

Abstract

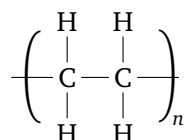
In this work several plastic objects have been studied both thermally and microstructurally: in particular, density measurements, crystallinity measurements, DSC, TGA and solvent effects have been studied. The aim of the work is to find a correlation between thermal properties, crystallinity and stability on heating and solvent attack.

1 Introduction

The laboratory activity concerns the analysis of several polymer materials in PP, PE, PS, PET, PLA, PMMA and tire rubber. Endothermic and exothermic transition of samples has been studied and it was also possible to determinate their degree of crystallinity by considerations on specific enthalpy of melting. Density measurements have been carried out, comparing results with theoretical ones and comparing found degree of cristallinity with one of thermal analysis. In order to study directly the thermal behaviour of samples, different heat treatments have been done. Thermal analysis of PMMA and tire rubber has been done in order to study the composition of samples and their residual mass at high temperature. Sample has been treated with solvents of different concentration in order to study their resistance to chemicals. The various samples used during the activity have been made by different processes. Cups have been produced by thermoforming, in which a plastic sheet is heated to a certain forming temperature, formed to a specific shape in a mold and cut to produce an usable product. Coffee sticks and bottle caps have been obtained by injection molding: the polymer is melted in a specif chamber, injected in a mold and then cooled and solidified. PET bottles have been produced by injection blow molding, a process in which a cylindrical preform is heated and then blown in a mold.

1.1 Materials

1.1.1 Polyethylene

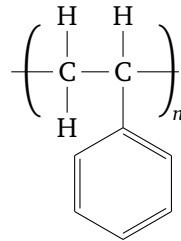


PE is a semicrystalline polymer and due to its low glass transition temperature (below room temperature) it shows a certain deformability.



Figure 1: PE sample.

1.1.2 Polystyrene



PS presents an aromatic ring in his structure that leads to a steric envelope responsable of the low mobility of the chain. Therefore it's an amorphus and rigid polymer.

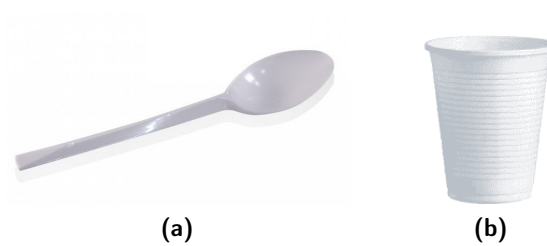
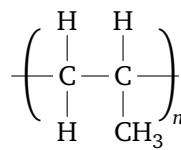


Figure 2: PS samples.

1.1.3 Polypropylene

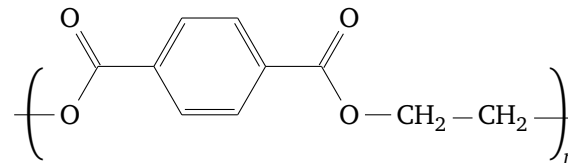


PP is a tough and rigid thermoplastic material. Isotactic conformation is obtained by Ziegler-Natta or metallocene polymerization. It shows an high thermal stability due to its semycrystalline structure.



Figure 3: PP sample.

1.1.4 Polyethylene terephthalate

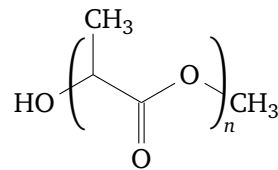


PET is a naturally colorless, semi-crystalline material. Some of its most important characteristics include: water resistance, high strength despite low density, shatterproofness and its wide availability as an economic and recyclable plastic.



Figure 4: PET sample.

1.1.5 Polyactic acid

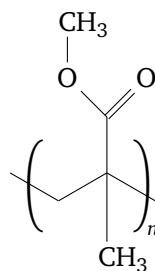


PLA is an amorphous, biodegradable and bioactive thermoplastic polymer derived from renewable resources like corn starch or sugar cane. It is principally made through condensation and ring-opening polymerization.



Figure 5: PLA sample.

1.1.6 Polymethyl methacrylate



PMMA is a transparent thermoplastic non-cross linked polymer often used as a lightweight or shatter-resistant alternative to glass.

2 Materials and methods

2.1 Materials

The polymeric materials that have been used are: plastic yogurt cup (PS), disposable coffee stick (PS), plastic coffee cup (PS), plastic water bottle (PET), plastic bottle cap (PE), plastic cups (PS, PP, PLA), disposable spoon (PS) and tire piece. In Table 1 main properties of the analyzed polymers are reported.

Table 1: Glass transition and melting temperatures.

Materials	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$
High density polyethylene (PE)	−110	138
Polystyrene (PS)	100	—
Polypropylene (PP)	−10	165
Polyethylene terephthalate (PET)	70	265
Polylactic acid (PLA)	50	140
Polymethyl methacrylate (PMMA)	105	—

Tire samples have been provided by Marangoni (Rovereto (TN), Italy) and are mainly composed by styrene-butadiene rubber (SBR), carbon black, sulfur, accelerators and other additives. All the others objects used in the experimental activity have been provided by University of Trento.

The solvents used in this laboratory experience to evaluate the effect on plastics are:

- acetone in different concentrations: 25%, 50%, 75% and 100%;
- ethyl alcohol;
- mixed solution of ethyl acetate, isopropyl alcohol, aqua, parfum, benzophenone-1, butyl acetate, glycerin, hydrolyzed keratin, CI 60725 ("*Levasmalto rapido*" by PSS Distribuzione srl, Alessandria (IT));
- mixed solution of acetone, aqua, benzophenone, phanthenol, ethyl acetate, parfum, D-limonene, butyl acetate, benzyl alcohol, CI 61565, CI 60725 ("*Levasmalto*" by PSS Distribuzione srl, Alessandria (IT));
- mixed solution of methyl acetate, acetone, toluene, xylene, ethyl acetate, heptane, ethyl lactate, methyl formate and methanol ("*Diluyente Nitro Antinebbia Top*" by Multichimica Spa, Padova (IT)).

2.2 Heat treatments

Samples of different types of polymers have been placed into a pressure cooker full of water for 20 minutes (heat treatment T1). In these conditions the samples have been heated at about 120°C, that corresponds to the boiling point of water in the cooker. Another different treatment that has been carried out is the locally heating of the samples through a hot air gun (heat treatment T2). In this case the maximum temperature reached is about 150°C. A third treatment has been done by filling the samples with 90°C hot water (heat treatment T3).

2.3 Sample preparation

In Table 2 sample coding is reported.

Table 2: Sample coding.

Sample	Description
PET	PET without heat treatment, from bottle threaded section
PET-T1	PET with heat treatment T1, from bottle threaded section
PET-T2	PET with heat treatment T2, from bottle threaded section
PLA	PLA without heat treatment, from a disposable plastic cup
PLA-T1	PLA with heat treatment T1, from a disposable plastic cup
PP	PP taken from a disposable plastic cup
PE	PE taken from a plastic bottle cap
PS	PS taken from a disposable plastic cup
PMMA	bone cement
T	tire rubber

3 Experimental activity

3.1 Effect of heat treatments on samples

Different heat treatments have been done on samples, as reported in Table 3. Their effects have been studied, with attention to crystallinity evolution and density.

Table 3: Heat treatments.

Sample	Description	Duration	Temperature
T1	Pressure cooker soaking	20 min	120°C
T2	Local heating through hot air gun	5 min	150°C
T3	Water filling	1 min	90°C

3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) has been carried out with instrument Mettler DSC30. Samples have been tested in inert nitrogen 100 ml/min flow, with a heating ramp of 0 – 300°C at 20°C/min. A first heating is followed by a cooling and eventually by a second heating. This is done in order to reset the thermal history of samples and to get informations about the degree of crystallinity (DC). From DSC analysis the specific enthalpy of melting (ΔH_m) and crystallization (ΔH_c) are obtained, together with melting temperature (T_m), crystallization temperature (T_c), glass transition temperature (T_g) and specific heat variation (Δc_p).

3.2.1 Melting enthalpy, degree of crystallinity and density

Degree of crystallinity (α_c) of polymers can be evaluated accordingly to Equation 1.

$$\alpha_c = \frac{\Delta H_m}{\Delta H_m^{\text{REF}}} \quad (1)$$

Where ΔH_m^{REF} is the reference value of specific melting enthalpy of a 100% crystalline polymer. Density (D) can be estimated knowing the crystallinity of polymers α_c , accordingly to empirical Equation 2.

$$D = D_0 + m \cdot \alpha_c \quad (2)$$

Where D_0 is the density of a completely amorphous polymer while m is the angular coefficient of the interpolating line passing from D_0 and the density at 100% crystallinity. Effect of DEG has been considered in order to calculate the right crystallization degree.

3.2.2 Effect of DEG in PET

Melting temperature of PET samples is affected by the presence of diethylene glycole (DEG) accordingly to the Equation 3.

$$T_m = 271 - 5.25 \cdot \text{wt}\%_{\text{DEG}} \quad (3)$$

3.3 Density measurements

The density measurements have been carried out using instrument Gibertini E42. Three samples have been tested: PET, PET-T2 and PET-T3. The normative for this type of test is the ASTM D792 [3] (Archimedean test), where each specimen has to be weighted in two different conditions, in air and liquid. In particular, for the measurement in the liquid, the sample have been placed inside a container filled with water, using an appropriate plate and mounting. Density of samples has been calculated using Equation 4.

$$\rho = \frac{m_a}{m_a - m_{acq}} \cdot \rho_w \quad (4)$$

where m_a and m_{acq} indicate respectively the mass in air and in water of the specimens and ρ_w indicates the water density, measured according to the normative.

A comparison with data from the DSC has been done. Having the densities of the samples PET and PET-T2 from Table 8 and the crystallinity from Table 7, using the straight line Equation 5 it was possible to calculate the densities of 0% and 100% crystalline samples.

$$\rho = \rho_0 + m \cdot \alpha \quad (5)$$

Density measurement of samples of PMMA of the previous lab session were also taking in account. The purpose was to understand how the presence of BaSO_4 and water affected the density of the samples, so some specimens of pure PMMA were also considered. The sampling group analyzed was of the polymerization P2 with and without thermal treatment.

3.4 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) has been carried out with instrument TGA Q5000. Samples have been tested in inert nitrogen 10 ml/min flow, with a heating ramp of 25 – 700°C at 10°C/min. Degradation of samples is observed, obtaining the residual mass percent at 700°C (m_r), the onset temperature of degradation (T_{onset}) and the temperature of maximum degradation rate (T_d).

3.5 Solvent effect

It has been investigated the effect of different solvents on coffee stirrer sticks and on two cups, PS and PP samples. The sticks have been put in test tubes filled with various solvents: acetone with subsequently higher concentrations (25%, 50%, 75%, 100%); two mixed solutions used in cosmetic field, one with acetone as principal constituent, the other with ethyl acetate and isopropyl alcohol; last solvent employed to test the cups is an aromatic diluent used with paints, this contains various mixture, in particular a percentage of toluene.

4 Results and discussion

4.1 Effect of heat treatments on samples

Polymers subjected to heat treatments show different behaviours.

From pressure cooker test, it has been noticed that PP has become more opaque since it has increased its degree of crystallization due to the exposure at high temperature for prolonged time. PE has not displayed any modification since it is already a semicrystalline polymer at room temperature and its melting point is higher than the temperature reached in this process. PLA has exhibited a process of crystallization since its glass transition has been overcome. Moreover its shape has changed trying to return back to the one before processing. PET has shown the same behaviour of PLA trying to return back to parison shape and crystallizing in its most dense parts (neck and bottom of the bottle). PS samples have been deformed reaching their pre-process plate shape. The degree of crystallization of these samples was not particularly evident since PS has high glass transition temperature close to that of process.

In the second heat treatment the local heating of samples of PET and PS through the hot air gun has lead to similar results already described for the first treatment. The PE sample, instead, has shown more rubbery behaviour: it could be deformed a lot with high extension of chains due to this local heating.

In the last heat treatment it has been observed that PLA, as soon as the contact with hot water, has been deformed itself since its T_g has been overcome. About PP and PS samples nothing has changed since the temperature of water was not so high enough to reach, respectively, their T_m and T_g . In Figure 6 samples after heat treatments are shown.

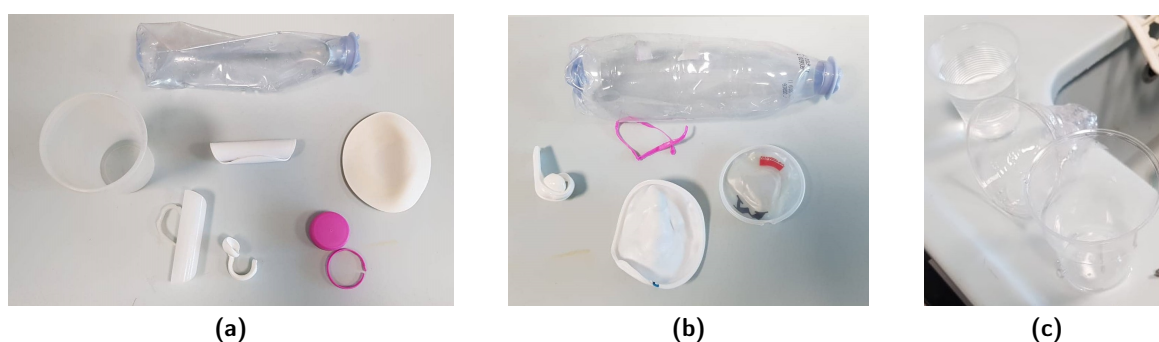


Figure 6: Samples after heat treatments:
a) T1, b) T2 c) T3.

4.2 Differential scanning calorimetry (DSC)

In Figure 7 the DSC thermogram of PET-T2 and PET samples is reported.

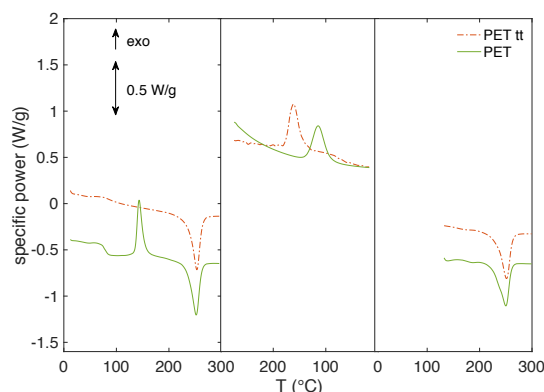


Figure 7: DSC thermogram for PET-T2 and PET samples.

From the chart it can be seen how the heat treated PET doesn't show a crystallization event during the first heating ramp. This event is related to the completion of crystallization shown by PET on heating, when the mobility of chains is enough for the system to reach a more stable and compact conformation, found in semi-crystalline one. This transformation releases energy since a more stable condition is reached compared to the amorphous one. Both PET-T2 and PET present a melting event but a difference in specific enthalpy of melting is seen: the heat treated sample has a higher value, sign that the grade of crystallinity of it is greater than the non treated PET sample. On cooling, due to a procedural error (run out of nitrogen), the cooling rate is lower than expected and the crystallization of PET sample is delayed with respect to PET-T2. Resulting values of specific crystallization enthalpy are found to be equal on cooling, as the thermal history of polymers has been canceled. For same procedural error as before, the second heating ramp starts later, at around hundred celsius, but both samples are seen to have comparable melting specific enthalpies, while no crystallization events are observed, as the polymer completely crystallized on cooling ramp.

In Figure 8 the DSC thermogram of PE, PP and PS samples is reported.

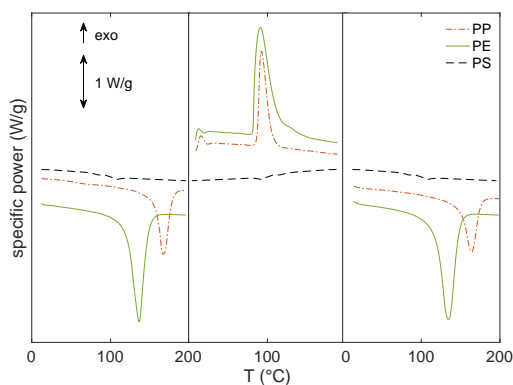


Figure 8: DSC thermogram for PE, PP and PS samples.

In the chart it can be seen how PS doesn't show any melting or crystallization event, since it's completely amorphous. Glass transition is instead observed either on heating and on cooling. PP and PE present very similar behavior with temperature: both present melting and crystallization while their glass transition temperatures are out of scale (below zero celsius) and thus not observed in the analysis. PE is found to release and absorb a lot of energy during respectively crystallization and melting.

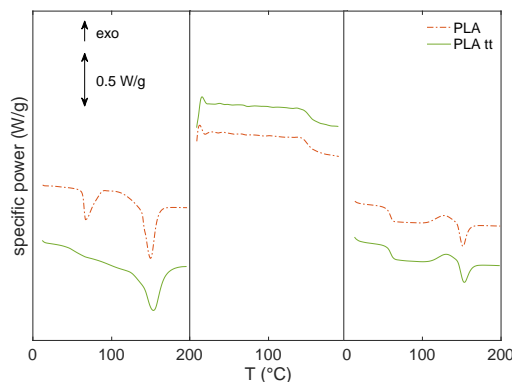


Figure 9: DSC thermogram for PLA-T1 and PLA samples.

In Figure 9 the DSC thermogram of PLA-T1 and PLA samples is reported.

From the chart it can be seen how the heat treatment in sample PLA-T1 is related to the disappearance of the crystallization event instead present in sample PLA at about 90°C. Glass transition is observed in both samples together with melting. A significant difference in the specific enthalpy of melting between these samples is observed: PLA-T1 shows a higher value with respect to PLA, evidence that the crystallization occurred during the heat treatment led to an higher level of degree of crystallization. During second heating ramp, the behavior of PLA and PLA-T1 is the same as the thermal hystory of both samples has been reset.

In Table 4 results of DSC analysis of the first heating on all samples are displayed.

Table 4: DSC results for all samples during the first heating.

Sample	$T_g(^{\circ}C)$	$T_c(^{\circ}C)$	$T_m(^{\circ}C)$	$\Delta H_c(J/g)$	$\Delta H_m(J/g)$
PET	76.1	143.4	251.8	23.9	35.4
PET-T2	82.4	—	253.0	—	41.2
PLA	64.8	90.4	149.2	26.0	21.3
PLA-T1	50.8	—	152.8	—	33.9
PE	—	—	136.2	—	169.6
PP	—	—	166.9	—	83.0
PS	104.5	—	—	—	—

In Table 5 results of DSC analysis of the cooling on all samples are displayed.

Table 5: DSC results for all samples during cooling.

Sample	$T_g(^{\circ}C)$	$T_c(^{\circ}C)$	$\Delta H_c(J/g)$
PET	—	114.0	30.7
PET-T2	—	161.3	30.7
PLA	52.4	—	—
PLA-T1	49.7	—	—
PE	—	108.7	182.4
PP	—	107.5	83.0
PS	86.8	—	—

In Table 6 results of DSC analysis of the second heating on all samples are displayed.

Table 6: DSC results for all samples during the second heating.

Sample	$T_g(^{\circ}C)$	$T_c(^{\circ}C)$	$T_m(^{\circ}C)$	$\Delta H_c(J/g)$	$\Delta H_m(J/g)$
PET	—	—	250.3	—	31.9
PET-T2	81.4	—	251.1	—	34.8
PLA	59.3	128.7	151.6	7.5	6.1
PLA-T1	59.7	130.8	153.3	6.8	6.6
PE	—	—	134.6	—	182.3
PP	—	—	164.1	—	84.5
PS	92.3	—	—	—	—

4.2.1 Melting enthalpy, degree of crystallinity and density

Reported values of melting enthalpy for PET, PLA, PE and PP are compared to reference values found in literature [1], contained in Table 7, considering completely crystallized polymers.

Table 7: Crystallization degree and density obtained from DSC analysis.

Sample	$\Delta H_m^{REF}(J/g)$	$\Delta H_m(J/g)$	$\alpha_c(\%)$	$D(kg/m^3)$
PET	145	11.5	8	1349
PET-T2	145	41.2	28	1385
PLA	93.7	4.7	5	1252
PLA-T1	93.7	33.9	36	1264
PE	293	169.6	58	922
PP	207	83.0	40	887

Values of density can be estimated knowing the degree of crystallinity of polymers, relating to reference values found in literature [1], using linear interpolation.

4.2.2 Effect of DEG in PET

Obtained melting temperature for PET is about 251 $^{\circ}C$, thus the amount of DEG can be estimated to 3.8%.

4.3 Density measurements

The water temperature has been measured obtaining a value of 22.6 $^{\circ}C$, so the water density used is 997.6351 kg/m³. For each sample, three specimens have been tested. Results for each sample are reported in Table 8.

Table 8: Density measurements of PET bottles with different thermal treatment.

Sample	$\rho(kg/m^3)$
PET	1313 \pm 6
PET-T2	1336 \pm 3
PET-T3	1327 \pm 3

This values can be compared with the ones obtained by literature [1], reported in Table 9:

Table 9: Density of PET from literature [1].

Cristallinity	ρ (kg/m ³)
Amorphus, non-oriented	1335
Calculated, crystal	1515

It can be observed that the amorphus PET density is different from the one calculated by Archimedean test. This can be explained by the presence of a certain amount of diethylene glycol (DEG), which increases the volume of samples by reducing the density. Starting from a different polymer with respect to the literature one, new values of density for totally crystalline and totally amorphus PET have been calculated. From Equation 5 results are shown in Table 10.

Table 10: Density and crystallinity of PET sample, considering the effect of DEG.

Sample	α (%)	ρ (kg/m ³)
Amorphus, non-oriented	0	1304 ± 10
PET	8	1313 ± 6
PET-T2	28	1336 ± 3
Calculated, crystal	100	1419 ± 36

The density values of the PMMA samples are reported in Table 11.

Table 11: Density of PMMA samples.

Sample	ρ (kg/m ³)
Pure	1183 ± 1
P2	1234 ± 12
P2-HT	1242 ± 15

As the table shows, the density is increased by the presence of BaSO₄.

4.4 Thermo-gravimetric analysis (TGA)

In Figure 10a-b the TGA thermograms of PMMA and T samples are reported.

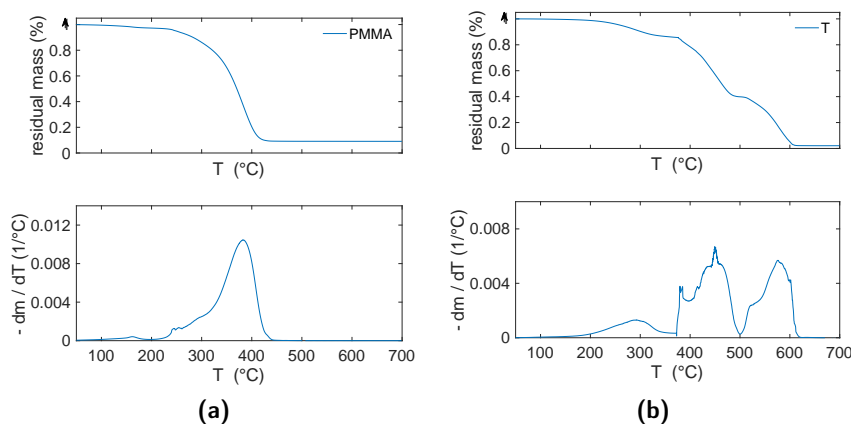


Figure 10: TGA thermograms for (a) PMMA and (b) T samples.

From Figure 10a it can be noticed that at 161.6°C the 2.35% of the total mass is lost, probably due to presence of water. At 382.9°C, degradation of the polymer (PMMA) occurs and thus a loss of 87.70% of the initial mass is registered. However a residue of 9.1% is left at the end of the process because the barium sulphate (BaSO_4) decomposes at much higher temperatures. This percentage of remaining mass is comparable with the value of the amount of sulphate found in the previous laboratory activity that was equal to 9.6% for the first polymerization.

From Figure 10b it can be observed that a first loss of mass of about 13.7% is present at 288.8°C due to decomposition of oils and other chemical products contained in the blend, while at 457.8°C the degradation of the rubber occurs with a mass loss equal to 45.8%. At about 575.9°C another loss of about 37.5% related to carbon black is seen. In this case a residual mass of 2.1% is left at the end of the analysis. These values of mass losses are comparable with the usual composition of a tire [2]. In Table 12 results of TGA analysis on all samples are displayed.

Table 12: TGA results for all samples.

Sample	$T_{onset}(^{\circ}\text{C})$	$T_{d,1}(^{\circ}\text{C})$	$T_{d,2}(^{\circ}\text{C})$	$T_{d,3}(^{\circ}\text{C})$	$m_r(\%)$
PMMA	—	382.9	—	—	9.1
T	—	288.8	457.8	575.9	2.1

Moreover, it has been evaluated the amount of natural and synthetic rubber present in the sample looking at the thermogram and its derivative: the derivative shows two peaks and the thermogram shows a slight difference in the slope, corresponding to the degradation of the two components. The amount has been estimated as 30% of natural rubber and 70% as synthetic rubber. These values of mass losses are comparable with the usual composition of the tire.

4.5 Solvent effect

Polystyrene stirrer sticks put in acetone show different responses depending on the concentration of the solution: in acetone 25% the specimen is softer but maintains its shape, with a concentration of 50% the stick is no more intact and the remaining part is spreaded on the sides of the test tubes. Increasing more the concentration (acetone 75%) the remaining polystyrene stick is less visible until it is completely dissolved by the solvent at the concentration of 100%. The specimen tested with the mixture of acetone shows a higher resistance to the commercial solvent, due to its lower concentration. These experimental evidences are in agreement with what expected, acetone can enter in polymer chains and can be absorbed by the stick according to the concentration of the solvent, this is more favorable in the case of polystyrene due to its amorphous structure. The same type of stick put in ethyl alcohol has maintained its features, showing the resistance of polystyrene to this solvent. The specimen put in the acetone mixture used in cosmetic becomes softer with the possibility to change significantly its shape and once it is deformed, if the solvent is left to evaporate, the specimen maintains the new shape. Polystyrene shows low resistance also to aromatic diluent that contains toluene, in fact the sticks and the cups filled with this solvent completely dissolved the part in contact. Otherwise the polypropylene cup submitted to the same experiment has maintained its shape and all other features. The polymer shows a higher resistance to this solvent, thanks to its semicrystallinity and therefore its more ordered structure able to reduce the absorption among the polymer chains.

5 Conclusions

The laboratory session has concerned the evaluation of some characteristic of common polymeric samples, such as cups, coffee sticks or water bottle, in order to compare theoretical values of different polymers with values of industrial products and to evaluate the composition of these samples. Through Archimedeian test was found out that the density of PET bottle threaded section, crystallized with heat treatment, was lower than the amorphous value of density of PET. This effect of decreasing of density is due to the presence of diethylene glycol in industrial composition, added to reduce crystallizability. The addition of DEG is also visible in DSC analysis in decreasing of melting point respect to theoretical value of PET. Density values of PET bottle estimated through DSC analysis are a little bit higher than values obtained with Archimedeian test since they don't take into account the presence of DEG and are calculated on the basis of pure PET. In DSC in PET and PLA heat treated, as expected, the crystallization peak disappears and this is related to the completion of crystallization in heat treatment. In heat treatments it has been noticed that samples trying to return back to parison shape in order to reduce stresses introduced in industrial processes. Those polymers in which T_g has been overcome in heat treatments has become more opaque due to the increase of crystallinity. In TGA analysis of PMMA at very high temperatures (above 600°C) can be noticed the presence of a residual mass due to the addition of barium sulphate in bone cement composition. This component is added in order to allow x-ray analysis. In TGA thermogram of tire sample has been evaluated the presence of different products contained in the blend added to the ABS rubber, such as oil and carbon black.

References

- [1] Polymer handbook, J. Brandrup, E.H. Immergut.
- [2] HF. Mark et al. Encyclopedia of Polymer Science and Technology.
- [3] ASTM D792 "Standard test methods for density and specific gravity of plastics by displacement".