attached to the C-C bond leads to the decrease of the thermal stability of C-C bond.

a). ESR investigation

We interested to observe by ESR spectroscopy the possible changes of the microscopic structure of the polyethylene in accordance with different thermal treatments. ESR spectra were registered immediately after the thermal treatment had stopped. We analyzed the witness sample in comparison with the thermal sample already damaged. The witness sample in characterised by an ESR signal without a hyperfine structure which means that there aren't unpaired electrons. Beginning with the first cycle of heating the registered spectra shows an additional signal at $B = 3350\text{ G}$, but it has a slight intensity. The slight amplitude of the signal doesn't allow the detection of a hyperfine structure (figure 8). It is possible that broken chains and oxidation to appear after the thermal degradation and also some cross-links in some cases [2-3]. This phenomenon is followed by the appearance of an unpaired electron.

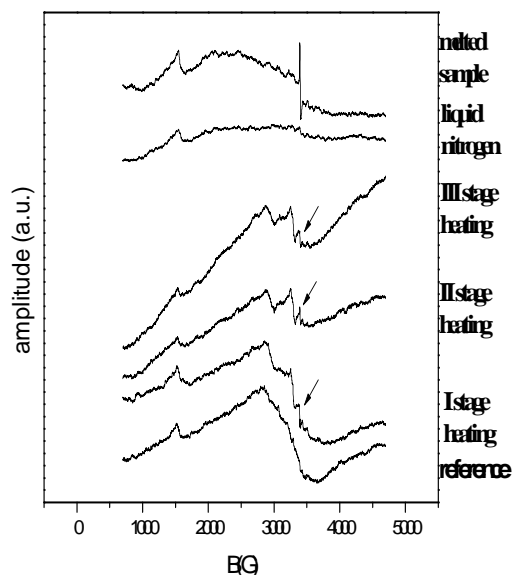


Figure 8. ESR spectra of HPDE after thermal degradation.

Similar behaviours have also the melted polyethylene sample. But the intensity of its signal is much bigger at this signal appears with the same value of magnetic field $B=3350$ G. In the case of the sample immersed in liquid nitrogen, the RES signal completely disappeared.

b). NMR investigation

The change of the spin-spin relaxation time T_2 is associated generally with the change of mobility of polymeric chains [34]. This mobility can be associated with the breakings within the polymeric chains, or by changes of neighboring of these groups. The reference sample in comparison with the sample which was thermal treated shows different evolutions of transversal magnetization which are associated with crystalline and amorphous components changes.

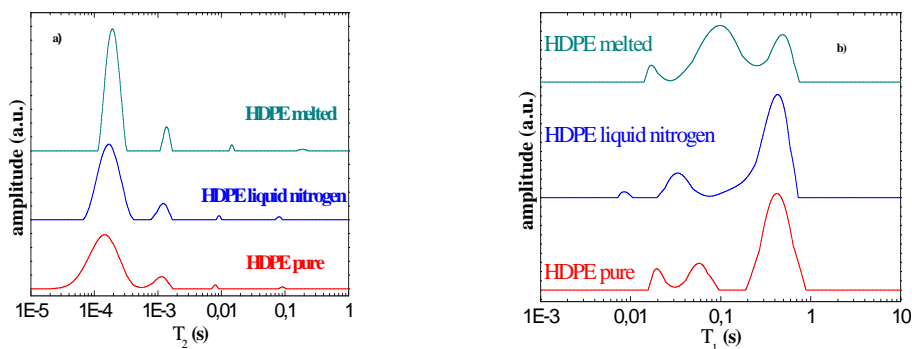


Figure 9. The corresponding a) T_2 , b) T_1 distributions for the pure and aged in liquid nitrogen, melted HDPE.

All distribution from the Laplace spectra presents four peaks (Figure 9). The main peak is located at the lowest T_2 values, around 200 ms, therefore characterized by a reduced mobility, and can be associated with the crystalline phase of HDPE. The second peak located between 1–2 ms, characterize the mobility of linked polymer chains therefore can be associated to the amorphous phase of HDPE. With one order of magnitude higher one can find a peak associated to the more mobile chain segments like the loose loops from the

amorphous phase, while with two orders of magnitude one can find peaks which can be associated with the extremely mobile polymer chain segments like the end chains. The positions of peaks in the T_2 distributions for HDPE aged in liquid nitrogen correspond with the peaks of pure HDPE. Nevertheless, the effect of 5 min cure in liquid nitrogen leads to a more organized chain distribution into the crystalline as can be observed from the corresponding narrowed peaks. The highest homogeneity is produced by melting the HDPE sample. This treatment will increase also the mobility of loose loops from amorphous phase. The melting cure lead to significant changes also into the saturation recovery build-up curve of the same pure and aged HDPE samples (see Only three components can be identified in the T_1 distributions and these can be associated from right to left (decreasing T_1 values) with the crystalline, interface and amorphous phase of HDPE [24]. The discrepancy between T_2 and T_1 distributions arises from different NMR sensitivity of these two parameters for describing multiphase in polyethylene. In contrast to the thermal treatment, irradiation with X-rays leads to a small ordering of HDPE network. The melting cure destroys a significant part of amorphous and crystalline phase and increase the interfacial high density polyethylene network.

2. The polystyrene (PS)

Polystyrene is a thermoplastic substance made of linear macromolecules without branches. It appears as a commercial product in 1937 and it is a colorless white substance and a good electric insulator. Polystyrene's chemical formula is presented in figure 10. The polystyrene is obtained through the radical polymerization of styrene, with the presence of a catalyser or without it, if the styrene is not mixed with inhibitors of polymerization.

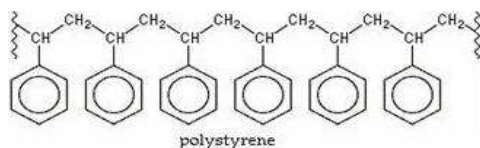


Figure 10. The molecular structure of the polystyrene.

2.1 The radioactive degradation

The researches regarding the effects of ionizing radiations of high energy (X and gamma), especially upon medical devices which consist in polystyrene, are increasing because of the requests of medical sterilization. The sample of solid polystyrene was exposed to the gamma radiation and also UV. The gamma irradiation was accomplished using a ^{60}Co source, from a 5,3 Gy/h dose rate, the accumulative doses being from 367 Gy to 8989 Gy and corresponding to times from 1 hour to 67 days. Some of the polystyrene proves was irradiated with X rays, accumulating a 367 Gy dose for 13 days. In this research I also irradiated the polystyrene prove with UV rays, using a VL lamp with a wavelength 254 nm for 1 hour to 4 hours and 30h [35].

a) ESR investigation

We followed through ESR the detection of free radicals formed during the gamma irradiation sample. ESR spectra were registered immediately after the irradiation had stopped. It was analyzed in comparison the unirradiated sample and the gamma irradiated sample. (Figure 11)

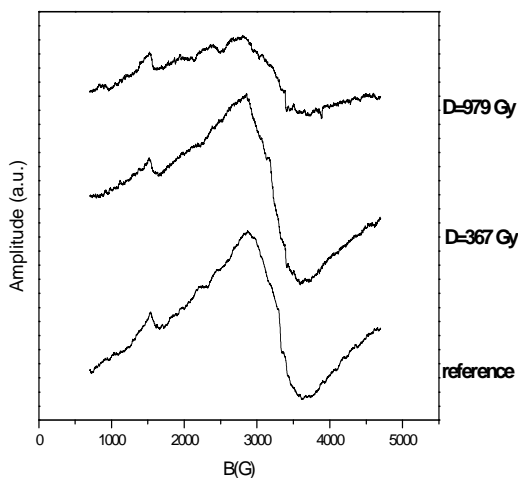


Figure 11. ESR spectra of PS gamma irradiated at different doses.

We can observe in the spectra of the unirradiated polystyrene a single signal without a hyperfine structure. This result shows the fact that there aren't free electrons. In the case of UV irradiated sample the ESR spectra were registered immediately after the irradiation

stopped. It can be noticed a large signal of 3400 G (Figure 12). This signal is still slight after 1h of irradiation and it has a relative low intensity, so we can conclude that the neighboring of unpaired electron is changed.

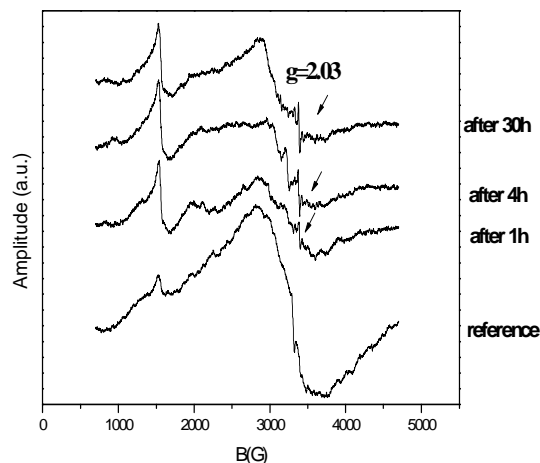


Figure 12. ESR spectra of the UV irradiated polystyrene at different periods of irradiation.

When the time of irradiation is increased this signal still persists, but it's a little bit more intense. The value of magnetic field is the same no matter of the time of the sample exposed to irradiation. It is possible that an electron to be set free from a chemical structure under the pressure of UV radiation. We can presume an effect of ionization occurred or even a broken chain [36-37].

b). NMR investigation

I compared the possible effect of the modification on the microscopic scale after gamma and X irradiation using CP MAS NMR method. The unirradiated sample present important maximum at 145 ppm associated to aromatic carbon group B₁, and also a maximum at 128 ppm associated to aromatic carbon group B₂ [40-43].

After the irradiation, the NMR signal shows the same maximum value of the frequency of the resonance but with a less amplitude (Figure 13).

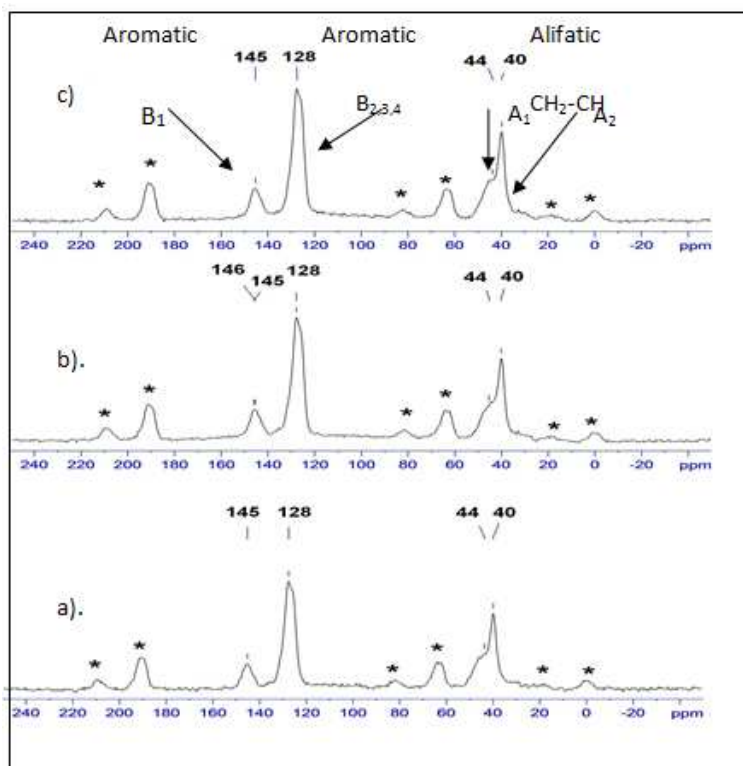


Figure13. NMR CP MAS spectra of ^{13}C for polystyrene
 a) pure state ; b) gamma irradiated; c) X rays irradiated.

The reduction of lines' intensity is associated generally with the reduction of number of spins which give a resonance signal. It is possible that a part of molecules to be chemically broken. The result is that the monomers or precursor monomers appeared and they have a signal for another research field than the studied one. So, we cannot identify modification of the chemical bonds till the $D= 979$ Gy irradiation dose. We don't have modified structures of the monomer, although it is possible to appear some structure modifications in the neighboring of the polymeric chain with the repercussions upon the dynamic. During the next stage we observed the effect of radiations upon the relaxation time of different functional, aromatic and aliphatic groups. We measured the relaxation of the ^{13}C carbon for the aliphatic and aromatic group. The gamma irradiated sample and the unirradiated one present different evolutions of transversal magnetization, and there are also different evolutions between aromatic and aliphatic groups. A general diminution of relaxation time can be observed after the irradiation.

The time for the aromatic group is half reduced in the case of the gamma irradiated polystyrene, and a much faster reduction of time, almost 5 times faster, takes place for the second part of the same group (Table 1).

Sampel	C aromatic		C metilen-metin
	T_{1p} (ms)	T_{1p} (ms)	T_{1p} (ms)
PS nonirradiated	1,9	81,3	63,8
PS gamma irradiated	0,7	14,3	32,7

Table 1

So the relaxation time and the irradiation decrease in the same time. The same effect can be observed in the case of the carbon from metilen-metin group, where the relaxation time is also half reduced. All these results can be associated with a reduced effect of crystallization induced by irradiation. The change of relaxation time is associated in general with the change of polymeric chains mobility [40-45].

c). Raman and IR investigation

The Raman and IR methods were used to emphasize the possible changes induced by the irradiation. The possible interactions within the polymer can be studied through comparing the initial state of samples with their state after irradiation. These spectra are presented in the figure 14.

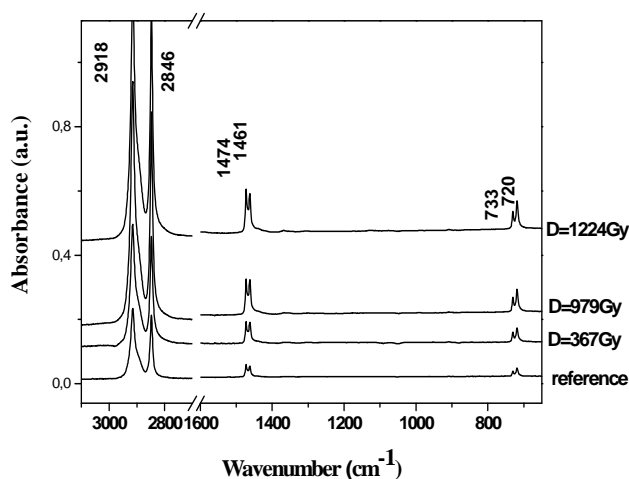


Figure 14. IR spectra of polystyrene with different doses of irradiation.

You can easily observe that the spectra of pure state polystyrene contains well distinguished bands at 720–2900 cm^{-1} . The aromatic ring C_6H_5 generates bands of vibration higher than 3000 cm^{-1} . The aspect and the amplitude of the spectra are slightly changed and the bands of vibrations appears at the same wavenumbers, as for witness sample. Also one may observe that the increasing of the irradiation time is in the same time with the increasing of Raman bands intensity which are at the same wavenumber [46-48]. The increasing of bands vibration is induced by the increasing of chemical chains number involved in this kind of vibrations.

2.2 The thermal degradation

The absorption of energy through heating may determine reversible or irreversible phenomenon which leads to the changes of physical and mechanical parameters or in the case of oxygen from the atmosphere, it leads to the changes of chemical properties. The polystyrene was under the effect of different thermal treatments, as follows: a) heating to its melting temperature of 250 $^{\circ}\text{C}$ b) immersion in liquid nitrogen at a temperature of -196 $^{\circ}\text{C}$. All these treated samples were brought at the temperature of the environment. We followed through ESR spectroscopy and NMR the possible modification of the microscopic structure of polystyrene which was under these thermal treatments.

a). ESR investigation

It is possible that after the thermal degradation free radicals to appear in this sample or to appear some kind of atoms with different spin state. We follow through ESR spectroscopy the possible changes of microscopic structure of polystyrene according to different thermal treatments. ESR spectra were registered immediately after the thermal treatment stopped. We analyzed in comparison the reference sample structure (Figure 15). In the case of the melted polystyrene, the registered spectra presents a supplementary signal at $B = 3450 \text{ G}$, but with a low intensity. This low intensity doesn't allow the observation of the hyperfine structure. We can assume that after the thermal degradation the broken chains can appear [49-50]. When the temperature is over 250 $^{\circ}\text{C}$, the polymer suffers processes of thermal degradation.

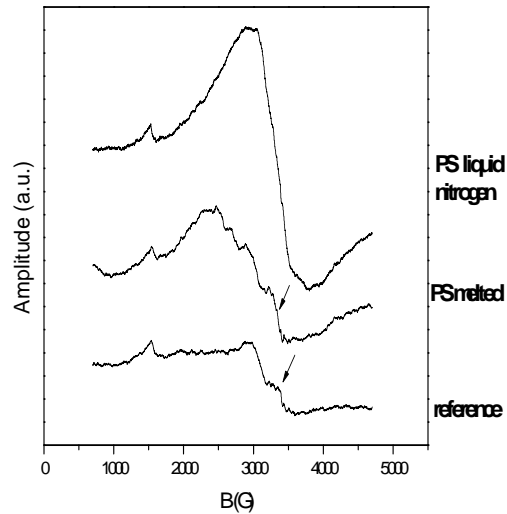


Figure 15. ESR spectra of PS after thermal degradation.

b). NMR investigation

We compared through this method the possible effect of changes of the polymer at molecular scale after different thermal treatments. In order to observe the possible effects on local dynamics we measured the relaxation spin-spin T_2 time and also measured the relaxation spin lattice T_1 time (Figure 16). One may notice the differences between the reference sample and the thermal treated samples.

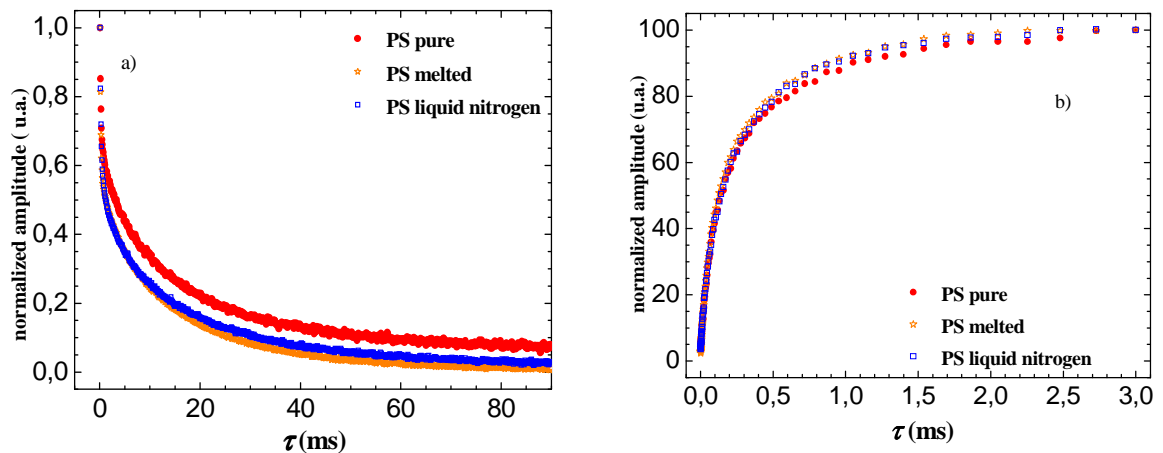


Figure 16. a).The transversal evolution of magnetization b). the longitudinal magnetization of polystyrene under the thermal treatments according to time.

Regarding the relaxation time, the differences between the reference sample and the immersed one in the liquid nitrogen are very few (Table 2). The melted sample shows a longer relaxation, so we can conclude that the dynamic of polymeric chains increases after melting, due to the breaking of chemical chains [42]. The fraction of higher dynamic states are much more after the melting.

Sample	Relaxion time T_2 (s)	Relaxion time T_1 (ms)
PS pure	0,44	53,87
PS melted	0,50	55,98
PS immersed liquid nitrogen	0,43	40,41

Table2.

3. The polypropylene (PP)

The polypropylene is a polymer similar with the polyethylene. It is a solid substance , white, thermoplastic. The molecular structure of the polypropylene is presented in Figure 17. Alike polyethylene, it can be considered a saturated molecular hydrocarbon (molecular weight of 80 000 – 200 000). It is a stable polymer at aggressive environments.

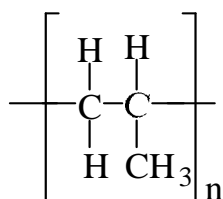


Figura 17. The molecular structure of polypropylene.

The polypropylene is an interesting thermoplastic substance from point of view of biomedical applications, because of mixture of some physical and chemical properties (a good chemical and thermal resistance, good electric and mechanical properties) with a slightly processing.

3.1 The radioactive degradation

There are two main modalities for forming free radicals in a polymeric chain, chemical methods and radiation methods with the help of electromagnetic medium and big energy. The gamma and X radiation produce the ionization of all solid substances.

a). ESR investigation

Electron spin resonance can be used for explaining from quality point of view the appearance of free radicals after gamma irradiation. The forming of free radicals in the polypropylene exposed to gamma radiation was the main topic for many specialized researches [51-53]. The ESR spectra were registered immediately after the irradiation had stopped. We analyzed the unirradiated sample and the irradiated one in comparison. The reference sample doesn't shows a convincing signal regarding a magnetic field of $B = 3400$ G. When the irradiated dose is 367 Gy, the registered spectrum shows a narrow signal. The value of magnetic field is the same 3400 G and the giromagnetic factor is $g = 2,01$. The result shows that the first unpaired electrons appeared. The low intensity of the signal doesn't allow the observation of the hyperfine structure. It is possible that because of the gamma radiation process an electron to be set free from the chemical chain, becoming in this way a free electron. This signal still persists when the radiation dose is increased and it has the same value of magnetic field, but the intensity of this signal increases (Figure 18).

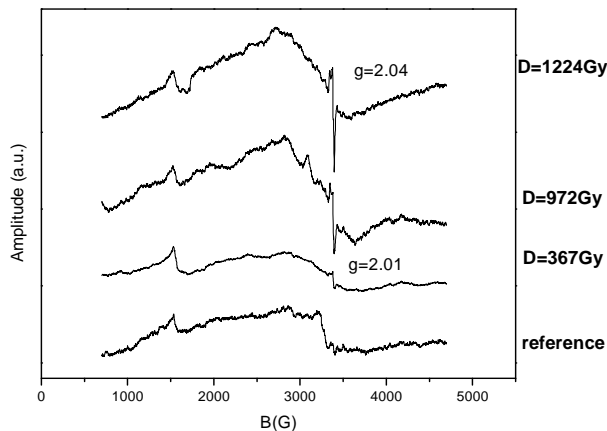


Figure 18. ESR spectra for PP gamma irradiated at different doses.

We observed that when the value of the dose is $D=1224$ Gy the value of the magnetic field is still $B=3400$ G, but the amplitude increases, so we can suppose that the number of free electrons increases and there can be possible a process of ionization.

b). NMR investigation

In order to emphasize the modifications induced by the effect of the gamma and X radiation over the polypropylene, we analyzed the gamma irradiated sample with a 8989 Gy dose and the X irradiated sample with a 353 Gy dose in comparison with the unirradiated sample. One may identify a high and narrow maximum of absorption of 26 ppm in the NMR CP MAS spectra. This maximum of absorption is associated to CH_3 group (Figure 19a). After the irradiation with gamma rays we observed a slight modification of the spectrum as an additional peak appeared at 32 ppm (Figure 19b). This peak can be associated with a cross-linking effect in the carbon-carbon group (C-C) [54-56]. The dose of gamma irradiation was 25 times lower than in the case of X ray sample.

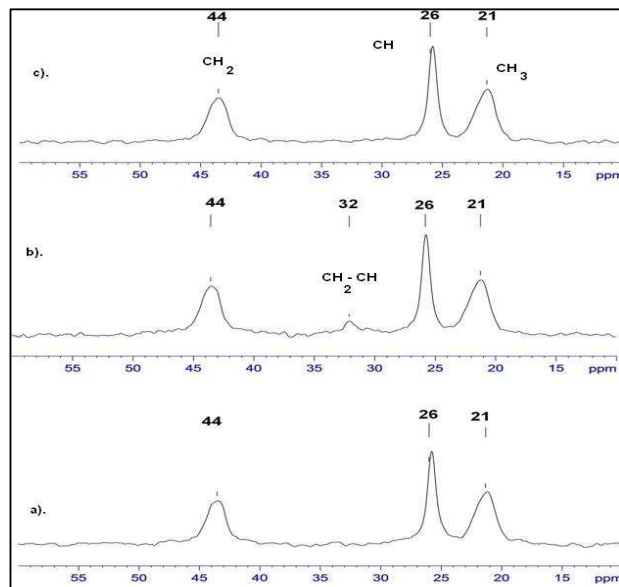


Figure 19. The R NMR CP MAS ^{13}C spectrum of the polypropylene
 a) pure ; b) gamma irradiated ; c) X ray irradiated

The NMR CP MAS spectra of irradiated sample with X rays is presented in Figure 19c and it can be observed that is identical with the spectra of the unirradiated sample. As in the case of the polystyrene this type of radiation produces a significant degradation bigger than in the case of gamma rays irradiation

c). Raman and IR investigation

The Raman spectroscopy provides information about the molecular structure of the material [57]. The effects of polypropylene's radioactive degradation can determine the modification of the vibration spectra noticed through Raman spectroscopy. An objective of our research was the analysing of Raman and IR spectra for the sample exposed at different doses of gamma radiation. One may observe that the IR spectra of the polypropylene unexposed to gamma irradiation contains think bands at $800\text{-}2954\text{ cm}^{-1}$. These bands are drawn in the figure 20. The most intense bands are as follows: $2954\text{-}2832\text{ cm}^{-1}$ -C-H (stretching vibration) and 1166 cm^{-1} -C-H deformation [58]. The doublet situated at $972\text{-}1000\text{ cm}^{-1}$ assigned to the amorph part of the polypropylene.

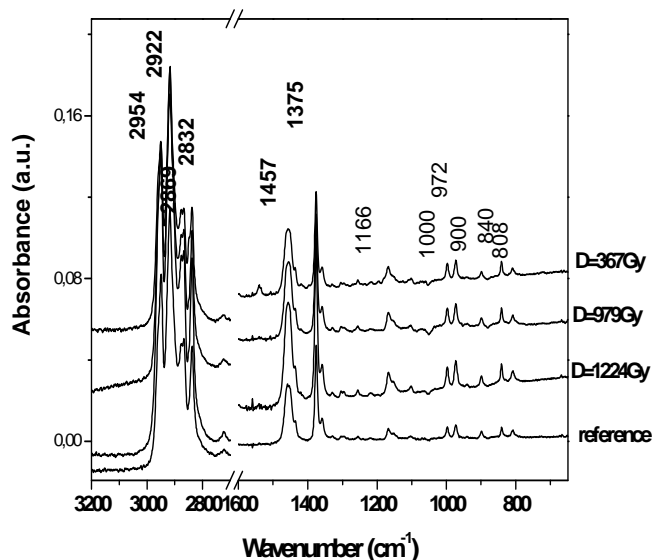


Figure 20. The IR spectra of the PP at different doses of gamma irradiation

In the case of the gamma irradiated sample, we can observe that the vibration bands appear at the same wavenumbers, but their amplitude increases simultaneously with the dose of gamma radiation. The increase of bands intensity is determined by the number of chemical bonds involved in these kind of vibrations. A possible effect of the gamma radiation is the split of chains and the effect is the increase of the local dynamics of the polymeric chain [58-61]. The Raman spectra of the polypropylene at different gamma irradiation doses is presented in the figure 21. The polypropylene in initial state spectrum contains thick bands of vibration at 390-3000 cm^{-1} .

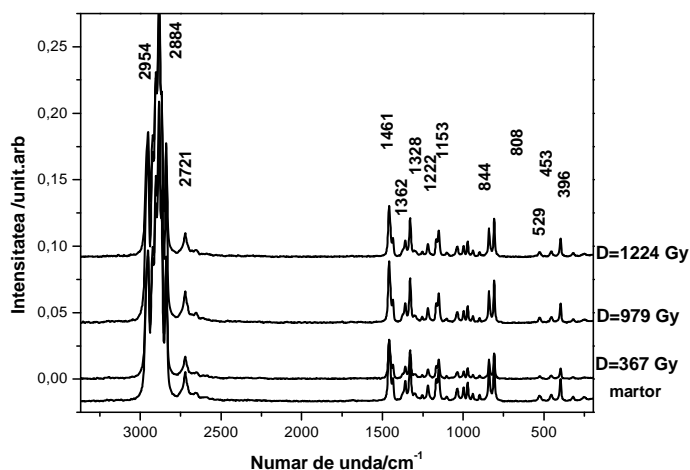


Figure 21. The Raman spectra of the polypropylene at different doses of gamma irradiation

The differences between the spectra at different irradiation doses are very small. The aspect and the amplitude of the spectra are slightly changed, the vibration bands appear at the same wavenumbers as in the case of the unirradiated sample, but their amplitude increases at the same time with the increasing of radiation dose.

3.2 The thermal degradation

Many polymers over the high temperature endure many physical changes which are not followed by the tearing of chemical bonds. When these polymers are heated the elimination of the substitute take place and it changes into a more stable polymer. The substances with a linear structure are the most thermostable. The branching polymers are less stable. At the next step the samples of polypropylene were under the influence of heating processes till the melting temperature 240 °C. After that they were cooled off till their temperature was very close to that of the environment. In this research I performed 3 cycles of sterilization. At the temperature of 134 °C, for 45 minutes. Then the samples were cooled off at the room temperature. In order to follow the possible changes of the damaged microscopic structure of the researched polymer, I put this sample under thermal shocks through the immersion on liquid nitrogen und at temperature of – 196 °C, for 5 minutes. After

that the sample was heated till the temperature of environment. I accomplished NMR, IR and Raman measurements over all these samples and I compared the registered spectra to the spectra of the reference sample.

a). NMR investigation

By nuclear magnetic resonance we wished to follow the possible changes of the local dynamic after the thermal degradation, we accomplished measurements of the relaxation time of the spin-spin proton T_2 , using the CPMG method and measurements of the relaxation spin lattice time T_1 , using the method of recovering of the longitudinal magnetization and saturation [25]. The relaxation times of the transversal magnetization, the relaxation time of longitudinal magnetization of the polypropylene sample over different thermal treatments are presented in the table 3.

Sample	Relaxation time	Relaxation time
	T_2 (s)	T_1 (s)
PP pure	0,15	9,8
PP melted	0,24	15,56
PP liquid nitrogen	0,20	10,67

Table 3.

One may observe a very small difference in the case of the spin-spin relaxation time of the sample after the thermal treatment. We can associate small changes of the local dynamic to these differences. In this case these measurements of the spin-spin relaxation time emphasize the effects of the thermal treatment over the polypropylene. In the case of the relaxation of the transversal magnetization, the spin lattice relaxation time for the melted sample is bigger ($T_1 = 15,56$ s) than the untreated sample ($T_1 = 9,8$ s). The melted sample presents a longer relaxation, so we can conclude that through melting process the dynamic of polymeric chains was encouraged, and also the scission of chemical bonds.

b). Raman and IR spectroscopy

The Raman spectroscopy provides information about the molecular vibration states[60]. I compared the Raman spectra of the initial state of sample during many cycles of thermal heating. The spectra of the polypropylene in initial state contain vibrated thick bands at 808-840 cm^{-1} . The bands of 808 and 840 cm^{-1} are associated with the crystalline state of the sample. In this way, at 808 cm^{-1} the vibration band is associated to the “helix” chain from the „crystalline” structure and there is a doublet with two parts at 840 cm^{-1} associated to, shorter helix chains 830 cm^{-1} , and to „unhelix” chains. In this domain the spectra look like in the figure 22.

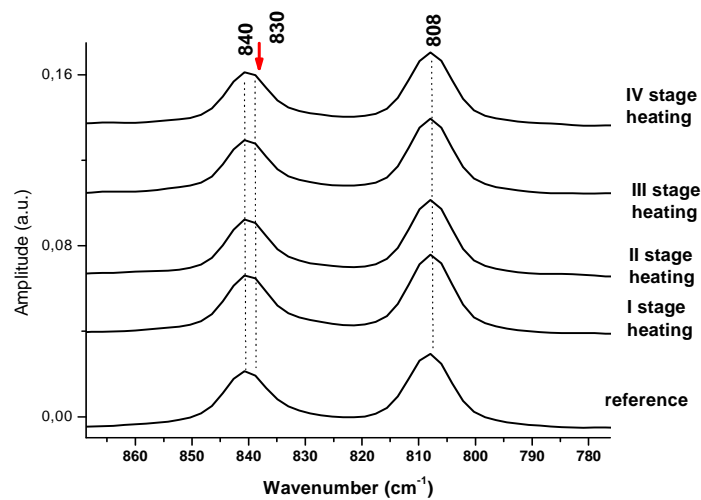


Figure 22. The Raman spectra of the polypropylene over the different cycles of heating

These bands appear also in the case of the sample exposed to the thermal treatment [61-62]. The crystallinity didn't change over these treatments.

CONCLUSIONS

The used methods (ESR, RAMAN, IR si NMR) emphasize the effects of degradation over the analyzed polymers.

The effect of X and gamma radiation over the polyethylene is the same as in the case of UV radiation and leads to the process of reorganized structure. Analyzing the ESR spectra of the gamma irradiated sample and those of unirradiated one, we observe that starting with the $D=1399$ Gy the first unpaired electrons appear, so we have an ionization effect or even the tearing of chemical bonds. The small amplitude of the signal doesn't allow the observation of the hyperfine structure. After the exposing to the gamma radiation stops, the polyethylene relaxed, which indicates the appearance of the recombination phenomenon of the free radicals. The relaxation spin-spin times T_2 and spin-lattice relaxation time T_1 measured emphasize the changes of mobilities of polymeric chains. The Raman analyze of the gamma irradiated polyethylene samples with doses of 1224 Gy doesn't show the modification of chemical structure. After the thermal degradation the scission of polymeric chains appears and the effect of the liquid nitrogen leads to more organized distribution of the crystalline and amorph phases. The biggest homogeneity is produced by the melting of the sample. As regards the Raman spectroscopy there aren't any changes after the irradiation. The vibration bands appear at the same wavenumbers before and after gamma irradiation, so there aren't any changes in the chemical structure of the polyethylene.

The gamma radiation produces a more significant degradation than X radiation in the case of the polypropylene. This fact is confirmed by the NMR. The Raman analysis of the polypropylenem sample over the thermal treatment doesn't indicate any changes of the chemical structure, its crystallinity didn't change. Although through the Raman spectroscopy one may observe the effect of the gamma irradiation over the polypropylene and also the increasing of the local dynamics of the polymer.

In the case of the UV irradiated polystyrene a ionization effect appears and even the scissio of some chemical bonds, showed by the ESR. There aren't any changes of chemical bonds till the $D=979$ Gy gamma dose. There is a reduced effect of crystallinity induced by gamma irradiation, also confirmed by NMR. The change of the relaxation time is associated in general with the change of the mobility of polymeric chains. This mobility can be modified through the scission of some chains or through the hanged of neighboring of polymeric

chains. The dynamic of polymeric chains was encouraged by melting. The polymer suffer thermal degradation processes at the temperature of 250 °C.

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