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**Sustainpack**

**Innovation and sustainable Development in the Fibre Based Packaging Value Chain**

Instrument: **IP**

**D5.37 Report on the ageing behaviour of composites samples**

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<b>PP</b>	Restricted to other programme participants (including the Commission	
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission	
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	

## WP 5.3 Composites characterisation

### D5.37 Report on the ageing behaviour of composites samples

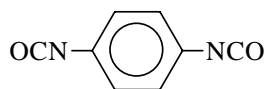
As part of the industrial and technological developments, new materials have to be developed and many researches show that composites play an increasingly important role among them (lighter, more efficient or both). In addition, many studies in the area seek to prevent the shortage of petrochemical resources in developing the use of natural fibers and the use of new biopolymer (from renewable resources).

In this report, we will focus on the ageing of new composite materials from Sub-Project 5 made with natural fibres (grafted or not) and biopolymer matrices. Indeed, it seems important to check the impact of new technologies of compatilisation between fibre (hydrophilic) and matrix (hydrophobic) like copolymerisation process (chemical grafting) developed in WP5.1.

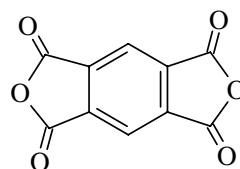
#### I. Materials and methods

##### Compatibilisation with co-polymerisation technique

The copolymerisation approach consists in grafting small bi-functional molecules onto the fibre surface. These grafting agents contain two identical functionalities and exhibit a rigid backbone structure. This will ensure that only one functionality will react with the fibre surface during grafting, leaving the other one to react with the matrix during composite processing. Examples of grafting agents are: 1,4-phenylene diisocyanate (PPDI), and pyromellitic dianhydride (PMDA).



PPDI



PMDA

Cellulosic materials used in this study is microcrystalline cellulose (Avicell), obtained as a powder of aggregates and which is used extensively in composite materials.

### **Composite films preparation**

A double-screw extruder (micro-compounder) was used for the preparation of composites with 30 wt% Avicell fibres. Both modified and unmodified fibres have been used to prepare composite with blend of polyester MaterBi and poly-l-lactide acid before extrusion. The blend properties with different compositions (25-75, 50-50 and 75 - 25 (PEM / PLLA)) have been analyzed and detailed in deliverable D5.48.

The mixtures of Avicell fibres and matrices have been introduced manually into the extruder at a temperature of 180°C for 15 min with 50 rpm rotation speed. An homogeneous materials is obtained when observing a constant torque value. After this, the extracted rod-shaped materials was dehydrated for 24 hours in a vacuum system at 50°C, in order to eliminate residual moisture content and then moulded by using a thermopress at 180°C for 2 minutes under 20 bar using siliconised paper coated steel plates. Samples are then rapidly cooled with water at 25°C and the thickness was measured.

### **Ageing of materials.**

The ageing study for these composite materials was made in climatic chamber with tropical condition at 35°C and 80% RH relative humidity for 45 days. These conditions simulate about 4 months (110 days) of ageing in normal conditions.

### **Characterizations**

Differential Scanning Calorimetry (DSC) experiments were carried out with a DSC Q100 differential calorimeter (TA Instruments) fitted with a manual liquid nitrogen cooling system. The composite samples with different compositions (25-75/50-50/75-25 PEM/PLLA) were placed in hermetically closed DSC devices. The heating and cooling rates were 10°C.min<sup>-1</sup> from -100°C to 200°C, respectively, in N<sub>2</sub> atmosphere. Sample weights were between 8 to 9.5 mg. Three samples were used to characterize each composite. No quenching has been made with materials which have been analyzed directly after extrusion process.

Dynamical Mechanical Analysis (DMA) of the composites films was carried out using a RSA3 (TA Instruments, USA) equipment working in tensile mode. The measurements were performed at a constant frequency of 1 Hz, strain amplitude of 0.05%, a temperature range of -100°C to 200°C, a heating rate of 5°C.min<sup>-1</sup> and distance between jaws of 10 mm. The width of the samples varied from 3 to 5 mm, which were measured before each analysis. Three samples were used to characterize each composite. To remove most of water from the

material, the specimens were immediately conditioned in the desiccators under vacuum, overnight before any measurement. It was checked that, under these conditions, a further conditioning did not modify the behaviour.

## II. RESULTS AND DISCUSSIONS

Several blend of biomatrices with different compositions (25-75, 50-50 and 75 - 25 (PEM / PLLA)) have been used as it was decided in previous SP5 meeting in order to find the best compromise. The properties of these blends have been analyzed and detailed in deliverable D5.48.

The aim of the study was to check **2 parameters after ageing**: the influence of the presence of natural fibres in the blend, and the influence of the grafting of the fibres.

Several characterisation techniques have been employed such as differential scanning calorimetric (DSC) measurements and dynamic mechanical analysis (DMA).

### II.1 DSC Analysis:

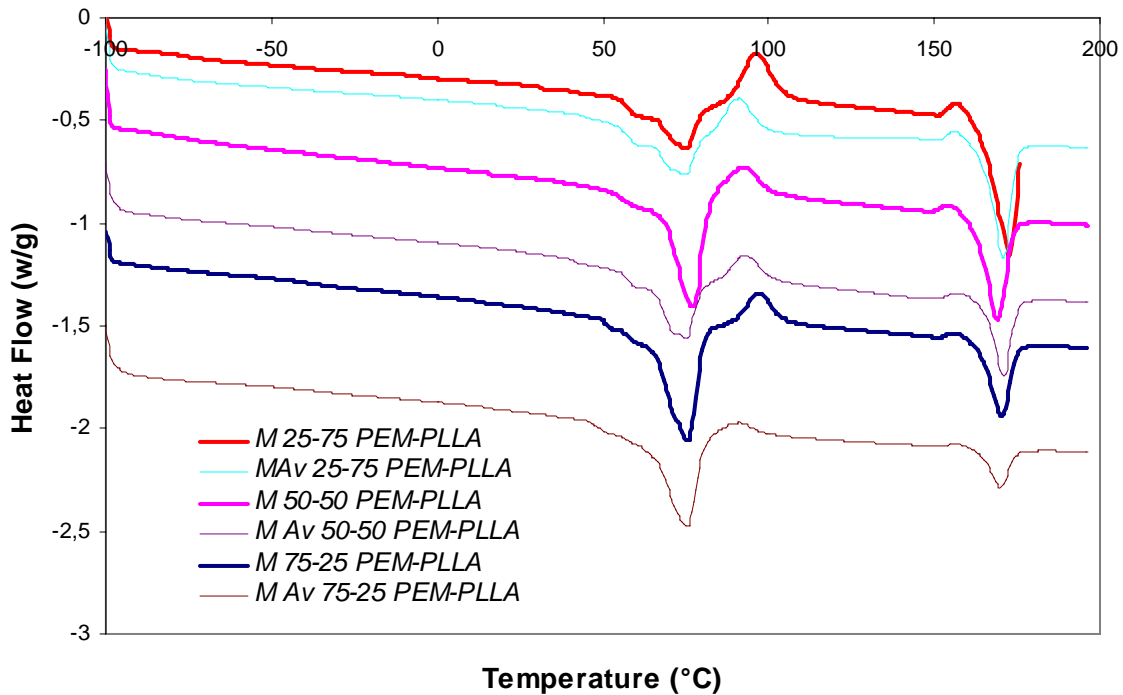
- *Influence of composites with ungrafted fibres:*

- . **Before ageing:**

Thermal characterization of composite films with different blends of Polyester Materbi (PEM) and poly-l-lactide acid (PLLA) containing 30% non-grafted Avicell fibre was carried out by DSC measurements.

DSC curves of unfilled blends (labeled “M 25/75 PEM-PLLA”) and blends reinforced with Avicell fibres (labeled “MAv 25/75 PEM-PLLA”) have been compared in Figure 1.

Two melting endotherms are observed which temperature position corresponds to those of the parent polymers. An exothermic peak is also observed in Figure 1 and it is ascribed to the crystallization of PLLA chains during the temperature scan. This phenomenon can be assigned to the molecular rearrangement of PLLA chains occurring above its glass transition.



**Figure 1:** DSC curves of blends with or without fibres before ageing.

Few differences between unfilled and filled materials are visually detected, except the fact that the low temperature melting endotherm is less sharp which means that the size distribution of crystallites is broader.

From the analysis of DSC curves, the total enthalpy of fusion ( $\Delta H_m$ ) and total degree of crystallinity ( $\chi_c$ ) were obtained for the different materials (Table 1).

	$X_{PLLA}$ (%)	$\Delta H_{f,tot}$ (J/g)	$\chi_{c,PLLA}$ (%)	$\chi_{c,PEM}$ (%)	$\chi_{c,tot}$ (%)
M 25/75 PEM-PLLA	75	68,7	58,3	46,8	55,5
M Av 25/75 PEM-PLLA	52,5	94,7	86,1	65,1	56,6
M 50/50 PEM-PLLA	50	78,3	66,4	53,6	60,0
M Av 50/50 PEM-PLLA	35	68,9	46,7	47,0	32,8
M 75/25 PEM-PLLA	25	81,5	67,0	55,8	58,6
M Av 75/25 PEM-PLLA	17,5	74,6	64,8	50,9	38,1

**Table 1:** Thermal data obtained from DSC curves. PLLA content ( $X_{PLLA}$ ); total enthalpy of fusion ( $\Delta H_{f,tot}$ ); degrees of crystallinity ( $\chi_{c,PEM,PLLA}$ ) for PEM and PLLA and total degree of crystallization ( $\chi_{c,tot}$ ).

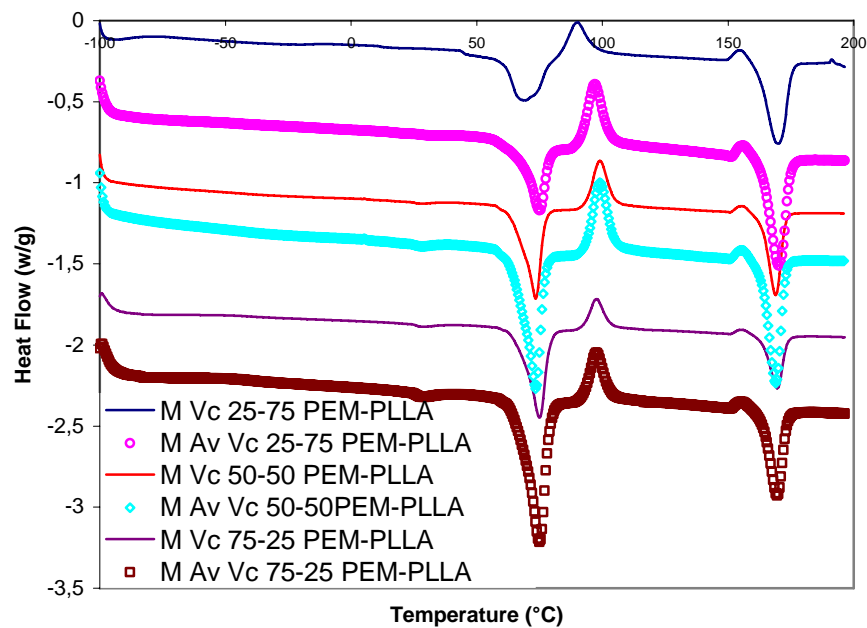
A decrease of the total degree of crystallinity is observed for composites reinforced with 30% ungrafted fibres regardless the composition of the matrix. Only the blend M Av 25/75 PEM-PLLA has a total degree of crystallinity that remains constant.

This decrease of crystallinity upon Avicell fibre addition is most probably due to the fact that fibres limit the possibility of polymeric chains rearrangement during the extrusion process avoiding their crystallization.

The presence of the fibres significantly reduces the crystalline phase in composite materials.

**. After ageing:**

DSC curves of unfilled and filled blends after ageing (labeled “Vc”) have been compared in Figure 2. The global aspect of the thermograms is similar to the one observed before ageing but the low temperature endothermic peak is sharper.



**Figure 2:** DSC curves of unfilled and filled blends after ageing.

From the analysis of DSC curves, the total enthalpy of fusion ( $\Delta H_m$ ) and the total degree of crystallinity ( $\chi_c$ ) were obtained for the different materials (Table 2).

	$X_{PLLA}$ (%)	$\Delta H_{f,tot}$ (J/g)	$\chi_{c,PLLA}$ (%)	$\chi_{c,PEM}$ (%)	$\chi_{c,tot}$ (%)
M 25/75 PEM-PLLA	75	95,6	83,1	65,7	78,7
M Av 25/75 PEM-PLLA	52,5	76,3	65,2	52,6	43,4
M 50/50 PEM-PLLA	50	93,7	83,3	64,9	74,1
M Av 50/50 PEM-PLLA	35	74,8	55,1	51,9	37,5
M 75/25 PEM-PLLA	25	90,0	74,6	62,9	65,8
M Av 75/25 PEM-PLLA	17,5	76,3	68,5	53,3	40,0

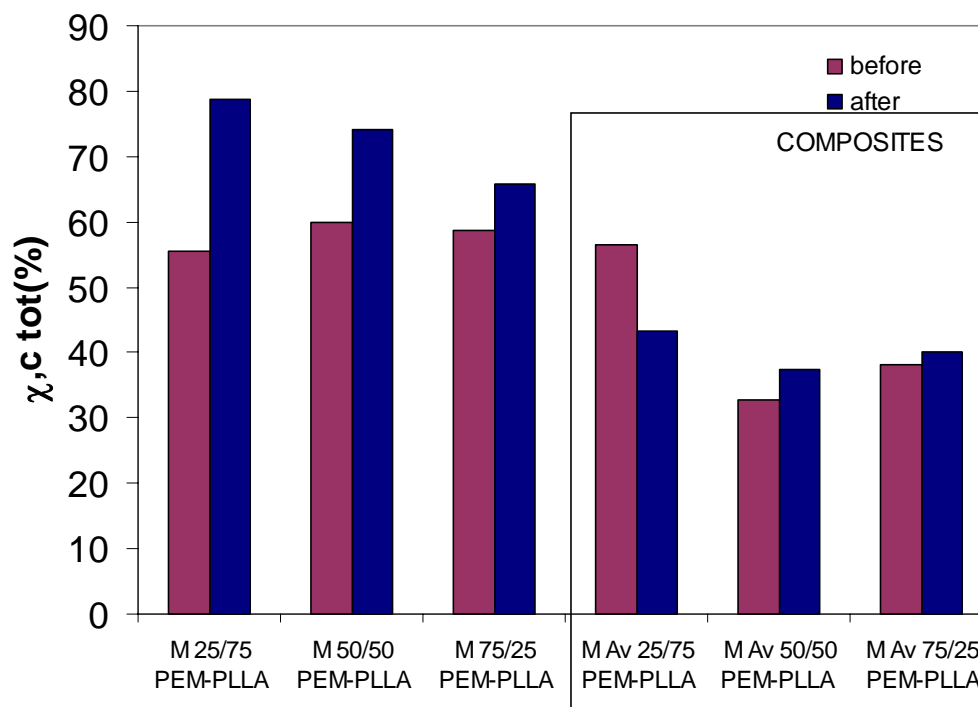
**Table 2:** Thermal data obtained from DSC curves after ageing for 45 days at 35 °C and 80% RH. PLLA content ( $X_{PLLA}$ ); total enthalpy of fusion ( $\Delta H_{f,tot}$ ); degrees of crystallinity ( $\chi_{c,PEM, PLLA}$ ) for PEM and PLLA and total degree of crystallization ( $\chi_{c,tot}$ ).

The difference between the unfilled matrix and composites is similar to the one reported for unaged materials. The decrease of the total degree of crystallinity upon fibres addition is even higher after ageing. This important decrease of the crystallinity of the matrix is observed regardless its composition. The value of the degree of crystallinity of the unfilled matrix after ageing is almost twice the one reported for composites.

It confirms that the fibres prevent the rearrangement of polymer chains even during ageing and then avoid any crystallisation.

Figure 3 helps to compare the influence of ageing on unfilled blend and composites. When adding fibres, the degree of crystallinity does not increase (or slightly increase) during ageing whereas it increases much more for the unfilled blend.

It is also worth noting that the degree of crystallinity after ageing decreases with the PLLA content in the material. This confirms that the PLLA is the polymer which crystallizes during ageing.

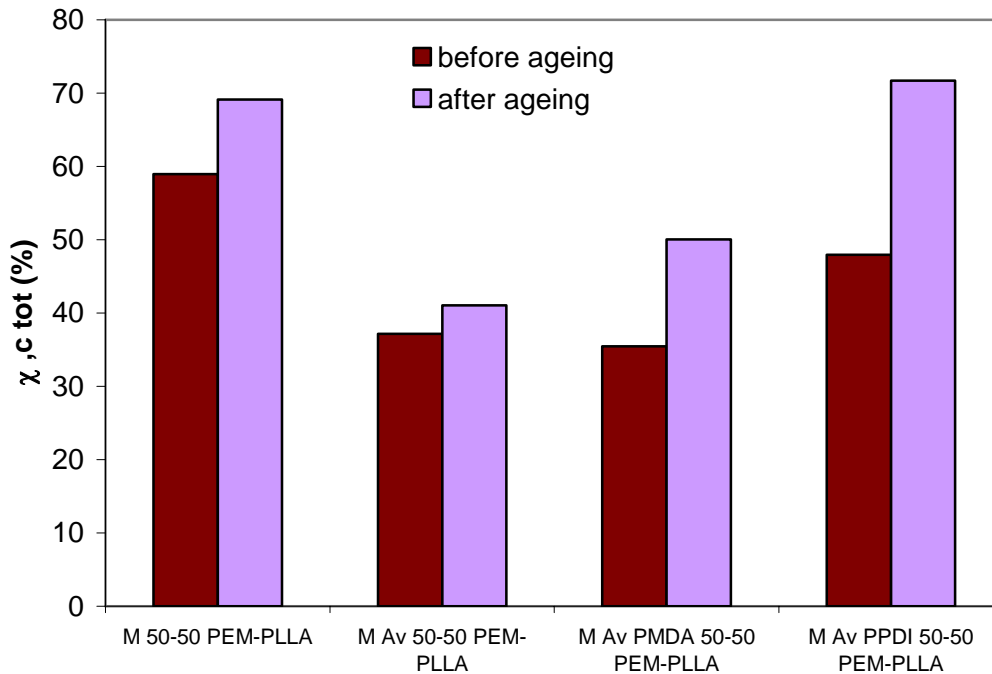


**Figure 3:** Degree of crystallinity for composites with mixture matrix before and after ageing.

- *influence of the grafting of the fibres:*

We have focused this part of the study on composite materials obtained with the 50-50 PEM-PLLA blend matrix and 2 kinds of grafted fibres (with PMDA and PPDI).

DSC curves are similar than those obtained for composites (Figures 1 and 2) and allows us to obtain the total degree of crystallinity ( $\chi_c$ ). Values before and after ageing are compared in Figure 4.



**Figure 4:** Degree of crystallinity for composites with 50-50 PEM-PLLA reinforced with ungrafted or grafted fibres before and after ageing.

After ageing the increase of the degree of crystallinity is more significant for composites reinforced with chemically treated fibres.

The higher  $\chi_c$  value is obtained for PPDI grafted fibres which allows to achieve almost the same degree of crystallinity than the one obtained for the unfilled blend.

The chemical modification tends to increase the degree of crystallinity certainly because of the induced compatibilisation between fibre and matrix. Indeed, as we use a copolymerization technique (“bridge” between fibre and matrices), fibre does not play anymore a role of reorganisation inhibitor but can follow and move in meantime than the polymer chain during crystallization rearrangement.

Another interpretation is also possible. Fibres in composite can absorb moisture present during the ageing process which prevents the plasticization of the blend and limits the polymer chains reorganisation. On the contrary, chemical grafted fibres are more hydrophobic, that means there are more water available for the blend which helps reorganisation by a plasticization effect.

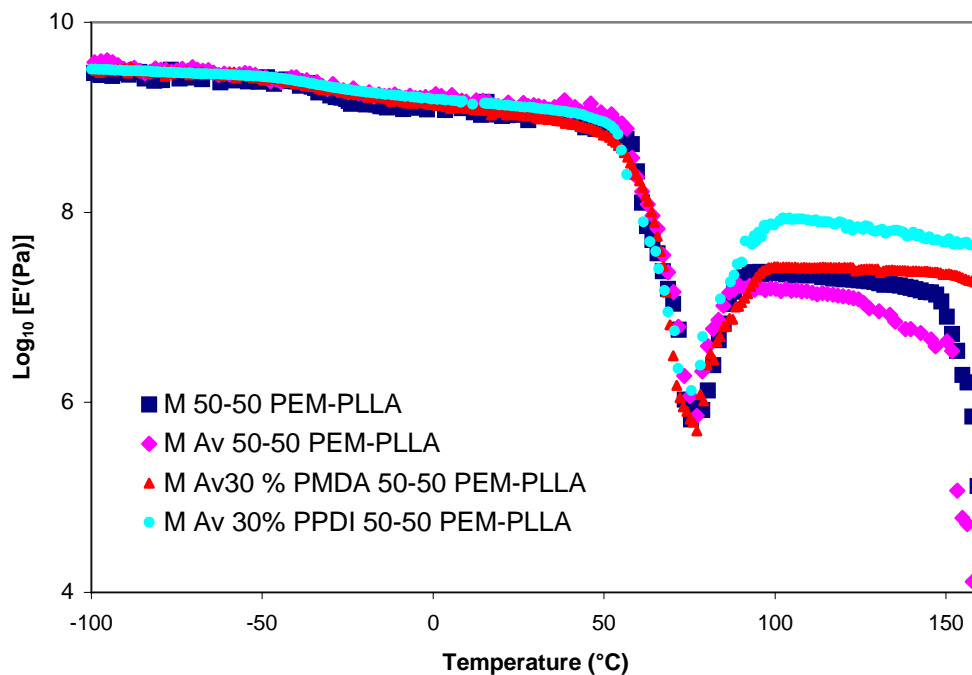
This thermal analysis gave us some important results concerning blend organisation and effect of fibre in crystallization. Let's see now the influence on mechanical properties.

## II.2 Dynamic Mechanical Analysis :

Dynamic mechanical measurements were performed on the unfilled 50-50 PEM-PLLA blend; and its composites reinforced with 30% ungrafted and grafted Avicell fibre.

### . Before ageing:

The evolution of  $\log (E'/\text{Pa})$  (logarithm of the storage tensile modulus) versus temperature at 1 Hz is displayed in Figures 5. For low temperatures, it was difficult to observe any change in the modulus for composites reinforced with Avicell fiber. To minimize this effect, the elastic tensile modulus,  $\text{Log}_{10} E'$  at  $-100\text{ }^\circ\text{C}$  was normalized for all the samples.



**Figure 5:** DMA curves for composite with 50-50 PEM-PLLA mixture matrix biopolymer reinforced with ungrafted or grafted fiber before ageing.

The DMA curves show a distinct relaxation phenomenon associated with the glass–rubber transition of Polyester Materbi around  $-40\text{ }^\circ\text{C}$ , and two modulus drops ascribed to a melting phenomenon. The first one, at about  $60\text{ }^\circ\text{C}$ , corresponds the melting of the Polyester MaterBi (almost in meantime than  $T_{g, PLLA}$ ) and the second one, at about  $170\text{ }^\circ\text{C}$ , corresponds the melting of the PLLA.

The storage modulus remains practically constant up to a temperature of 50 °C. But the rubbery moduli are decreasing for higher temperatures and depend on the degree of crystallinity of the material.

We can notice that the addition of ungrafted fibres results in a slight decrease of the rubbery modulus. This decrease can be ascribed to the decrease of the degree of crystallinity of the matrix previously reported from DSC measurements. This phenomenon seems to overcome the expected reinforcing effect of the fibres.

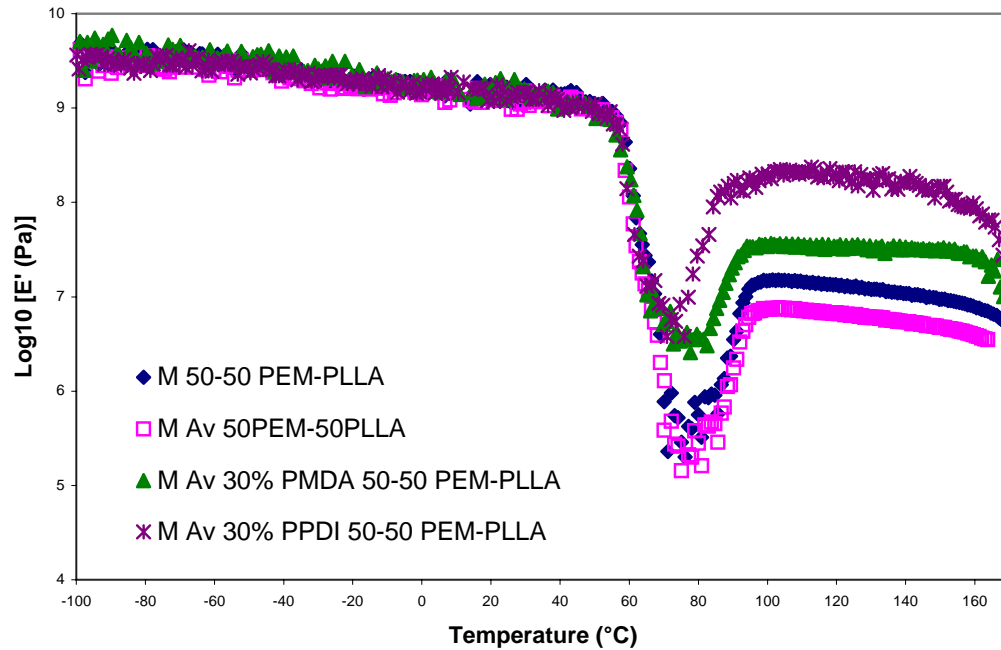
After chemical modification with PMDA and PPDI, we observe a significant increase of the rubbery modulus. DSC measurements have shown that these materials display a lower degree of crystallinity of the neat matrix (35% for PMDA and 45% for PPDI, compared to 60% for the unfilled matrix). That means there is an important reinforcement effect of the modified fibres.

This reinforcement is really higher than the one of the ungrafted fibre as the degree of crystallinity of the latter (35%) is similar than the one reported for modified fibres.

We can conclude that the compatibilization treatment between fibre and matrix has a positive effect on the mechanical properties of composite. Let's check now that it will not decrease after ageing.

**. After ageing:**

The curves of storage shear modulus versus temperature at 1 Hz have been made for composites and blends directly after ageing (see Figures 6).



**Figure 6:** DMA curves for composite with 50-50 PEM-blend reinforced with grafted or ungrafted fibres after ageing.

After ageing, we can observe the same evolution than before ageing. We still have several phenomena. However, as the degree of crystallinity of the unfilled blend and blend reinforced with PPDI-grafted fibres is almost the same, we can notice the importance of the reinforcement effect.

Both the degree of crystallinity and the rubbery modulus is lower for the composite reinforced with ungrafted fibres. It could be due to the fact that the fiber absorbs water from the ageing chamber. This water is not anymore available for biopolymer rearrangement (plasticizer role). On the contrary with hydrophobic fiber, water helps reorganisation (chain crystallisation) of the biopolymers. The chemical link between the fibre and the matrix could help also this rearrangement or at least does not have negative influence after ageing.

Nevertheless, as several phenomena are present in this part of curves (temperature superior to  $T_{g, PLLA}$  and  $T_{g, PEM}$ ), further experiments are necessary to have better understanding.

### **III. Conclusion:**

The study of ageing has allowed us to quantify the influence of grafted or ungrafted fibre in blend of biopolymers. In the case of composite, the addition of the fibre prevents the rearrangement of polymeric chains before and after ageing. Nevertheless, our first results show that chemical grafting allows chain polymer rearrangement and does not destroy the material integrity even after ageing. Therefore the best solution seems to use PPDI-grafted fibres which allow crystallisation of the matrix and confer an important reinforcement effect.

Further experiments have to be performed in order to confirm this point, for instance tensile tests. For a better understanding of dynamical mechanical analysis, other series of tests will be carried out and reported in D 5.37 (part II, Month 46). Ageing of other composite materials will be also tested.