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Shifts: 3	Local contact(s): Cyrille Rochas	
Names and affiliations of applicants (* indicates experimentalists): S. Ouchiar*, G. Stoclet*, L. Leroy* Unité Matériaux Et Transformations (UMET) Equipe Ingénierie des Systèmes Polymères (ISP), Villeneuve d’Ascq, USTL (France)		

Report:

This report deals with the results obtained from WAXS and SAXS experiments carried out to characterize the structural evolution upon uni-axial stretching of biodegradable polymer nanocomposites. Besides Alginate and Poly (Lactic Acid) polymer matrix filled with natural clays were studied.

Starting from these experiments, two main conclusions have been drawn. On the one hand, the presence of a filler didn't significantly infer on the strain-induced structural evolution upon uni-axial stretching in the rubbery state as well as on the plastic deformation mechanisms involves upon cold drawing. On the other hand, for higher clay contents, the presence of the filler strongly infer on the strain-induced structural evolution. Particularly, filler seems to restrict molecular mobilities and consequently hinderer the strain-induced structural evolution phenomenon currently observed in the neat matrix.

Background:

Over the last few years, one assist to remarkable developments in the field of packaging films made from renewable and natural polymers. Particularly, polymers issued from renewable resources, ignored until nowadays now received an increasing interest as they could replace synthetic polymers in many applications, including the packaging field. Nevertheless these kinds of polymers don't intrinsically have the sufficient properties for some of these applications. Besides, both their barrier and mechanical properties remain lower than the ones of commodity polymers. To outclass this lack, one way consists in incorporating nanofillers into the material. In this way this study is devoted to develop new bio-based polymer nanocomposites based on Alginate (A) and Poly (Acid Lactic) (PLA) polymer matrix filled with natural clays, i.e. Talc (T) or Kaolin (K). These polymers have been chosen as they can be extracted from the biomass by a green chemistry route.

The characterization of the mechanical behaviour of these materials recently carried out has highlighted particularly interesting results. Indeed, when clay is added into the alginate matrix, a significant increase of the Young's modulus (E) is observed without loss of the elongation at break. This result is quite surprising as the incorporation of the filler is generally known to decrease this value. This properties enhancement is very interesting especially for application in the packaging field. Nevertheless, the origin of this behaviour remains undetermined.

Regarding the PLA matrix, mechanical analyses carried out in our laboratory has shown that a significant increase in the modulus is observed with the incorporation of the clays, especially for clay contents above 10%wt. Modulus is nearly doubled when 30 wt% of talc is added as compared to neat PLA while E remains nearly constant for fillers contents around 5 wt%, that's to say for contents generally used in the case of nanocomposites. Consequently, both WAXS and SAXS experiments have been performed in order to characterize the structural evolution at both atomic and nanometric scales of these composites when drawn below and above their glass transition temperature (T_g).

To summarize, the main goals in this study were:

- to study the plastic deformation mechanisms involved during stretching of Alginate films and its nanocomposites in order to explain why no loss of ductility is observed when clay is added.
- To study the influence of the presence of clays on the strain-induced structural evolution of PLA when stretched above its glass transition temperature (T_g) (to assess the impact of the filler on the processability of PLA) but also below T_g (to determine the origin of the embrittlement induced by the presence of Talc)

Hence, a particular interest will be paid at studying both plastic deformation mechanisms occurring upon stretching as well as crystalline phase transitions. In this way, it is expected to determine the effect of the incorporation of clays into a bio-based polymer matrix.

Experimental:

The alginate composites were elaborated by casting. The corresponding quantities of materials were dissolved into hot water under stirring until a complete dissolution. The solution was then cast in a petri dish. The point here is also to study the effect of the amount of plasticizer in the materials. For this purpose, 0; 10 and 30 wt% of glycerol were tested. The abbreviation used for samples is AXG where X is the quantity of plasticizer.

The nanocomposites based on PLA were prepared by melt extrusion at 180°C using a twin screw microextruder. Films were elaborated by compression-moulding. 0, 5 and 30 wt% of fillers were studied. The samples notation for these composites is PLAX where X corresponds to the percentage of talc. Samples were stretched at a constant rate of 1.28 mm/min at room temperature using a homemade stretching device adaptable on the beamline.

Results:

▪ *Clays based alginate composites*

This part is focused on the characterization of the structural evolution of alginate composites filled with talc or kaolin in presence or not of glycerol (G).

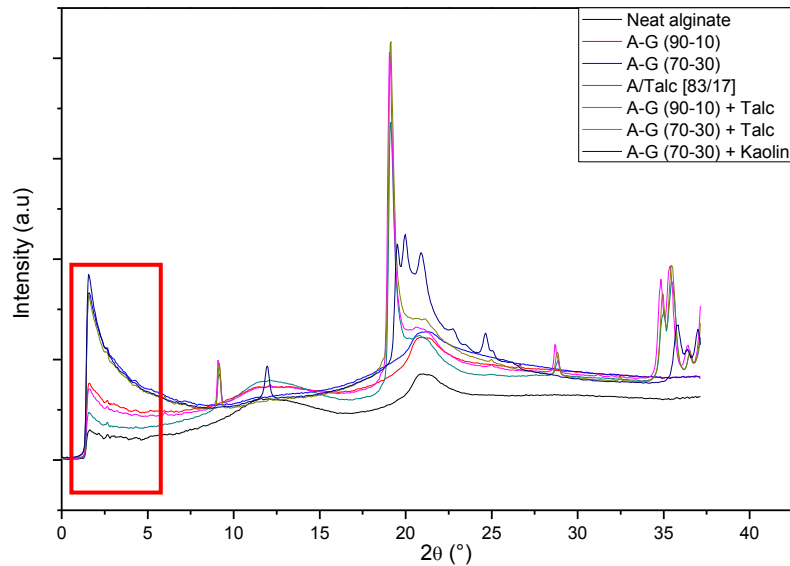


Figure 1: Waxes diffractograms of clays based alginate composites

Figure 1 depicts integrated intensity profiles computed from the WAXS patterns for neat alginate, alginate with different amounts of plasticizer (10 and 30 wt%) and filled with clays. Neat alginate exhibits two broad halos characteristic of an amorphous material.

Addition of glycerol did not significantly change the intensity profile in the WAXS angle region. Nevertheless it can be seen that it influences scattering at low angle. This scattering, due to the presence of an electronic density contrast arises from the presence of heterogeneities into the material. Particularly it seems that there's an, at least partial, phase separation between Alginate and Glycerol. The latter point is still under investigation but it can be assumed that incorporating glycerol into Alginate involves the formation of nodules composed of a blend of glycerol and Alginate into the neat Alginate matrix.

Moreover it appears that the incorporation of clays did not infer on the structure of Alginate. Indeed, the diffraction peaks observed on figure 1 are only related to the ones of clays.

In order to better understand more the behaviour at these small angles and characterize the scattering objects, the intensity profiles of the diffuse scattering were calculated. For example the intensity profiles obtained for the A10G sample is reported in figure 2.

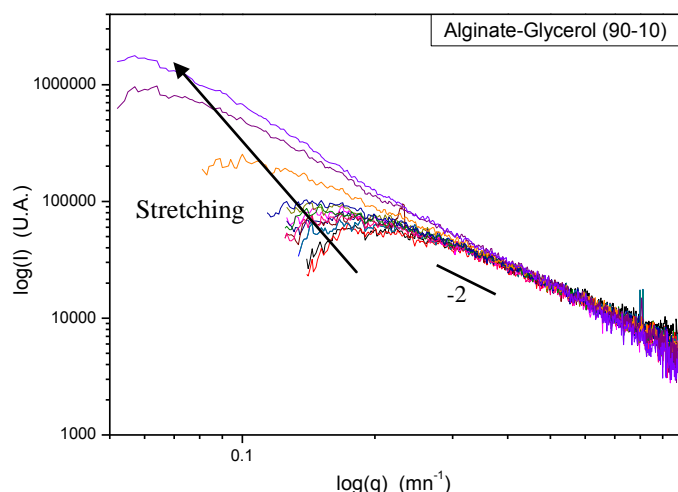


Figure 2: Logarithmic representation of $I = f(q)$ of the diffuse scattering observed on the SAXS patterns of Alginate-Glycerol (90-10) material during drawing

The analysis of the intensity profile of the unstretched sample indicates that the low angle scattering observed in the case of glycerol filled samples, arises from the presence of heterogeneities having a disk like shape with nanometric characteristic lengths. Upon stretching, it appears that these heterogeneities grown up which induce plasticity and then the break. This means that the heterogeneities deforms in the meantime that the polymer matrix.

Complementary analyses carried out by means of Dynamical Mechanical Analysis (DMA) on the composites shows that neat alginate presents only one glass transition temperature around 60°C. When glycerol is added to the alginate, another transition appears around -40°C. This indicates that the sample correspond to a two phases system that confirms the phase separation. More precisely, the sample is composed of a neat Alginate matrix into which rubbery nodules composed of a mix of alginate and glycerol are dispersed.

This result is of prime interest as it reveals that Glycerol do not act as a “conventional” plasticizer in the case of Alginate. Indeed conventionally a plasticizer disperses itself into the polymer matrix leading to the formation of a one-phase system. In our case, Glycerol rather involves the formation of rubbery nodules, in a glassy matrix (at room temperature). This is comparable to (High Impact PolyStyrene) HIPS materials where rubber nodules are dispersed into the PS matrix. This is this particular morphology which is responsible of the mechanical behaviour observed, to know no loss of ductility when clay is added.

Indeed, it is well known that clays act as stress concentrators which promote the formation of cracks into the polymer matrix. It is true here but the growth of the crazes is hindered by the presence of rubbery nodules that stop cracks growth. Consequently, as can be seen in figure3, no loss of ductility is observed for the alginate based composites.

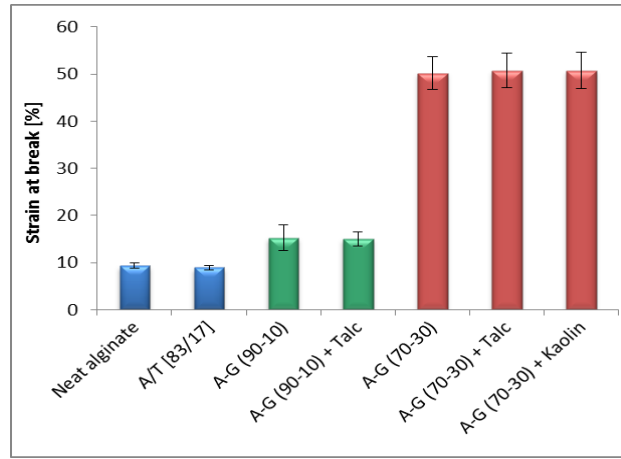


Figure 3: Deformation at break of the alginate based composites

▪ *Clays based PLA composites*

Influence of filler content on the plastic deformation mechanisms

In order to explain the origin of the embrittlement of PLA when clays are added, SAXS experiments have been carried out to characterize the plastic deformation involved upon cold drawing. The first set of experiments was carried out at 25°C. Typical SAXS patterns recorded just before sample's break are depicted in figure 4. For neat PLA, SAXS patterns are characteristic of the occurrence of the crazing mechanism as previously reported by Stoclet et al. [1]. The pattern is composed of an intense horizontal scattering arising from the cracks and of a diffuse vertical scattering arising from the diffusion by fibrils that bridge the cracks.

In opposition, when clays are added, SAXS patterns differ and are characteristic from the presence of voids into the material. Indeed scattering from fibrils is no more observed. This tends to show that filler avoid the formation of crazes or in other words that the incorporation of filler involves a craze to crack transition.

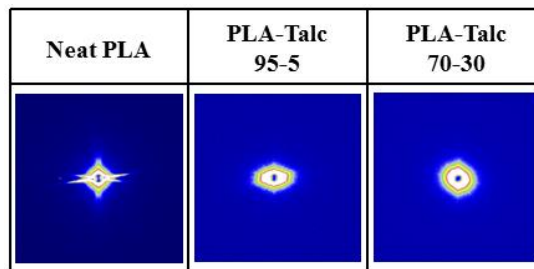


Figure 4: SAXS patterns taken before sample's break for neat PLA, PLA5 and PLA30 at Td = 25°C (the tensile axis is horizontal)

In order to corroborate this point, experiments were carried out at Td = 50°C, temperature just before the glass transition temperature. Figure 5 illustrate SAXS patterns of neat PLA at drawn temperature of 25 and 50°C taken before sample's break.

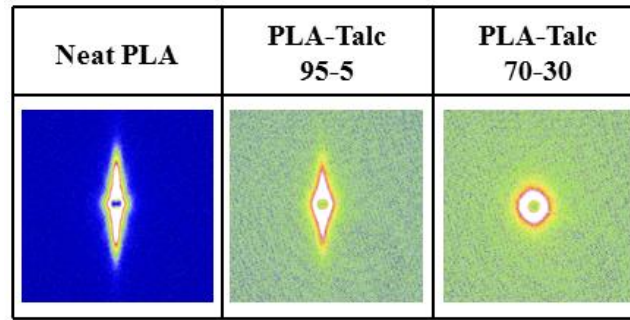


Figure 5 SAXS patterns taken before sample's break for neat PLA, PLA5 and PLA30 at $T_d = 50^\circ\text{C}$ (the tensile axis is horizontal)

SAXS pattern at 50°C presents are different behaviour than at 25°C . For PLA0 and PLA5, the SAXS patterns are quite similar and typical of the presence of crazes into the materials. In opposition, the SAXS pattern recorded for PLA30 is clearly different and characteristic of the presence of cavities. Consequently, at $T_d = 50^\circ\text{C}$ it appears that a low clay content has no significant effect on the deformation mechanism involved while there's a clear impact for higher clay content.

Influence of filler content on the strain-induced structural evolution upon uniaxial stretching in the rubbery state

In order to assess the role of clay on the strain-induced structural evolution upon stretching in the rubbery state, WAXS experiments were carried out at $T_d = 70^\circ\text{C}$ and 80°C respectively. These drawing temperatures were chosen as they are currently used during processing of PLA. Figure 6 and 7 depicts mechanical behaviour recorded at $T_d = 70^\circ\text{C}$ and WAXS patterns recorded at the beginning of drawing and before sample's break respectively. It appears that the same mechanical behaviour is observed for neat PLA and PLA5. In these cases plastic deformation first starts by the formation of a neck until $\varepsilon = 50\%$, then plastic deformation occurs at constant stress before the apparition of a strain-hardening phenomenon around $\varepsilon = 150\%$. This strain-hardening continues until sample's break around $\varepsilon = 450\%$.

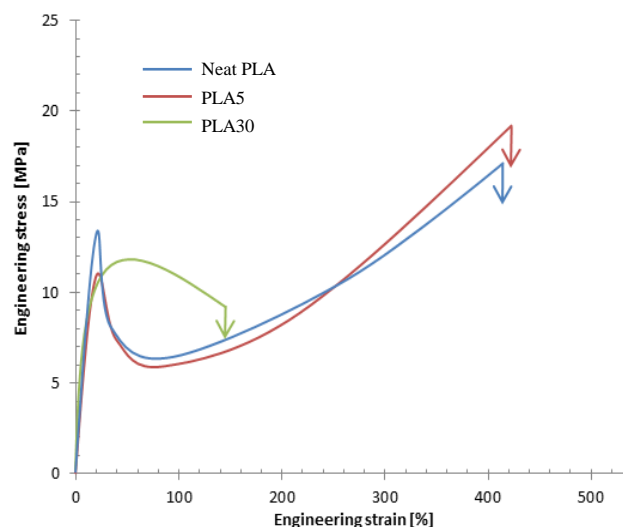


Figure 6: Engineering stress-strain curves of neat PLA, PLA5 and PLA30 drawn at $T_d = 70^\circ\text{C}$

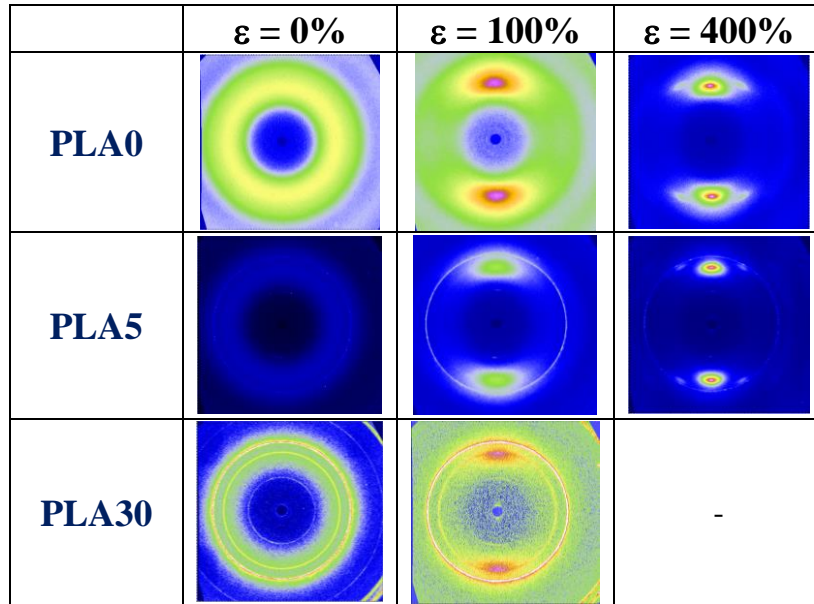


Figure 7: WAXS patterns of neat PLA, PLA5 and PLA30 drawn at $T_d = 70^\circ\text{C}$

WAXS patterns recorded at $\varepsilon = 400\%$ for PLA0 and PLA5 are quite similar. Thin diffraction spots are observed in both cases indicating that a strain-induced crystallization phenomenon occurred. Crystallinity ratios computed from the integrated intensity profiles (not shown here) also indicate that the same crystalline form, i.e. α' , and similar crystallinity ratios are achieved in both case.

At $T_d = 80^\circ\text{C}$, as can be seen in figure 8, the same kind of behaviour is observed in the case of neat PLA. Besides, for $\varepsilon = 400\%$, the WAXS pattern recorded is characteristic of a fibrillar structure with well-defined diffraction spots indicating a pronounced orientation of the strain-induced crystals.

When 5 wt% of talc is added, the WAXS patterns are different. Indeed diffraction arcs rather than spots are observed. This indicates that even if a strain-induced crystallization still occurs, strain-induced crystals are less oriented in the presence of Talc as compared to neat PLA. Same results are obtained for PLA30.

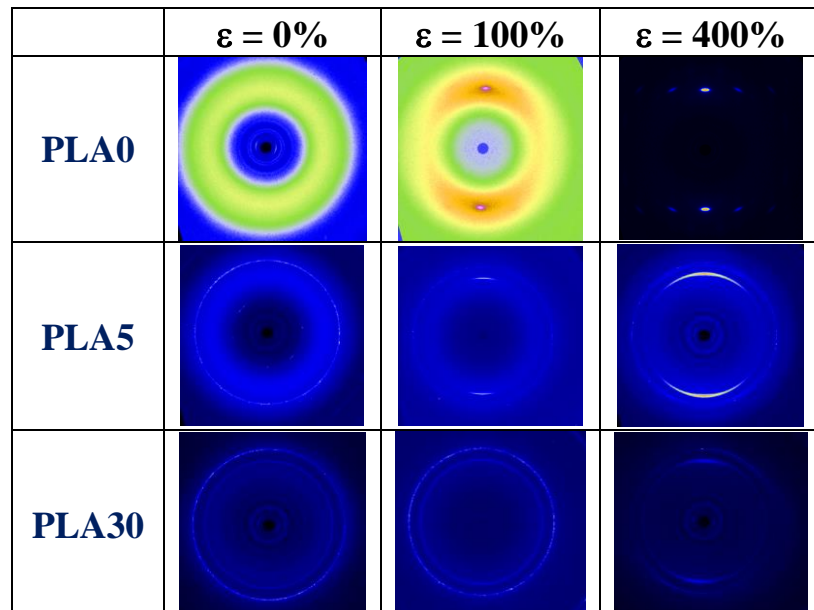


Figure 8: WAXS patterns of neat PLA, PLA5 and PLA30 drawn at $T_d = 80^\circ\text{C}$

Consequently it appears in this case that the presence of clays influence the orientation of the strain-induced crystals. This can be attributed to a local decrease of molecular mobility due to the presence of the clay platelets.

Conclusions:

To conclude, SAXS and WAXS experiments carried out during this beamtime allocation allowed us to show that:

- Incorporation of Glycerol into Alginate lead to a two phase system constituted of rubbery nanometric disk like nodules into a pure Alginate Matrix.
- This is this particular morphology which explains the mechanical behaviour observed in the case of clay filled composites. Indeed the rubbery nodules dissipate the plastic deformation energy propagated by the craze, allowing thus significant plastic deformation
- The embrittlement observed in the case of PLA-Talc nanocomposites arises from a craze to crack transition
- Incorporation of high Talc contents can strongly modify mechanical behaviour of PLA and particularly reduce its processability.
- Incorporation of low Talc contents infers on the strain-induced structure even if the mechanical behaviour is not deeply affected.
- The drawing temperature also plays a key role in addition to the one of Talc. In other words the influence of the filler is strongly dependant of the drawing conditions. For example while for $T_d = 25^\circ\text{C}$ the plastic deformation mechanisms are different for PLA0 and PLA5, they are the same at $T_d = 50^\circ\text{C}$
- The influence of the clay platelets on the strain-induced structural evolution arises can be ascribed to a local modification of molecular mobility. Besides clay platelets restrict macromolecular motions leading to the formation of a less perfect structure.

Note: Two publications based on these results are in preparation.

References:

[1] Stoclet, G., Lefebvre, J. M., Séguéla, R., & Vanmansart, C. (2014). In-situ SAXS study of the plastic deformation behavior of polylactide upon cold-drawing. *Polymer*