TRABAJO ESPECIAL DE GRADO

PREPARACION Y CARACTERIZACION DE NANOCOMPUESTOS DE REX-PLA.
(PREPARATION AND CHARACTERIZATION OF REX-PLA NANOCOMPOSITES)

Presentado ante la Ilustre
Universidad Central de Venezuela
Por el Br. Blanco M. Andreina A.
Para optar al Título
de Ingeniero Químico

Caracas, 2015

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PREPARACION Y CARACTERIZACION DE NANOCOMPUESTOS DE REX-PLA. (PREPARATION AND CHARACTERIZATION OF REX-PLA NANOCOMPOSITES)

TUTORES ACADEMICOS: Prof.Giulio Malucelli (Politecnico di Torino)
Prof. Jose Angel Sorrentino (UCV)

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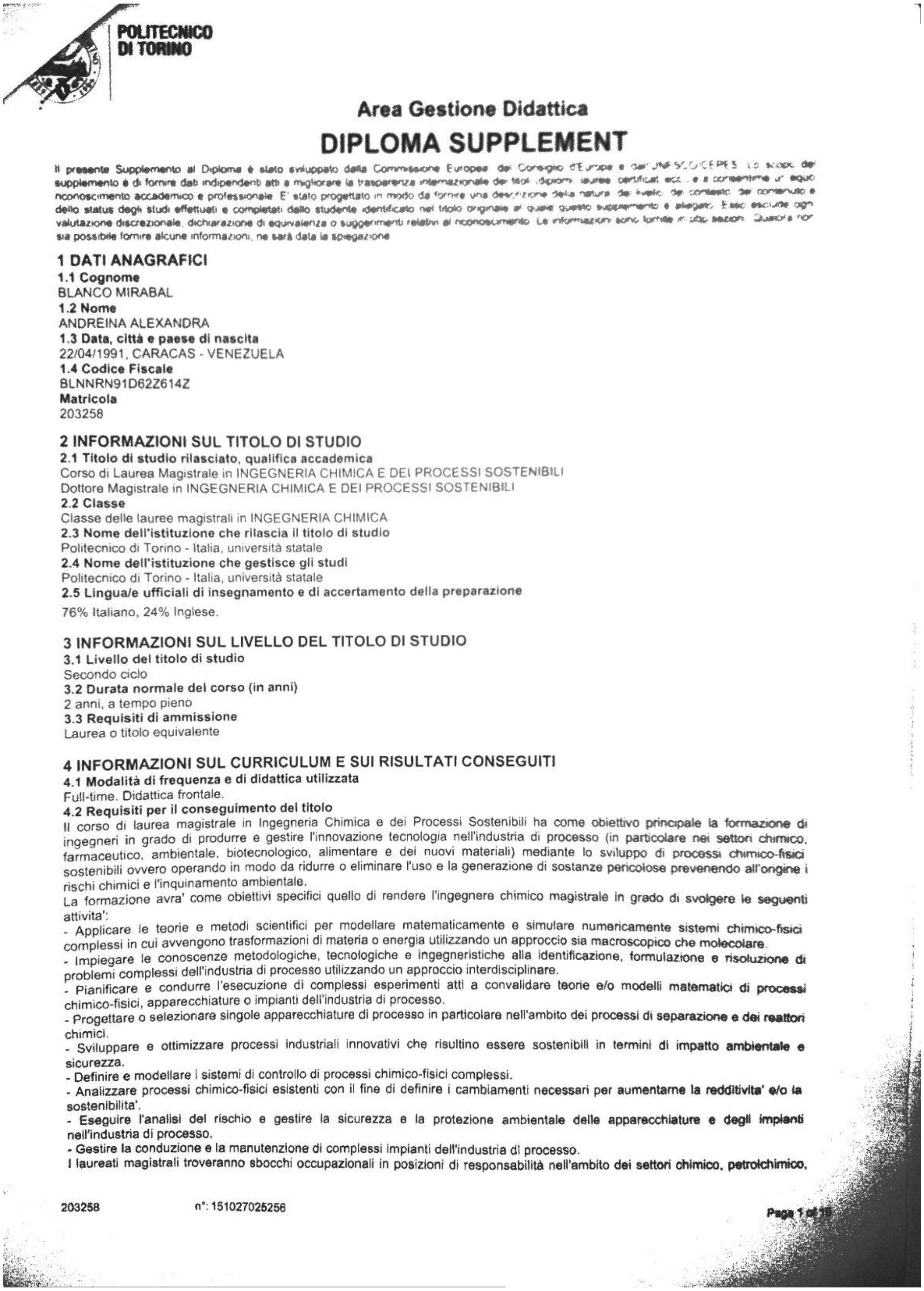
Politecnico di Torino
Por el Br. Blanco M. Andreina A.
Para optar al Título
de Ingeniero Químico y de los Procesos Sostenibles

Caracas, 2015



POLITECNICO DI TORINO

Area Gestione Didattica

DIPLOMA SUPPLEMENT

Il presente Supplemento al Diploma è stato sviluppato dalla Commissione Europea, dal Consiglio d'Europa e dall'UNESCO/CEPES. Lo scopo del supplemento è di fornire dati indipendenti atti a migliorare la trasparenza internazionale dei titoli (diplomi, lauree, certificati ecc.) e a consentirne un equo riconoscimento accademico e professionale. E' stato progettato in modo da fornire una descrizione della natura, del livello, del contesto, del contenuto e dello status degli studi effettuati e completati dallo studente identificato nel titolo originale al quale questo supplemento è allegato. Esso esclude ogni valutazione discrezionale, dichiarazione di equivalenza o suggerimenti relativi al riconoscimento. Le informazioni sono fornite in otto sezioni. Qualora non sia possibile fornire alcune informazioni, ne sarà data la spiegazione

1 DATI ANAGRAFICI

1.1 Cognome
BLANCO MIRABAL
1.2 Nome
ANDREINA ALEXANDRA
1.3 Data, città e paese di nascita
22/04/1991, CARACAS - VENEZUELA
1.4 Codice Fiscale
BLNNRN91D62Z614Z
Matricola
203258

2 INFORMAZIONI SUL TITOLO DI STUDIO

2.1 Titolo di studio rilasciato, qualifica accademica
Corso di Laurea Magistrale in INGEGNERIA CHIMICA E DEI PROCESSI SOSTENIBILI
Dottore Magistrale in INGEGNERIA CHIMICA E DEI PROCESSI SOSTENIBILI
2.2 Classe
Classe delle lauree magistrali in INGEGNERIA CHIMICA
2.3 Nome dell'istituzione che rilascia il titolo di studio
Politecnico di Torino - Italia, università statale
2.4 Nome dell'istituzione che gestisce gli studi
Politecnico di Torino - Italia, università statale
2.5 Lingua/e ufficiali di insegnamento e di accertamento della preparazione
76% Italiano, 24% Inglese.

3 INFORMAZIONI SUL LIVELLO DEL TITOLO DI STUDIO

3.1 Livello del titolo di studio
Secondo ciclo
3.2 Durata normale del corso (in anni)
2 anni, a tempo pieno
3.3 Requisiti di ammissione
Laurea o titolo equivalente

4 INFORMAZIONI SUL CURRICULUM E SUI RISULTATI CONSEGUITI

4.1 Modalità di frequenza e di didattica utilizzata
Full-time. Didattica frontale.
4.2 Requisiti per il conseguimento del titolo
Il corso di laurea magistrale in Ingegneria Chimica e dei Processi Sostenibili ha come obiettivo principale la formazione di ingegneri in grado di produrre e gestire l'innovazione tecnologia nell'industria di processo (in particolare nei settori chimico, farmaceutico, ambientale, biotecnologico, alimentare e dei nuovi materiali) mediante lo sviluppo di processi chimico-fisici sostenibili ovvero operando in modo da ridurre o eliminare l'uso e la generazione di sostanze pericolose prevenendo all'origine i rischi chimici e l'inquinamento ambientale.

La formazione avra' come obiettivi specifici quello di rendere l'ingegnere chimico magistrale in grado di svolgere le seguenti attivita':

- Applicare le teorie e metodi scientifici per modellare matematicamente e simulare numericamente sistemi chimico-fisici complessi in cui avvengono trasformazioni di materia o energia utilizzando un approccio sia macroscopico che molecolare.
- Impiegare le conoscenze metodologiche, tecnologiche e ingegneristiche alla identificazione, formulazione e risoluzione di problemi complessi dell'industria di processo utilizzando un approccio interdisciplinare.
- Pianificare e condurre l'esecuzione di complessi esperimenti atti a convalidare teorie e/o modelli matematici di processi chimico-fisici, apparecchiature o impianti dell'industria di processo.
- Progettare o selezionare singole apparecchiature di processo in particolare nell'ambito dei processi di separazione e dei reattori chimici.
- Sviluppare e ottimizzare processi industriali innovativi che risultino essere sostenibili in termini di impatto ambientale e sicurezza.
- Definire e modellare i sistemi di controllo di processi chimico-fisici complessi.
- Analizzare processi chimico-fisici esistenti con il fine di definire i cambiamenti necessari per aumentarne la redditivita' e/o la sostenibilita'.
- Eseguire l'analisi del rischio e gestire la sicurezza e la protezione ambientale delle apparecchiature e degli impianti nell'industria di processo.
- Gestire la conduzione e la manutenzione di complessi impianti dell'industria di processo.

I laureati magistrali troveranno sbocchi occupazionali in posizioni di responsabilità nell'ambito dei settori chimico, petrolchimico, *A Dios por siempre acompañarme en el camino que he escogido.*

A mi Familia por brindarme el amor inagotable que sobrepasa fronteras y mares.

En especial a mi Madre que ha significado a lo largo de toda mi vida la voz que guía mis pasos y nutre mi alma.

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Agradezco a la Universidad Central de Venezuela, la casa que vence las sombras, por ser universo de aprendizaje y buenas experiencias, por haberme brindado el privilegio ser parte de esta gran comunidad y más aún por formar bases firmes de conocimientos que me permitieron llegar a donde he llegado. Igualmente, doy gracias al Politecnico de Torino por darme la oportunidad de crecer como estudiante y profesional.

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Blanco M., Andreina A.

PREPARACION Y CARACTERIZACION DE NANOCOMPUESTOS DE REX-PLA

Tutores Académicos: Prof. Jose Angel Sorrentino (UCV) y Prof. Giulio Malucelli (Politecnico di Torino). Tesis. Caracas, U.C.V. Facultad de Ingeniería. Escuela de Ingeniería Química. Torino, Politecnico di Torino. Departamento de Ciencias Aplicadas y Tecnología. Año 2015, 107 p.

Palabras Claves: Polímeros, Biodegradable, PLA, Extrusión reactiva, REX-PLA, Nanosílice, Nanocompuestos, TGA, DSC, Tracción, Envejecimiento.

Resumen. La industria del plástico ha logrado un crecimiento increíble en las últimas décadas: el plástico se utiliza en muchas áreas de la vida diaria. Sin embargo, varias décadas han causado altos niveles de contaminación del aire y el agua. Esto ha hecho el estudio de la utilización de polímeros biodegradables una prioridad hoy en día, para tratar de limitar y controlar el problema medioambiental de reciclado de plásticos convencionales. A pesar de ello, la aplicabilidad de la nueva generación de materiales biodegradables no es equivalente a la de los polímeros sintéticos derivados del petróleo. Buscando ampliar la aplicación de los polímeros bio-basados, algunos intentos se han llevado a cabo, con el fin de encontrar formas de mejorar las propiedades de uno de los polímeros biodegradables más prometedor en la actualidad, el ácido poliláctico (PLA). En la búsqueda para la optimización de estas propiedades, se ha aplicado la extrusión reactiva de ácido poliláctico con diferentes compuestos, incluyendo Joncryl, un extensor de cadena, que promueve mejoras mecánicas, térmicas y reológicas significativas, resultando un material de calidad superior, llamado REX-PLA. El objetivo de este trabajo es preparar y caracterizar nanocompuestos basados en REX-PLA obtenidos mediante extrusión reactiva con tres tipos de nanopartículas: nanosílice sin modificar (SiO_2), nanosílice modificada con grupos amino ($Am.SiO_2$) y nanosílice modificada con grupos epoxi ($Ep.SiO_2$). Después de la producción de REX-PLA y la encapsulación de las nanopartículas en PLA, cuatro tipos de materiales fueron producidos por extrusión reactiva en forma de películas (incluyendo el REX-PLA sin nanocarga). Fueron sometidos a un analisis térmico (DSC y TGA) y a caracterización mecánica (ensayos de tracción); Además, se evaluó la sensibilidad al envejecimiento físico del material. Desde un punto de vista general, la utilización de nanopartículas de sílice modificadas con grupos amino parecen ser la forma más eficaz para mejorar las propiedades térmicas y mecánicas de la REX-PLA. De hecho, estas nanopartículas aumentan la cristalinidad y la resistencia a la tracción de la matriz polimérica, extendiendo así su facilidad de uso a nivel industrial así como también su almacenamiento.

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INTRODUCCIÓN

La industria del plástico ha logrado un crecimiento increíble en las últimas décadas: el plástico se utiliza en muchas áreas de la vida diaria, tales como envases de alimentos, área automotriz, muebles, aparatos eléctricos y electrónicos, decoración, etc. Sin embargo, tantas décadas de uso han acumulado grandes cantidades de residuos para el medio ambiente que causan los altos niveles de contaminación del aire y el agua, que tendrán un fuerte impacto en las generaciones futuras. Aproximadamente el 5% del petroleo extraído se usa en la industria del plástico. Según las proyecciones actuales, la demanda y el precio de los combustibles fósiles aumentarán, los pozos existentes se agotaran y aparentemente no existen nuevos pozos rentables para la extracción, por lo que es imposible aumentar la producción. Esto convierte el estudio de la utilización de polímeros biodegradables una prioridad para tratar de limitar y controlar el problema medioambiental de reciclado de plásticos convencionales.

La nueva generación de materiales biodegradables se ha estudiado en los últimos años y hoy es un reto para la Ingeniería Química y de Materiales, sobre todo porque la aplicabilidad de los polímeros con características de biodegradabilidad no es equivalente a la de los polímeros sintéticos derivados del petróleo. **La motivación de este trabajo se basa en la necesidad de poner en práctica los conocimientos químicos y de producción, tratando de ampliar la aplicación de biopolímeros**. En este contexto, algunos intentos se han hecho con el fin de encontrar formas de mejorar las propiedades de uno de los polímeros bio-basados más prometedores en la actualidad, el ácido poliláctico (PLA), estabilizando su estructura macromolecular y optimizando así su manipulación industrial.

El ácido poliláctico (PLA) es un termoplástico que se deriva del monómero natural L-ácido láctico o D- ácido láctico. Es un polímero de base biológica con alta resistencia a la tracción y alto módulo de Young en comparación con otros materiales biodegradables. El polímero es especialmente adecuado para aplicaciones que deben soportar una carga, como las suturas y ligaduras ortopédicas, envases biodegradables y compostables para bebidas frías, bolsas y más. Tiene un alto punto de fusión y temperatura de transición vítrea de entre 60 y 65 ° C. Actualmente se están realizando muchos estudios para la mejora de las propiedades del polímero: en particular, la extrusión reactiva con diferentes compuestos, incluyendo Joncryl, un extensor de cadena, que genera mejoras mecánicas, térmica y reológicas significativas, el material resultante de dicho proceso de extrusión se ha llamado REX-PLA. Sin embargo, para ampliar aún más la aplicabilidad del polímero, las propiedades del mismo deben mejorarse. Esta es la razón por la cual se decidió evaluar, en este trabajo experimental, el efecto de la incorporación de diferentes nanoparticulas en la matriz de REX-PLA, obteniendo así los llamados nanocompuestos.

El propósito de este trabajo es **preparar y caracterizar nanocompuestos de REX-PLA obtenidos mediante extrusión reactiva con tres tipos de nanopartículas: nanosílice no modificada (SiO_2), nanosílice modificada con grupos amino (Am.SiO_2) y nanosílice modificada con grupos epoxi (Ep.SiO_2).**

La atención se dirige específicamente a nanocompuestos reforzados con sílice por su alto grado de interacción con la cadena de PLA y por consiguiente una capacidad de dispersión mayor que otras nanocargas. Los experimentos con nanocompuestos de PLA con nanosílice han proporcionado buenos resultados en lo que respecta al comportamiento térmico del material; Sin embargo, a pesar del aumento del porcentaje de cristalinidad de la PLA, la dispersión de las nanopartículas no era suficiente para lograr mejoras significativas en las propiedades mecánicas. La modificación de la superficie de nanosílice podría representar una solución para mejorar la adhesión y la dispersión de nanopartículas y asi optimizar significativamente el material resultante.

Este trabajo experimental se desarrolló en uno de los centros de investigación más importantes de Barcelona, el **Centro Catalá Plástico (CCP)**, conocido por el gran número de publicaciones y consultoría industrial. En la actualidad, el CCP ha estado trabajando en el proyecto **REX-BIOBLEND (MAT2013-40730-P)**, que es financiado por el Ministerio de Economía y Competitividad del Gobierno español. Es importante señalar que esta tesis es una parte del proyecto mencionado y futuras investigaciones continuarán en el centro de investigación.

Las fases de este trabajo experimental para lograr los objetivos son las siguientes:

1. Acondicionamiento de la materia prima: extrusión reactiva de PLA con Joncryl. A continuación, la encapsulación de nanosílice en el PLA (masterbatch) para hacer la nanocarga adecuada para el proceso de extrusión reactiva.

2. La obtención de nanocompuestos REX-PLA: extrusión reactiva de REX-PLA con cada lote de nanosílice encapsulado. Esta etapa consta de dos pasos: la obtención de Pellets de polímero (primera extrusión) y la homogeneización y la producción de la película polimérica (segunda extrusión).

3. Caracterización de las propiedades mecánicas y térmicas de los materiales obtenidos.

METODOLOGIA

1.1 Acondicionamiento de la materia prima

1.1.1 Preparación del REX-PLA

El primer paso es la molienda y homogeneización de tamaño de particula del JONCRYL. Para obtener el REX-PLA se ha empleado un proceso de extrusión reactiva de PLA con JONCRYL, utilizando una extrusora de doble husillo. Antes de la extrusión, el PLA se secó a 80°C durante 4 horas en una tolva PIOVAN para evitar posibles fenómenos de hidrólisis. El JONCRYL se debe almacenar al vacío en un desecador de laboratorio para evitar la humedad. El proceso se ilustra en la **Figura 1**:

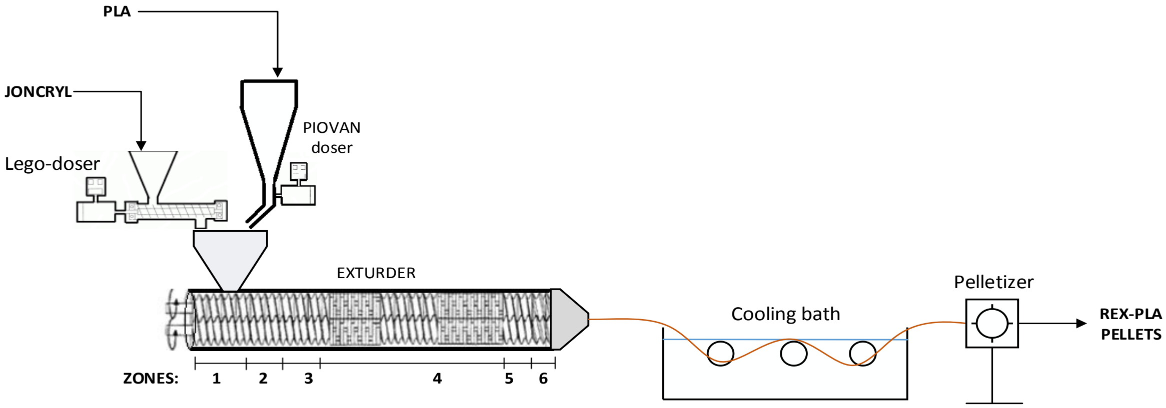

Figura 1. Esquema de producción de REX-PLA.

Para la dosificación de la JONCRYL (**0,5-0,6 g/min**), se utilizó un Lego-dispensador diseñado específicamente para este proceso con el objetivo de obtener un porcentaje de JONCRYL alrededor del 1% en el polímero (evitando ramificaciones y reticulación); La alimentación del PLA se llevó a cabo mediante el dispensador PIOVAN a **44,6 g/min**.
En cuanto a las condiciones de extrusión, la rotación de los husillos se fijó a 35 rpm. En la zona de alimentación, se aplicó un flujo constante de nitrógeno a 2,5 bar, para evitar la presencia de humedad en el proceso y los posibles fenómenos de degradación del PLA. Durante la extrusión, se introdujo un trazador inerte para medir el tiempo implementado por el componente más rápido en salir del reactor, que fue igual a 4 min. El perfil de temperatura para cada área se muestra en la **Tabla 3** de este trabajo.
En esta fase experimental que se produjeron 48 kg de REX-PLA después de 5 días de extrusión (aproximadamente 10 kg/día). Todo el material obtenido (en forma de gránulos/pellets) se sometió a un tratamiento térmico (recristalización) durante 4 horas a 90 ° C, agitando manualmente cada 30 minutos.

1.1.2 Primera encapsulación de nanopartículas en PLA

Se prepararon tres diferentes masterbatch a 30% en peso de nanopartículas: nanosílice sin modificar, nanosílice modificados con grupos amino y nanosílice modificados con grupos epoxi. Para este fin, se siguió el procedimiento descrito en la **Figura 23**, repitiendolo hasta obtener aproximadamente 200 g de cada masterbatch. Luego, cada uno se cristalizó a 100 ° C durante 2 horas en un horno para facilitar la molienda y homogeneización de tamaño de partícula posterior.
Se realizó luego un análisis termogravimétrico (TGA) para verificar que la encapsulación era correcta. Para cada material, se tomaron 10 mg de muestra y la

temperatura se aumentó gradualmente desde 30 hasta 1000 ° C a 10°C/min. Se determina entonces, la fracción inorgánica de la nanosilice (residuo) y se añade el porcentaje de materia orgánica en el nanosílice degradado durante la prueba (dato del proveedor). Se ha obtenido aproximadamente 28% en peso de nanosílice en cada masterbatch (**Tabla 6**).

1.2 Preparación de nanocompuestos de REX PLA.

Antes de la extrusión, cada masterbatch de nanosílice se secó a 90 ° C durante 4 horas en un desecador de vacío de laboratorio. Del mismo modo, el REX-PLA se secó una tolva PIOVAN a 80 ° C durante 4 horas para eliminar cualquier humedad durante la extrusión.

1.2.1 Preparación de pellets

2.2.1.1 Primera extrusión

Antes de proceder a la extrusión, algunas pruebas reológicas fueron realizadas con el fin de evaluar el comportamiento del par de torsión como función del tiempo a una temperatura dada y comprobar si los materiales eran adecuados para la extrusión. Luego de ello se dio inicio al proceso de extrusión. La dosificación de las nanopartículas encapsuladas se realizó usando un dosificador de doble husillo. El REX-PLA se dosificó con el dispensador PIOVAN. El esquema de producción seguido en cada caso se muestra en la **Figura 24** del presente trabajo.

La primera prueba de extrusión REX-PLA/SiO_2, con una tasa de dosificación continua de masterbatch de PLA/SiO_2 igual a 17 g/min (velocidad mínima del dispensador de doble husillo) y 43 g/min de REX-PLA, resultó en problemas de agregación de la nanoparticula, lo que trajo como consecuencia perdidas de 123 g de masterbatch PLA/SiO_2. En las extrusiones sucesivas la dosificación del masterbatch se redujo realizando descargas discontinuas del mismo durante la extrusión, evitando así aglomeración excesiva.

Para este proceso, el husillo de la extrusora se hizo girar a 45 rpm, la zona de alimentación trabajó bajo 2,5 bar de presión de nitrógeno, para evitar la presencia de humedad en dicha zona y también fue conectada una bomba de vacío la última zona para eliminar los compuestos volátiles formados, favoreciendo desgasificación. El trazador inerte empeño unos 4 minutos y 30 segundos aproximadamente en salir de la extrusora. El perfil de temperatura en la extrusora se muestra en la **Tabla 8.**

La dosificación de marterbatch con cada nanosilice se aumentó gradualmente a fin de alcanzar el porcentaje de nanosílice deseada en el material resultante (2% en peso). Como puede verse en la **Tabla 11**, sólo en el caso de nano-sílice modificada con grupos epoxi ha alcanzado el valor deseado; Por lo tanto, se procedió a una segunda encapsulación y extrusión con el fin de aumentar el porcentaje de nanosílice no modificada (REX-PLA/SiO_2) y modificada con grupos amino (REX-PLA/Am.SiO_2) en el REX-PLA.

1.2.1.2 Segunda encapsulación de nanosílice en PLA

Los masterbatches se prepararon con 40% de nanocargas siguiendo el procedimiento descrito en la **Figura 23**, se produjeron aproximadamente 80 g por cada masterbatch. Cada lote se trató térmicamente a 100°C durante 2 horas en un horno y luego fueron molidos y homogeneizado su tamaño de particula.

1.2.1.3 Segunda extrusión

Los masterbatches de PLA con 40% nanosílice y El REX-PLA se secaron con las mismas condiciones mencionadas antes de la primera extrusión. Y se siguió el mismo esquema de producción (**Figura 24** del presente trabajo).

Los husillos en la extrusora se hicieron girar a 45 rpm durante la extrusión; la zona de alimentación trabajó bajo atmósfera de nitrógeno a 2,5 bar y una bomba de vacío se conectó la última zona. El tiempo empleado por el trazador inerte en salir de la extrusora fue cerca de 4 minutos y 3 s. El perfil de temperatura en la extrusora se muestra en la **Tabla 8** y Las condiciones de flujo de alimentación en la **Tabla 14** del proyecto.

Posteriormente, los pellets de cada material se mezclaron manualmente, resultando un porcentaje de alrededor de 2 % en peso de nanopartículas en cada uno. En esta fase, se extrujo igualmente, 600 g de REX-PLA sin nanopartículas, con el fin de tener una referencia para las caracterizaciones posteriores. Inmediatamente, el material obtenido se recristalizó a 90 ° C durante 5 horas, agitando manualmente cada 30 min.

1.2.2 Homogeneización y la preparación de las películas poliméricas: tercera extrusión

Para preparar las películas poliméricas se ha empleado la extrusora de doble husillo con un cabezal de extrusión plano ajustado a 0,6-0,7 mm de espesor. Antes de este proceso, el material se secó a 80 ° C durante 4 horas en una tolva PIOVAN. El proceso se muestra esquemáticamente en la **Figura 26** del proyecto.

3. Caracterización

En esta fase se ha evaluado el contenido de nanosílice en cada película, por análisis termogravimétrico (TGA), comparando con los valores teóricos. En adición, el análisis termogravimétrico ha permitido obtener información acerca de la estabilidad térmica de los materiales producidos. Luego se realizó un análisis DSC (Calorimetria diferencial de barrido) en todos los materiales. Por último, el comportamiento mecánico se evaluó por medio de ensayos de tracción, teniendo en cuenta también el efecto del envejecimiento en las películas obtenidas. Todas las técnicas de análisis mencionados se explican en detalle en el capítulo **TECNICAS DE ANALISIS**.

RESULTADOS Y DISCUSIÓN

1. Inspección sensorial

El color de las películas es muy similar, independientemente del tipo de nanocarga utilizado; en REX-PLA/SiO_2 se evidenciaban aglomerados.
Algunas diferencias en la textura de la superficie fueron observados: REX-PLA/Am.SiO_2 y REX-PLA mostraron una superficie lisa; REX-PLA/SiO_2 y REX-PLA/Ep.SiO_2 tenían una superficie rugosa.

2. Análisis térmico de las películas

2.1 Análisis termogravimétrico (TGA)

2.1.1 Composición de los materiales

El análisis termogravimétrico se realizó con muestras de una masa aproximada de 10 mg. La temperatura se varió de 0°C a 1000°C a una velocidad de 10°C/min en una atmósfera de nitrógeno.
La fracción en peso de nanopartículas en cada polímero obtenido se determinó utilizando los residuos de muestras a 1000°C, que corresponden a la porción en el polímero inorgánico (sílice). A ese porcentaje se añadió la parte orgánica de la nanosílice (información del proveedor), que ha sido degradada en la prueba.
El porcentaje de nanosílice en el REX-PLA/SiO_2 fue igual a 1,89 ± 0,29 % (**Tabla 18**), resultados aceptables en relación con el valor teórico (2%). El REX-PLA/Am.SiO_2 resultó contener 2,20±0,16% de nanosílice modificado con grupos amino (**Tabla 19**). De nuevo, esto es un resultado aceptable con respecto al esperado teóricamente (2,34%). El REX-PLA/Ep.SiO_2 mostró un contenido de nanosílice modificado con grupos epoxi igual a 2,49 ± 0,26% (**Tabla 21**), que se aproxima al valor ideal calculado (2,5%).

2.1.2 Estabilidad térmica

El REX-PLA/Ep.SiO_2 mostró la $T_{95\%}$ más baja, con un valor aproximado de 325°C; REX-PLA sin modificar tuvo un valor cercano a 330°C. Los valores de $T_{95\%}$ en los materiales que contienen nanosilice sin modificar y modificada con grupos amino fueron ligeramente superiores (alrededor de 335 y 332 °C respectivamente) a la registrada para el REX-PLA sin nanocarga. Esto significa que la adición de tales nanopartículas puede mejorar las propiedades térmicas de la matriz polimérica ya que se empieza a degradar a temperaturas más altas. Sin embargo, este aumento no es tan elevado como para incrementar significativamente la temperatura de procesamiento del REX-PLA.

2.2 Calorimetría diferencial de barrido (DSC)

Se prepararon tres muestras de aproximadamente 5 mg para cada material en crisoles de aluminio sellados utilizando una prensa. Se tomaron muestras de la película, al principio, en medio y al final de la extrusión . Los ciclos fijados en la prueba se encuentran descritos en la **Tabla 22** en el proyecto. Es importante recordar que todas las pruebas se llevaron a cabo en una atmósfera inerte de nitrógeno a 10°C/min.

2.2.1 Primer barrido de calentamiento (directamente del proceso de extrusión)

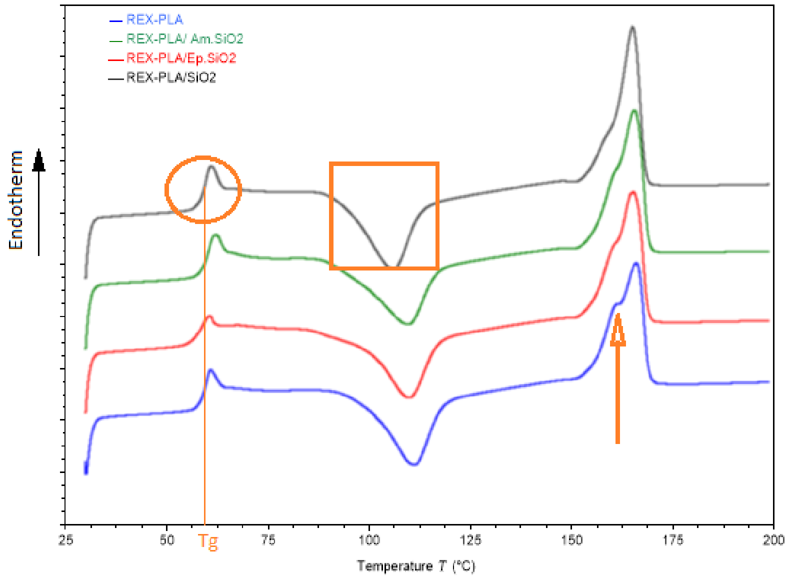

Figure 2. Comparacion del primer barrido de calentamiento en cada material (eje Y modificado).

La temperatura de transición vítrea (Tg) no se ve afectada significativamente por la presencia de las nanopartículas, siendo de 58 ° C.

Todos los materiales mostraron un fenómeno de "cristalización en frío", la entalpía de este proceso aumentó en el caso de nanosílice no modificada (32,61 ± 0,99 J/g) en comparación con REX-PLA (31,60 ± 1,34 J/g) y más baja en el caso de la nanosilice modificado con grupos amino (31,40 ± 0,71 J/g) o grupos epoxi (31,10 ± 1,15 J/g). Este resultado puede ser debido al impedimento estérico causado por grupos sustituyentes en la nanosilice, que dificultan la movilidad macromolécular.

Antes de alcanzar el máximo del pico del proceso de fusión, todos los materiales han mostrado una "hombro" (Tsm) a aproximadamente 160°C, que puede ser el resultado de polimorfismo, es decir, la presencia de diferentes poblaciones cristalinas.

En cuanto a la cristalinidad, todos los materiales son semicristalinos. En el caso de REX-PLA/SiO_2, la cristalinidad fue menor (2,68%) que el material sin nanocarga (3,54%). Por otra parte, se observó un ligero aumento en el grado de cristalinidad en el caso de

REX-PLA/Am.SiO_2 (4,43%) y REX-PLA/Ep.SiO_2 (3,96%), apoyando así la hipótesis que la nanosílice modificada aumenta la velocidad de cristalización debido a una mayor interacción de la interfaz orgánica-inorgánica.

2.2.2 Fase de enfriamiento

Los materiales capaces de cristalizar en estas condiciones de enfriamiento son el REX-PLA, que alcanza aproximadamente el 12% de cristalinidad y el REX-PLA/SiO_2, que a su vez alcanza aproximadamente 28% de cristalinidad. Esta diferencia en cristalinidad evidencia el efecto nucleante de la nanosílice sin modificar. Este efecto parece ser perdido cuando la nonosilice es modificada superficialmente

2.2.3 Segundo barrido de calentamiento (Historia térmica eliminada)

A excepción del REX-PLA/SiO_2, todos los materiales mostraron una cristalización en frío, mostrando un "retraso" en la temperatura de inicio de este proceso (Tc-o) cuando se utilizó nanosilice modificada.

Se observó que la nanosílice modificada reduce marcadamente el porcentaje de cristalinidad debido a que los sustituyentes voluminosos limitan la movilidad en la estructura polimérica evitando un empaquetamiento eficiente.

3. Evaluación de las propiedades mecánicas

Ensayo de tracción

La prueba se realizó según la norma ASTM D638-02. Los ensayos se realizaron a temperatura ambiente (25°C) con una velocidad de deformación de 10 mm/min. Las probetas realizadas fueron del tipo I según la norma (**Figura 47**) y tuvieron un espesor de 0,6-0,7 mm,. Las muestras fueron tomadas de los laterales y el centro de la película tal como se muestra en la **Figura 48**.

El método de selección de muestras a analizar (4 y 5 para cada material) se realizó en función del punto de ruptura de la misma, que debe estar entre las líneas de los límites establecidos (tramo útil).

En este análisis se han estudiado las propiedades mecánicas de cada material y el efecto del envejecimiento sobre dichas propiedades del polímero, teniendo por ende probetas rejuvenecidas (de-aged) y probetas envejecidas (aged).

El tratamiento térmico de rejuvenecimiento aplicado a las muestras fue el siguiente:

1. La película se colocó entre dos placas de metal ajustadas (precalentado a 60°C)
2. Se mantuvo durante 40 min a 60 ° C en un horno.
3. Finalmente, se enfrió en un baño de agua fría durante 15 minutos.

Inmediatamente después de este procedimiento, se cortó cada muestra en la máquina de fresado y directamente fue sometido a ensayos de tracción en el caso de **probetas**

rejuvenecidas. Las **probetas envejecidas**, por su parte, se almacenaron durante 1 semana a temperatura ambiente después del tratamiento térmico.

3.1 Probetas rejuvenecidas.

La **figura 3** muestra los resultados para muestras con menores desviaciones de la media.

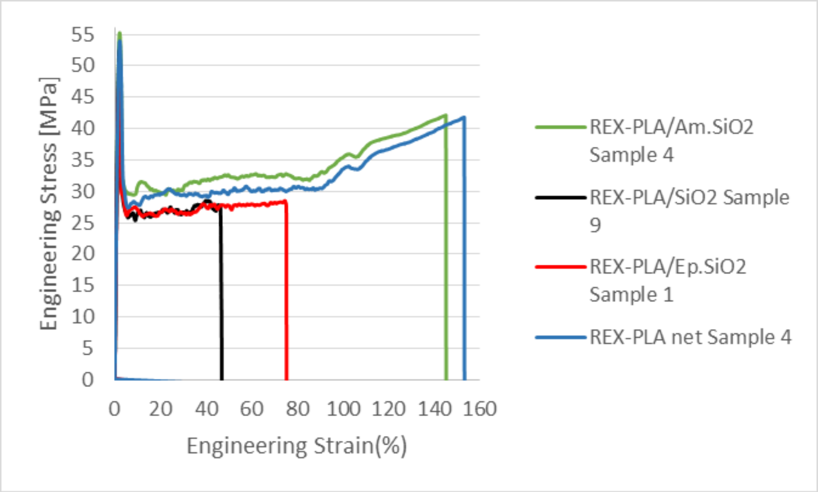

Figura 3. Resultado de la prueba de tracción para muestras rejuvenecidas.

El REX-PLA/Am.SiO$_2$ es el material que presentó la mayor relación entre la tensión aplicada y la deformación (módulo de Young: 2.94 GPa) por lo que es el candidato más prometedor en términos del comportamiento mecánico.

Los valores de alargamiento a la rotura mostraron dispersiones importantes, esto en el caso de los nanocompuestos, puede ser debido a que las nanopartículas actúan como núcleos de ruptura.

3.2 Probetas envejecidas

Las muestras preparadas se ensayaron después de una semana de almacenamiento a temperatura ambiente (25°C). La **figura 4** muestra los resultados para muestras con menores desviaciones de la media.

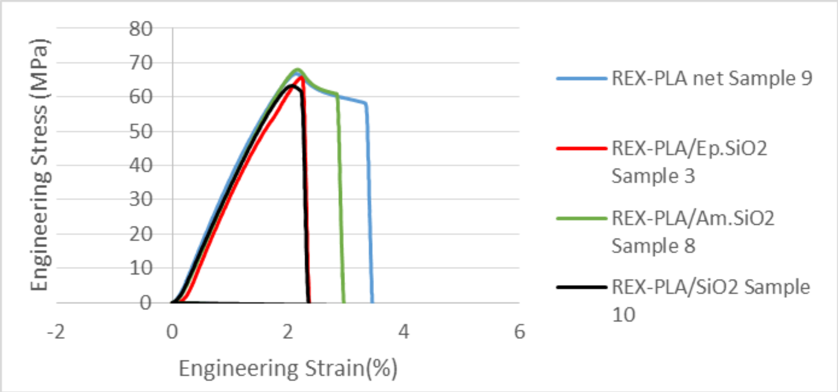

Figure 4. Resultado de la prueba de tracción de las muestras envejecidas.

El REX-PLA tiene un módulo de Young ligeramente superior (3,11 GPa) en comparación con modificado con grupos amino (2,88 GPa). Esto significa que después de algún tiempo el REX-PLA rápidamente se convierte en un material más frágil que el REX-PLA/Am.SiO$_2$.

3.3 Factor de envejecimiento

Se evaluó la variación percentual de las propiedades debido al envejecimiento de los materiales (**Tabla 35**).

Desde un punto de vista general, el REX-PLA/Am.SiO$_2$ es el material con mejor comportamiento, ya que sus propiedades tienen una variación menor con el paso del tiempo. Esto significa que es probable que la nanosilice modificada con grupos amino retrase el envejecimiento del material a temperatura ambiente.

CONCLUSION

El objetivo general de esta investigación fue estudiar el efecto de la presencia de nanosilice modificada en las propiedades termomecanicas de ácido poliláctico (PLA); para este propósito se prepararon nanocompuestos basados REX- PLA por medio de extrusión reactiva con tres tipos de nanosílice : nanosílice sin modificar, nanosílice modificada con grupos amino, nanosílice modificados con grupos epoxi.

A. Análisis térmico

Para evaluar el comportamiento térmico de los diversos compuestos, se ha realizado análisis TGA y DSC. A partir de estos resultados se puede concluir que, con la adición de 2% en peso de nanopartículas en la REX-PLA, la temperatura de degradación no cambia significativamente. Sin embargo, se observó un aumento en la cristalinidad del material, que puede ser reflejada sobre las propiedades mecánicas.

B. Análisis mecánica.

Las muestras de cada material fueron sometidas a un tratamiento térmico con el fin de evaluar el efecto de envejecimiento a temperatura ambiente. Los ensayos mecánicos han mostrado que la nanosílice modificada con grupos amino es capaz de aumentar la resistencia a la tracción de la matriz de polímero y de reducir el efecto del envejecimiento.

Desde un punto de vista general, el uso de nanopartículas de sílice modificados con grupos amino parece ser la alternativa más eficaz para mejorar las propiedades térmicas y mecánicas del PLA-REX. De hecho, este tipo de nanopartículas aumentan la cristalinidad y la resistencia a la tracción del polímero, extendiendo así la capacidad de uso a nivel industrial. También facilitan el manejo y almacenamiento, reduciendo el efecto del envejecimiento sobre las propiedades físicas del polímero.

Nomenclature used

PLA: Polylactic acid (PLA 4032D)

PLA/SiO$_2$: Concentrate of nanosilica in PLA matrix

PLA/Am.SiO$_2$: Concentrate of nanosilica surface modified with amino group in PLA matrix

PLA/Ep.SiO$_2$: Concentrate of nanosilica surface modified with epoxy group in PLA matrix.

REX-PLA: Reactive Extrusion of PLA 4032D and Joncryl ADR4300F

REX-PLA/SiO$_2$: PLA 4032D, Joncryl ADR4300F and Cab-O-Sil EH5 (Untreated Nanosilica)

REX-PLA/Am.SiO$_2$: PLA 4032D, Joncryl ADR4300F and SiO$_2$ 6851HN (Nanosilica surface modified with Amino group).

REX-PLA/Ep.SiO$_2$: PLA 4032D, Joncryl ADR4300F and SiO$_2$ 6852HN (Nanosilica surface modified con Epoxy group).

$\boldsymbol{E}$: Young's modulus

$\boldsymbol{\sigma}$: Engineering stress

$\boldsymbol{\varepsilon}$: Engineering Strain

$\boldsymbol{\sigma y}$**:** Yield stress

$\boldsymbol{\varepsilon}$**y:** Yield strain

$\sigma \boldsymbol{b}$: Strain at brake

ε**b**: Tensile Strength at Break

%σ_y: Percentage of change of the yield stress

%ε_y: Percentage of change of the yield strain

%E: Percentage of change of Young's modulus

Tg: Glass transition temperature

Tc-o: Temperature in which start the cold crystallization process.

Tc-peak: Temperature of maximum speed in the cold crystallization process.

ΔHcc: Cold crystallization enthalpy

Tm-o: Temperature at which start the melting process.

Tsm: Temperature corresponding ti the shoulder on melting endotherm

Tm-peak: Temperature of maximum speed in the melting process.

ΔHm: Melting enthalpy

ΔHc: Crystallization enthalpy

Tc: Temperature corresponding to the maximum crystallization rate

Xc: Percentage of crystallinity.

ΔHm°: Melting enthalpy of 100 % crystalline PLA.

%PLA: Percentage of pure PLA in the material.

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I. INTRODUCTORY CHAPTER

I.1 Introduction

The plastics industry has achieved an amazing development in recent decades, as plastics are used in many areas of daily life, like packaging, automotive, furniture, electrical and electronic equipment, decoration, food packaging, etc. However, several decades have accumulated large quantities of plastic wastes in the environment causing high levels of air and water pollution that will have a great impact on future generations. In addition, this kind of plastic entirely derives from non-renewable fossil resources. Of the total amount of oil produced in the world, about 5% goes to the plastics industry. According to current projections, the demand and price for fossil resources will increase, the current wells run out and no new ones seem to be at disposal, making an increase in production unfeasible. This has made the study of the use of biodegradable polymers a priority in order to try to limit and control the environmental problem of recycling of conventional plastics.

The generation of new biodegradable materials has been a challenge for Chemical Engineering and Materials Engineering in recent years. Many technological efforts have been directed mainly to solve problems in the environment area. While natural polymers are generally associated with the term biodegradability, their applicability cannot be compared to synthetic ones derived from petroleum. **The motivation of this work is based on the need to implement chemicals knowledge and processing, looking to expand the application of the bio-based polymers. In this context, some attempts have been carried out in order to find ways to improve the properties of one of the most currently promising bio-based polymer, polylactic acid (PLA), stabilizing its macromolecular structure and thereby optimizing its industrial handling.**

Polylactic acid (PLA) is a thermoplastic material derived from a natural monomer, L-lactic or D-lactic acid, is a bio-based polymer with high tensile strength and a high Young's modulus in comparison to other biodegradable materials. The polymer is well suited for applications that have to withstand a load, such as sutures and orthopedic bindings as well as biodegradable and compostable disposable cups for cold drinks, bags and more. Its thermal characteristics are defined by a high melting point and glass transition temperature ranging between 60 and 65°C. In the seeking for optimizing these properties, other studies have exploited the reactive extrusion of polylactic acid (PLA) with different compounds, including Joncryl, a chain extender, which generates significant mechanical, thermal and rheological improvements, giving a higher quality material, which has been called REX-PLA. However, for achieving a wider polymer use in the industry, the properties of the material must still be improved. This is the reason, for which we decided to explore, in this experimental work, the effect of the incorporation of various nanocomposites in the REX-PLA matrix.

In recent years similar studies applied to PLA without reactive extrusion, (i.e. the original material without the processing that makes REX-PLA) have been carried out, directly introducing into the molecular structure different nanocomposites, reaching moderate mechanical and thermal improvements as compared to the pure polymer. Unlike these previous studies, this work relies on the experimentation with REX-PLA as the base material.

The aim of this work is to prepare and characterize the REX-PLA nanocomposites obtained by reactive extrusion with three types of nanoparticles, i.e. unmodified nanosilica (SiO_2), surface modified nanosilica with amino group ($Am.SiO_2$), and modified with epoxy group ($Ep.SiO_2$), in order to compare their mechanical and thermal properties of the polymer matrix.

Nanocomposites can act as mechanical reinforcement and as a barrier to prevent degradation of the material during processing. Attention has been given specifically to the nanocomposites reinforced with silica due to its high interaction degree with the PLA chain and hence to a greater dispersibility in relation to other nanocomposites.

The PLA nanosilica composite experiments provided good results regarding the thermal behavior of the material; however, despite increasing the percentage of crystallinity of the PLA, the dispersion of the nanoparticles is not enough to achieve significant enhancements in the mechanical properties. The surface modification of the nanosilica might represent a solution to ameliorate the nanofiller dispersion and due to the increase in the interactions between the polymer matrix and the reinforcement, it could be possible to obtain various improvements in the resulting material.

It is expected that the dispersibility of modified nanosilica remarkably increases because of the additional chemical interactions between functional groups and Joncryl added to the PLA structure. High dispersion could be beneficial for the optimization of the physico-mechanical properties of the resulting material.

This experimental work has been developed in one of the most important research centers in Barcelona, Centre Catalá del Plàstic (CCP), known for its high number of publications and industrial consulting. Currently, CCP is working on the REX-BIOBLEND project (MAT2013-40730-P), which is funded by the Ministry of Economy and Competitiveness of the Government of Spain. Is important to remark that this work is a portion of the mentioned project and future investigations will continue in the research center.

The step of the present experimental work for the achievement of the objectives can be listed as follows:

1.-Feedstock conditioning step: First reactive extrusion of PLA with Joncryl. Successively, encapsulation of the nanosilica in a PLA network.

2.-Gathering of REX-PLA nanocomposites step: Reactive extrusion of REX-PLA with each batch of encapsulated nanosilica. This step consists of two sub-steps: the first one is to obtain pellets (first extrusion) and the second phase refers to the homogenization and obtainment of the polymer film (second extrusion).

3.-Characterization step: Characterization of the mechanical and thermal properties of the materials obtained.

The results of the characterization will be analyzed and evaluated in order to confirm the hypothesis.

This project consists of five chapters: the **Introductory chapter** is aimed at getting familiar with important related concepts. The **Experimental chapter** is a description of the raw materials, as well as of the procedure followed during the experimental work. The **technical analysis** chapter will show the analyses that will be applied to the product; The **results and discussion** of these analyses will be exposed as well. Finally, the **Conclusion chapter** will summarize and point out the results.

I.2 Objectives

I.2.1 General Objective

The main goal is to improve the thermal and mechanical properties of polylactic acid, PLA, preparing and characterizing the REX-PLA nanocomposites by reactive extrusion with three types of nanosilica: modified amino group, epoxy group and nanosilica unmodified, contributing to research for optimization of its industrial handling.

I.2.2 Specific objectives

- Evaluate the rheology of materials to be extruded
- Characterize thermally the material produced and compare these properties with the neat polymer (i.e. without nanofiller) subjected to the same processing conditions.
- Evaluate and compare the mechanical properties of the polymers.
- Evaluate the aging factor of each material.
- Propose the best nanofiller alternative for the polymer treated (REX-PLA).

I.3 Hypothesis

- If nanofillers are added to the polymer matrix of REX –PLA, the degradation temperature of the material will be higher.
- The presence of the nanofiller should increase the crystallinity of the REX-modified PLA.
- If the nanosilica surface is modified, the mechanical properties of the polymer matrix will be improved as a consequence of a better dispersion and adhesion of the nanofiller.
- The aging factor will be reduce with the addition of nanoparticles.

I.3 Theoretical framework

Since the focus of this work will be on improving the properties of one of the most promising bio-based polymers, such as polylactic acid (PLA), stabilizing its macromolecular structure and thereby optimizing its industrial handling. It will be necessary to raise some central concepts to support the interpretation that is intended.

First of all, plastics belong to a category defined as polymeric materials. The polymers are presented regularly in our daily life: nowadays it would be unimaginable to live in a world without the polymeric materials. These are manifested in a single container of water, medicine or food packaging, etc. Unfortunately, they usually show a serious problem of resistance to degradation after use, making them difficult to dispose.

Depending on their base structure, the polymeric materials may be classified into natural and synthetic. Natural polymers are based on materials from the animal or plant kingdom. Synthetics are man-made, usually derived from petroleum. From a scientific point of view, a polymer is a macromolecule composed of large numbers of repeated subunits called monomers and depending on its origin, the material will be classified as **plastic, Bio-plastic or Bio-based plastic**.

I.3.1 Classification of polymers by origin

I.3.1.1 Plastic: Polymeric material obtained from monomers derived from fossil fuels.

I.3.1.2 Bio-plastic: It is obtained by direct conversion of polymeric materials already present in nature.

I.3.1.3 Bio-based plastic: polymer obtained through biotechnology " Building Blocks" (chemical synthesis) of natural monomers, chemical modification of natural polymers or mixture of synthetic and natural polymers.

Currently, polyethylene terephthalate (PET) and polystyrene (PS) are two of the most produced and used in the plastics industry. They have a large range of applicability; both are used in food packaging, personal care products and medicine. In addition, they have the advantage of bearing microwave heating. PS use expands to areas like construction, home appliances, toys, garden equipment, and others.

I.3.2 Classification of Polymers by molecular structure

Due to the high molecular weight of the polymers, completely crystalline polymers do not exhist. Hence, the classification according to their molecular structure is of significant importance in this regard; more specifically:

I.3.2.1 Amorphous polymers: they do not show any order or pattern in their structure. Due to their difficult packaging, light can easily pass through them, making them transparent materials. It is noteworthy that amorphous materials are not crystallizable.

I.3.2.2 Semi-crystalline polymers: their structure shows ordered chain parts and amorphous parts, resulting in an opaque material that has more resistance to light transmittance. In their neat crystalline parts, the chains fold to form sheets defined as **lamellae**. Furthermore, lamellae usually give rise to spherical structures called **spherulites**, the amount of which will increase or decrease the polymer crystallinity. These types of materials are **crystallizable**: in other words, depending on the cooling conditions (°C/min) from melt, the structural order can be increased. This concept opens a new classification of polymers, which corresponds to their behavior in relation to the applied heat.

I.3.3 Classification of polimers by heat applied:

I.3.3.1 Termoplastics: these are moldable by increasing the temperature and pass to glassy state when cooled. A good advantage of such plastics is that, once they are cooled, they can be moldable again by heating, since their bonds are weak (Van Der Waals, dipole – dipole interactions).

I.3.3.2 Thermosets: these polymers can be subjected to the above process only once, because upon the solidification they give rise to a highly rigid material that tends to degrade when heated. This is caused by the covalent bond present in the material.

I.3.3.3 Elastomers: Unlike the previous classes, they show a low glass transition temperature. Because of this, they hold a great elasticity that allows fully recovering their original shape.

Once outlined the general concepts of relevance, we will proceed to the definition and description of some properties of PLA.

I.3.4 Polylactic Acid definition

Polylactic acid, hereinafter referred as **PLA**, is a bio-based thermoplastic quite similar to polystyrene (PS) or polyethylene terephthalate (PET). It can be synthesized from renewable resources. It is completely biocompatible and has advantageous thermal, mechanical and optical properties compared to other biodegradable polyesters [1]. **PLA** is produced by condensation polymerization, that is to say, directly from its basic structure of lactic acid (sugar fermentation from carbohydrate sources). However, there is an alternative and more effective process that is generally used in the medical area: the ring-opening polymerization (ROP) of lactide (cyclic dimer of lactic acid) catalyzed by tin (II) octoate (Lewis acid). Such a monomer may be obtained from the short chain PLA (prepolymer) under reduced pressures. PLA prepolymer is derived from the dehydration and polycondensation of lactic acid under vacuum and high temperatures.

PLA has a Young modulus (elastic limit upon application of mechanical stress) relatively high, but it is brittle (low elongation) due to steric effect in its structure, promoting a lower melting resistance compared to conventional polymers, this impedes its applications in some areas particularly like packaging materials[2]. The improvement of these properties is necessary in order to widen its application in the market of polymers, successively reviewing its biodegradation process.

I.3.4.1 PLA Degradation

The PLA degradation process is extremely complex. It has been classified into different types according to the agent that causes it: thermal degradation, degradation by radiation (UV rays or heat-induced) and biodegradation. Factors that influence in the degradation rate of PLA can be summarized as follows: the steric configuration and possible crystallinity, relative hydrophobicity of the polymer matrix and the presence of substituents [1].

Hydrolysis of PLA is generally the main material degradation; this process is illustrated in the **Figure 1.**

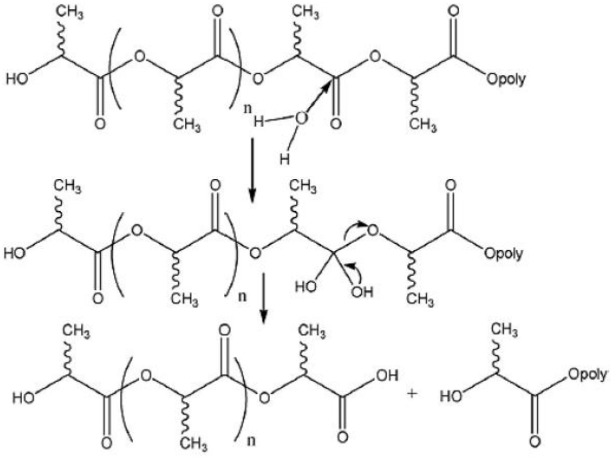


Figure 1: PLA Hydrolysis. [3]

I.3.4.1.1 PLA Thermal Degradation

The decrease of molecular weight of PLA occurs at temperatures below its melting point: this justifies that it tends to degrade during the thermal processing. As is known, the rate of this process is inversely proportional to the degree of crystallinity and molecular weight [3]; in addition, it depends on the substituent groups and their distribution in the polymer matrix.

According to earlier investigations, it has been found that the reactions that occurred during the processing of this material are hydrolysis, depolymerization, oxidative degradation and transesterification reactions.[3]

PLA degradation may represent an advantage by being environmentally-friendly. However, the main problem is the low temperature, at which this process is carried out (from 180 to 220°C), promoting an undesirable reduction of molecular weight [4].

I.3.4.1.2 PLA Biodegradation

Such degradation occurs in the environment by the action of natural factors (UV, soil, water bodies, etc.) and microorganisms. It happens due to enzymatic or non-enzymatic hydrolysis (pH degradation).

It has been found that PLA biodegradation occurs in between 6 months to two years. Clearly, this depends on its structure and molecular weight.[3]

This process occurs in two steps: the first step of the biodegradation is promoted by both temperature and moisture (H_2O). PLA high molecular weight chains are hydrolyzed becoming oligomers with lower molecular weight. The next step is the plastic fragmentation, which takes place when the molecular weight decreases to less than about 40,000[4]. Here, the microorganisms in the environment continue the biodegradation process by converting the components into CO_2, water, and humus.

I.3.4.2 PLA Physical Properties

PLA is a copolymer of poly (L - lactic acid) and poly (D- lactic acid) monomer. The polymer properties are related to the proportion of each enantiomer [4].

Lactic acid (2-Hydroxypropanoic acid) has a chiral carbon, resulting in two enantiomeric forms. Depending on the optics, positive (S or L) and negative rotation (R or D), the physical properties will change. That is why the R/S notation is used to characterize it. If the content of poly (L - lactic acid) is greater than 90%, the polymer will be crystalline. This means that the crystallinity is inversely proportional to the percentage increase in D- lactic acid [1].

The thermal and mechanical properties of PLA depend of the molecular weight, polymerization condition, thermal history and purity of the polymer.

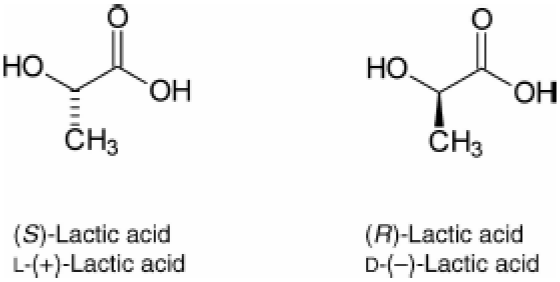


Figure 2: Enantiomeric forms of Lactic Acid**.**

The glass transition temperature of pure PLA (94% of L) is around 60° C and the melting peak point is equal to 140°C [4].

I.3.4.3 PLA Chemical Properties

The lactic acid molecule contains a hydroxyl functional group and a carboxylic acid group, which leads to inter and intramolecular esterification reactions. This makes difficult to obtain an enantiomerically pure lactic acid, being only possible by crystallization method [4]. The amount of water removal is important to control the monomer ratio of lactic acid, lactoyl (lactic acid dimer), higher oligomers of lactic acid, lactide and therefore the properties of the resulting polymer.

I.3.4.4 PLA Miscibility with different solvents

Miscibility (mixing two substances) is the property that measures the rate, at which they form a homogeneous phase (are visually indistinguishable). When two substances are miscible, this means that when combined, no physical or chemical transformation between them occurs: in other words, they respectively retain both their chemical composition and physical properties.

This property can be represented by a distribution coefficient (K_d) that represents the ratio of total solid concentration in the organic phase (HLA)o and the aqueous phase (HLA)w.

$$\mathbf{Kd} = \frac{(\mathbf{HLA})\mathbf{o}}{(\mathbf{HLA})\mathbf{w}}$$

(I.1)

The distribution coefficient K_d of PLA in chloroform ($CHCl_3$) at 25°C is equal to 106 and in relation to different organic solvents it is the best candidate for the encapsulation process of a composite structured PLA.

I.3.4.5 Lactic acid Production

There are different processes for the production of PLA, which may provide different properties, hence addressing its end-use.

Lactic acid, as mentioned above, is the monomer of PLA. Its properties are extremely important because it is the base of the material structure. Since it has a chiral carbon, according to how is obtained it, a certain enantiomeric purity will result.

I.3.4.5.1 Lactic acid Production by chemical way

This alternative production is based on the reaction between acetaldehyde and hydrogen cyanide, resulting in the production of lactonitrile. Lactic acid is obtained by exploiting a subsequent hydrolysis.[5]

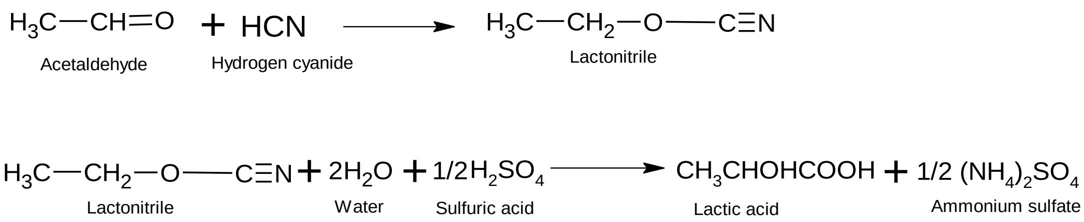


Figure 3: Lactic acid from chemical reactions.

The disadvantage of the chemical synthesis is that a mixture of L-lactic acid and D -lactic acid is obtained without particular predominance, which affects the physical and chemical properties of the final material. Given that there is not enantiomeric pattern, predicting the behavior of the future PLA becomes difficult.

I.3.4.5.2 Lactic acid production by fermentation

In the production of lactic acid by fermentation of substrates rich in carbohydrate, lactobacilli (bacteria) and Rhizopus (filamentous fungi) microorganisms are the most frequently used because they consume the substrate without major nutrient requirements. Production tending to a single enantiomeric form depends intimately on the pH control, temperature, type of microorganism used, type and concentration of the substrate, etc. This large amount of variables to control makes it an extremely delicate process.

The obtained product contains impurities as esters, sugar and trace metals. To solve this, such techniques as esterification with methanol, purification with ion exchange resins, solvent extraction, membrane technology (ultrafiltration), reverse osmosis and electrodialysis can be applied. The profitability of this process depends on the type of raw material and substrate used. In particular, it must gather economic requirements, pretreatment, demanding performance and pollutant levels.

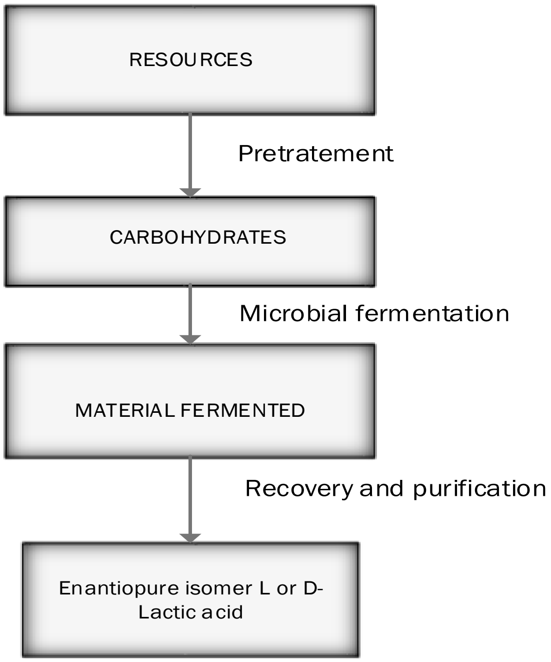


Figure 4: Block scheme lactide acid production by fermentation.

I.3.4.6 High molecular weight PLA Industrial production:

The PLA for industrial use should have a high molecular weight. This is why several techniques have been designed, each showing advantages and disadvantages.

I.3.4.6.1 Polycondensation based on Lactic acid polymers

As a first step, the amount of water in the feed of lactic acid should be eliminated because it favors the formation reaction of PLA. Then lactic acid is converted into low molecular weight PLA: this process involves the catalyzed reaction of hydroxyl group and carboxylic acid of the lactic acid. At this point the water removal is not critical due to the low viscosity of the mixture. It is advisable to take in this step the residence time fixed to obtain a pre-polymer with a low molecular weight dispersion.

The third step is the polycondensation, wherein the removal of water formed (by vacuum) becomes critical to avoid the transesterification reaction. The optimal mixing and effective heat transfer are important parameters in this step.

Clearly, side reactions that reduce the molecular weight of the obtained polymer may occur. The same effect is also caused by the lactide formation, which can be avoided reintroducing it into the feed stream. The resulting PLA with a yield of 50% has a molecular weight approximately about 79,000 g/mol.

In order to increase the efficiency of the direct polymerization, fusion/solid polycondensation has been studied. This process adds a fourth step, in which the PLA is cooled below its melting point, forming solid particles that are then subjected to a crystallization process. With the addition of this last step, the molecular weight of PLA obtained is above 100,000 g/mol.

With the same purpose the azeotropic distillation of PLA with Sn component has been assessed: a higher molecular weight of about 100,000 g/mol has been achieved. [4]

The PLA resulting from this production method is used mostly in food and beverage biologically based package, envelopes and textile area.

I.3.4.6.2 Production based on chain extensors

The most widely used is 1-6-Hexamethylene diisocyanate (HDI) (bifunctional compound) because it has a lower toxicity compared to other chain extenders [4]. The amount of chain extender, the proportion of carboxylic acid present in the pre-polymer and catalyst are the main parameters to control in this process.

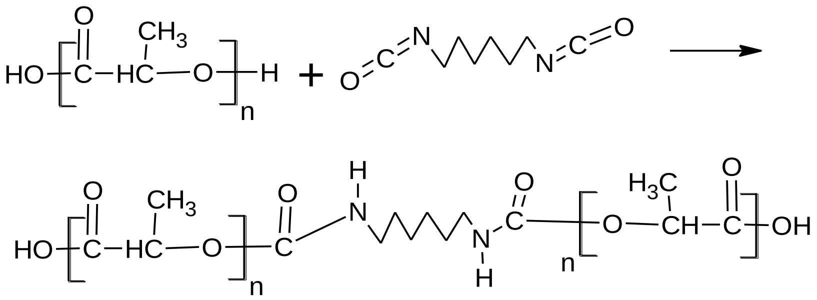


Figure 5. PLA from chain extension production.

The PLA obtained by this method proves to be of high molecular weight; however, their properties depend on the procedure used and, hence, on the future usefulness.

I.3.4.6.3 Polymerization by ring opening

This procedure involves three steps: polycondensation, lactide manufacturing and ring opening polymerization. The most important parameters to control are esterification, purity of the lactide and the monomer residual percentage.

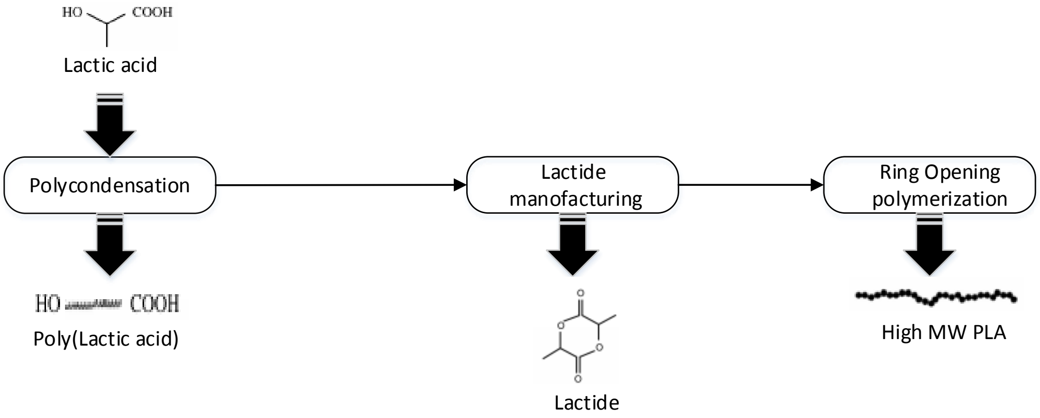


Figure 6. PLA from chain extension production.

The typical manufacture of lactide at an industrial scale involves heating the PLA between 130°C and 230°C at reduced pressures in the presence of 1% of Sn.
The ring opening polymerization (ROP) allows obtaining a high molecular weight PLA by controlling effectively many variables. Tin carboxylates and alkoxides are used as most studied catalysts.[4]

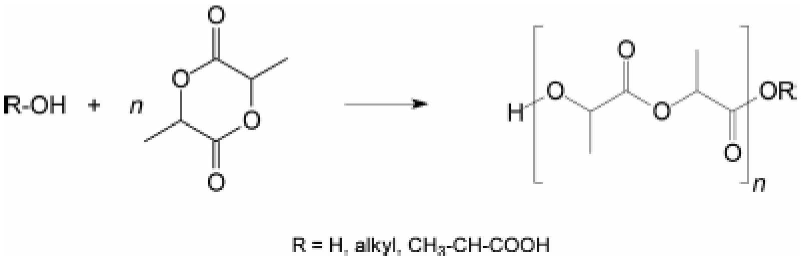


Figure 7. Ring opening of Lactide by an alcohol [4].

This alternative production of PLA is performed in order to improve properties such as melting point, crystallinity and mechanical strength, which seem to be affected by the stereochemical purity of the resulting polymer. This technique is used on small scale, generally in the area of medicine.

All procedures described above allow obtaining high molecular weight PLA, which is very useful today, even in the area of technology, on the manufacture of small-sized computers components, CDs, etc. However, it cannot be compared with the uses of polymers derived from petroleum. To be competitive, it is necessary to improve their thermal and mechanical properties.

I.3.5 Modification of PLA

Chemical and structural modifications of PLA make possible an increase of the molecular weight, crystallinity, thermal stability, among other factors. As a consequence, the macroscopic properties are improved.

The possible modifications regard the variation of the process conditions, using chain extenders, PLA compounds, plasticizers, copolymers, etc. However, the present research is limited to the study and analysis of chemical modification using chain extenders, starting from the PLA and the nanocomposite derived from the resulting material.

I.3.6 Chemical modification of PLA by Reactive Extrusion

Aiming at improving the PLA properties, the reactive extrusion has been exploited as an extremely useful technique in polymer processing. It involves the occurrence of controlled and induced reactions during the extrusion process. The PLA is extruded with various compounds that promote the desire improvements.

Extruders have been used for many years, like in the manufacture of polymers in mass, rheology and chemistry modification and polymer recycling. The most used is the co-rotating twin-screw extruder, due to its high performance in the treatment of viscous mixtures. **Figure 8** shows the main parts that integrate this extruder.

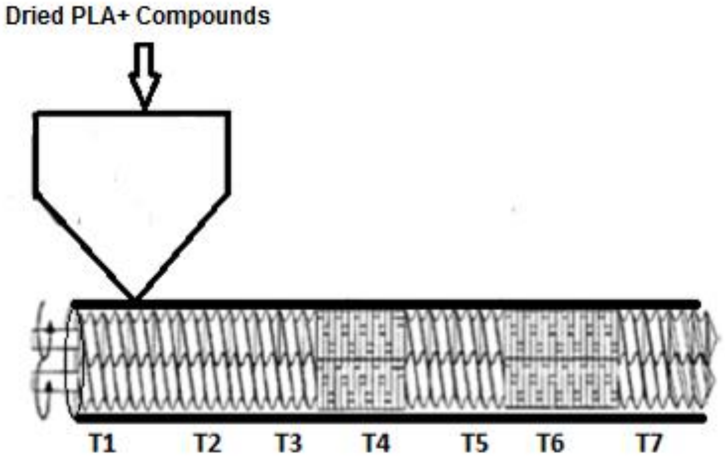


Figure 8. Twin-screw extruder.

In the reactive extrusion process the temperature increases as the extruder progress advances. The temperature profile can be divided into three general zones [6]:

- ✓ First zone: it’s the melting zone aimed at reaching the reaction temperature. In this area no significant reactions occur.
- ✓ Second zone: the reactions take place. The mechanical mixing is used to disperse the components, homogenizing the mixture. At this point, the viscosity of the system increases. A vent can be used to release volatile compounds formed.

- ✓ Third zone: here, the necessary pressure to overcome the resistance of the outlet nozzle of the product is provided. Furthermore, a unit of volatilization (vacuum) may be employed to obtain the desire levels of volatile component.

The properties of the resulting polymer will depend on the process conditions adopted for the extrusion, such as temperature, retention time, rotation speed of the spindles, and pressure.

The residence time distribution (RTD) of the twin-screw extruder has been previously studied to predict their behavior with changing process conditions. There are complex models that can be used to achieve a good estimation. Many authors have compared the models reactor "CSTR cascade" and twin screw extruders, which represent an acceptable simplification [7] as shown below in **Figure 9.**

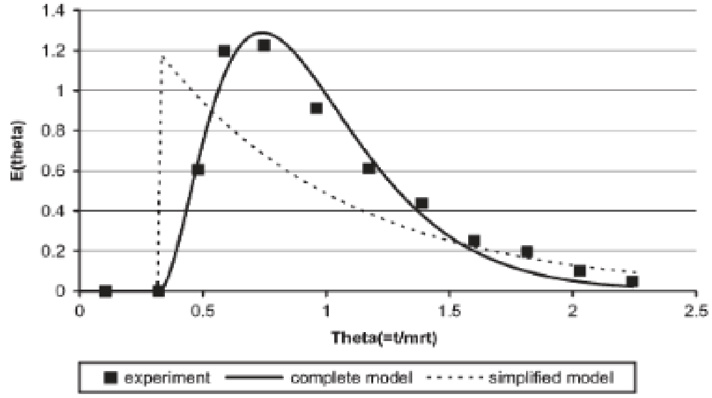


Figure 9. Comparison between predictive models.

Yeh and Jaw (1999) proposed a "simplified model" assuming plug flow reactors in series with a CSTR as dead volume fraction. The complete model of extruding assumes several plug flow reactors in series, with a finite number of stirred tank reactors (CSTR 2 or 3) as dead volume fractions (d), adjusting better to the experimental results (**Figure 9**). It was found that the moisture content, the screw rotation speed, barrel temperature and nozzle diameter had significant effects on the RTD [7]. Studies show that the rheology of the material has a negligible impact on the half-time resistance, being more sensitive to the mass flows along the screws, which depend mainly on their geometry [8].

Extrusion can be accomplished using different compounds, which are defined below:

I.3.6.1 Reactive extrusion with Joncryl

In the recent years a method to reduce the effect of PLA degradation has been investigated. This may be possible by modifying the polymer structure by using additives, called chain extenders, generating covalent bonds between chains or branches of the polymer due to reactions between functional groups of the chain extender and end-groups of the polymer. The suitable reactive groups, according to the literature, are -COOH/epoxy, OH/epoxy, -COOH/ isocyanate, -COOH/amine, -OH/-COOH, -OH/-OH pyromellitic dianhydride PMDA and Triglycidyl isocyanurate TGIC [9]. As shown in **Figure 10**, the epoxy functions may react with both end groups (-OH and -COOH) of PLA in a simple way, which may be desirable in the polymer chain extension.

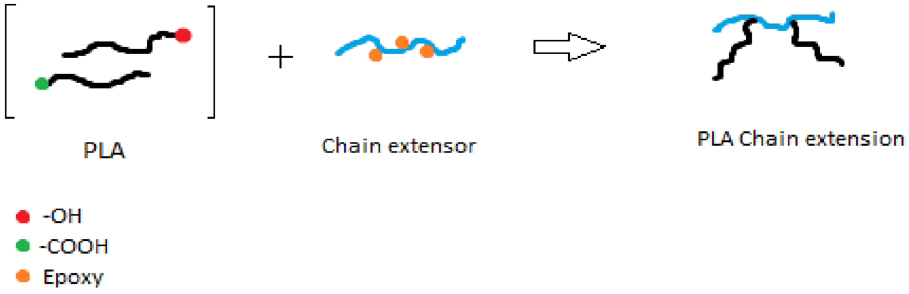


Figure 10. PLA Chain extension scheme.

An attractive multifunctional oligomer of styrene acrylic-epoxy, called Joncryl, has been proposed as an agent for chain extension for PLA during reactive extrusion, resulting a complex called **REX-PLA**. This compound has proved be the most efficient extender chain for poly lactic acid [9], providing an acceptable thermal stability without adversely affecting the dispersion of particles in the PLA. The molecular structure of Joncryl is shown in **Figure 11**.

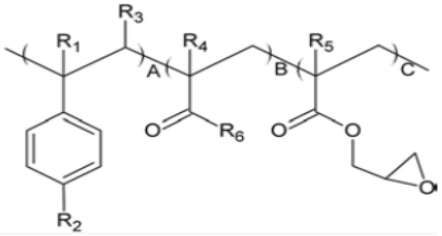


Figure 11. Joncryl-ADR-4300F. R1-R5 are H, CH3, a higher alkyl group, or combination of them. R6 is an alkyl group. A and B are each between 1 and 20 and C between 1 and 12.

The chemical interaction between PLA and Joncryl can build two types of chain extension [10]:

- Linear chain extension: shortly added chain extender or polymer with a few reactive groups.

- No-linear chain extension: the numbers of branches are directly proportional to the amount of chain extender and functional groups of the polymer.

This causes different ways of reaction and thus various structures, as it is shown in **Figure 12**.

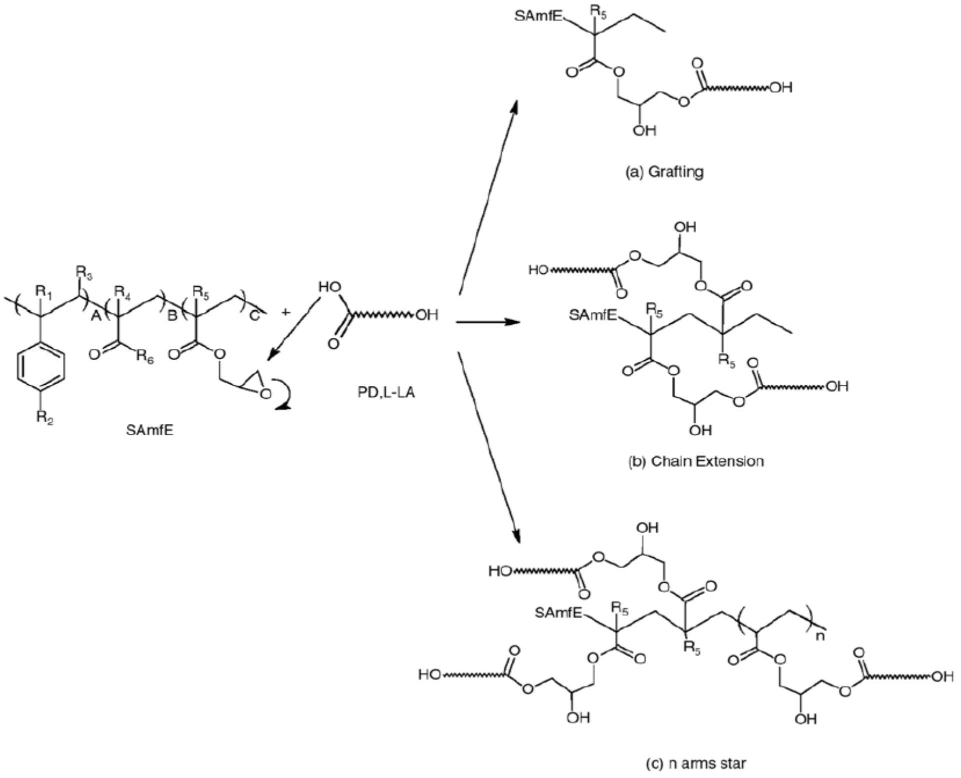


Figure 12. Joncryl and PLA reactions [11].

The characterization of the resulting polymer shows a significant increase in viscosity and excellent rheological properties [8]. Clearly, in the REX-PLA, unreacted epoxy groups can continue to react in a subsequent process, like, for example, the addition of nanocomposites by reactive extrusion.

I.3.6.2 Preparation of PLA nanocomposites

The nanocomposites are an extreme case of composite materials (which are derived from the combination of two or more different elements in order to take advantage of their properties), where the interactions are maximized at the interface [4] due to the small size of the embedded particle (nanoscale). The aim of this type of materials is to disperse the nanoparticles of organic or inorganic materials homogeneously in the polymer matrix. It is important to note that the rheological behavior of the polymer is strongly influenced by the particle size and hence the interfacial characteristics. The larger the surface area of the nanocomposite, the higher will be the degree of dispersion, strengthening and transparency of the resulting material.

Frequently, PLA nanocomposites are able to modestly improve their mechanical and thermal properties compared to the pure polymer matrix. Studies indicate an increase in the average melting temperature, thermal stability and extension process of degradation, as well as the decrease of gases permeability.

The nanocomposite acts as a mechanical reinforcement for the polymer chains and as a mass transport barrier of volatiles products generated during the decomposition, thus increasing the initial degradation temperature [9]. According to the above experiments, the typical amounts of nanocomposite material should be less than 5% by weight, in order to have an effective improvement [12].

Reactive extrusion is the method commonly used in industry for the PLA nanocomposite preparation.

Nowadays, one of the nanofillers that have arisen more interest in the plastics industry is nanosilica. Silica is a natural component in minerals such as quartz and flint, and plants such as bamboo, rice and barley. Also, it can be synthesized, depending on the application, as fibers, sheets, gels and powders [13].

Synthetic amorphous silica (SAS) can be divided into two groups according to the manufacturing process, which can follow the wet route (precipitated silica, silica gel) or the thermal route (fumed silica) [14].

In the present work, pyrogenic amorphous nanosilica (fumed silica) will be used.

The pyrogenic amorphous silica (SiO_2), also called silicon dioxide or amorphous synthetic silica, consists of amorphous silicon dioxide particles produced by oxidation of silicon tetrachloride at high temperatures in an oxygen-hydrogen flame [15].

Table 1: Properties of pyrogenic Silica.[16]

Property	Pyrogenic Silica
Purity	>99.8
Color	white
Specific surface area (BET)	50-400 m2/g
Primary particle size	0,005-0,05 μm

Specific gravity	2,2 g/cm3

The reactivity of the silica depends on the functional groups on the solid phase surface. Basically, two chemical groups compose the synthetic silica: relatively unreactive and hydrophobic units, siloxane (-≡Si -O - Si≡-), and hydrophilic silanes groups (≡Si - OH), with high affinity for polar media [14]. The structure can be schematized as in **Figure 13**.

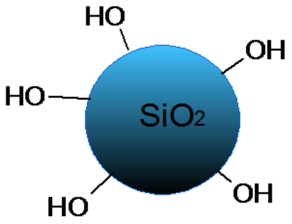


Figure 13. Silica molecular structure.

The main component of silica that is produced industrially is SiO_2 (99.8% purity), notwithstanding that traces of other metals can be found.

Table 2: Composition of pyrogenic Silica[16]

Component	% bby weight
SiO_2	>99,8
Al_2O3	<0,05
Fe_2O3	<0,003
TiO_2	<0,03
Na_2O	<0,0009
Chlorides as Cl	<0,025

The manufacturing process for the pyrogenic silica is based on the hydrolysis of volatile silanes, particularly silicon tetrachloride ($SiCl_4$) in a burner of oxygen – hydrogen flame. In this flame, the following reactions take place [13]:

$$2H_2 + O_2 \longrightarrow 2H_2O \qquad \text{Ec. 1}$$

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl \qquad \text{Ec. 2}$$

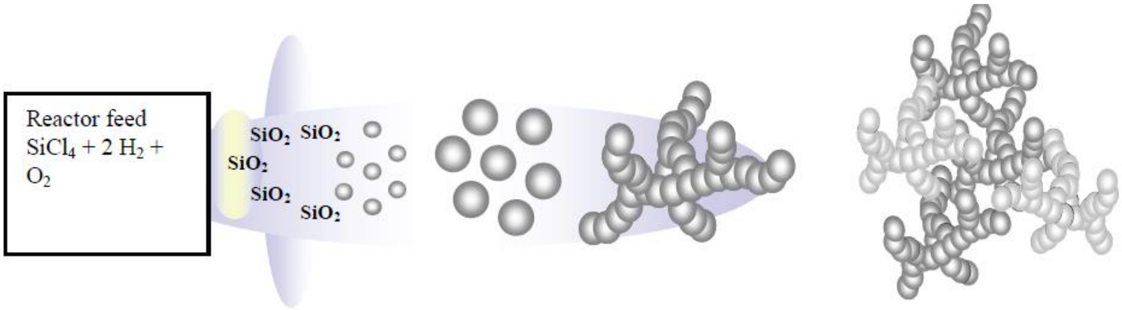


Figure 14. Pyrogenic Silica production.

The characteristics of the produced silica can be controlled by varying the concentration of reactants, flame temperature and residence time in the combustion chamber [4].

Silica dusts are essentially non-toxic by oral ingestion, skin or eyes contact, or inhalation. Epidemiological studies show little evidence of adverse health effects (no personal protection) which can cause mechanical irritation of the eyes and drying/cracking of the skin [14].

I.3.6.3 Advantages of Nanosilica

Experiments that have been performed in the biopolymer industry indicated that the addition of nanoscale silica compounds based on PLA structure improves the thermo-mechanical properties (most stable crystalline structure) by increasing the dispersion of the composite material and the polymer/filler interaction compared to other particle sizes. In addition, it has been detected a certain protective action of the silica in the PLA degradation. The silica particles make a barrier effect to heat transfer and diffusion to the gas phase of the decomposition products [15].

The rol of the nanosilica is to to get specifically localized at the interface within the polymeric matrix and thus the overall material performances [2]

The use of silica in the polymer matrix is based on the high interaction between them, as well as the crystallization rate in the distribution of the polymer and the resulting silica. These factors depend on viscosity, surface active, hardness, and other properties of the silica. At present, in order to improve the compatibility between the polymer matrix and the inorganic silica surface, the chemical modification of this latter has been thoroughly assessed by using organosilane groups (particularly containing epoxy or amino functionalities), because they have adequate affinity to the filler surface [17].

Modification of silica surface with silane coupling agents is a famous tecniche. Silane-coupling agents ($Si(OR)_3R$) are used, with the ability to bond inorganic materials (silica nanoparticles) to organic polymer. Essentially, the $Si(OR)_3$ portion of the silane-coupling agents reacts with the inorganic reinforcement, while the organofunctional group (R) reacts with the polymer.[18]

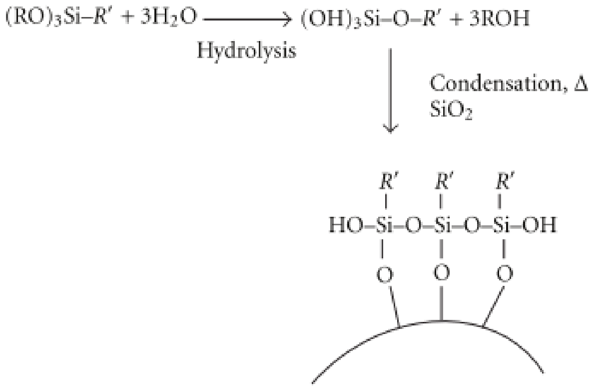


Figure 15. Modification of silica surface with silane coupling agents(aqueous system)[18]

I.3.6.4 Nanosilica modified with epoxy group

Epoxy resins have several unique features such as high adhesive strength, high resistance and hardness. That's why they are widely used in industry, acting as a reinforcement of various polymer matrixes [19].

Recently, a new technology has been developed to improve the mechanical properties of thermoset polymers. The combination of the silica and epoxy properties can exhibit substantial improvements in the fracture toughness of the polymer.

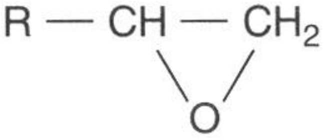


Figure 16. Epoxy group structure.

The compatibility between the modified particles and the polymer matrix could be improved by adding epoxy groups in the silica structure. Thereby, this modification prevents agglomeration of the nanoparticles and leads to a better distribution of silica [19]. The nanosilica modified with epoxy group can react with the epoxy and the hydroxyl group in the REX-PLA matrix.

Previous work showed that the addition of epoxy to the modified nanosilica can improve the heat resistance properties of the resulting material. Indeed, the system crosslinking density increases due to the strong interaction between the nanosilica modified particles with the epoxy and the polymer matrix, causing a better distribution of the components and inhibition of the thermal decomposition of composites [19].

I.3.6.5 Modified Silica with Amino Group

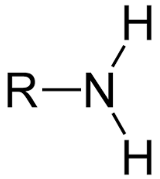


Figure 17. Amino group structure.

The addition of the polar group NH_2 has been studied in order to avoid agglomeration of nanosilica and resulted in a good dispersion of particles in different polymeric matrices. This behavior may be due to the steric effect in comparison with other substituents, which promotes a a good distribution of the nanofiller in the polymer network [20].

The amino group can react with the epoxy and carboxyl group present in the polymer REX-PLA and could improve the interaction between matrix and particles.

I.3.7 CCP - Centre Catalá del Plàstic

This experimental work is done in one of the most renowned research centers in Cataluña, Spain, the "**Centre Catalá del Plàstic** ". Thus it is important to outline a short review of this center.

The Centre Catalá del Plàstic (CCP) is an entity of consortium character composed of the Generalitat of Catalunya, the Ajuntament de Terrassa, the Universitat Politècnica de Catalunya and the most representative industry associations in the plastic sector. Created in 1996, the CCP was founded with the vocation of being a tool for improving business, coordinating its activities around four main objectives: technical training, continuous improvement, dissemination of technological innovation and promoting internationalization of business activity. At present, the CCP has become a recognized center of excellence in plastics, with a team that forms a consolidated group of Research of the Generalitat de Catalunya and belongs to TECNIO.

Research lines developed in the “Centre Catalá del Plàstic”:

- Investigation and development
  - ✓ Reactive Extrusion
  - ✓ New compounds and nanocomposites
  - ✓ Polymer mixtures
  - ✓ Biopolymers
  - ✓ Cellular polymers
  - ✓ Halogen free Fireproofing

- Characterization
  - ✓ Relationship processing / structure / properties
  - ✓ thermal and mechanical behavior
  - ✓ Fracture and advanced techniques of impact
  - ✓ Rheology
  - ✓ Microscopy
  - ✓ Fire behavior

- Technological innovation
  - ✓ Comprehensive design of plastic parts
  - ✓ Injection process window
  - ✓ Multicomponent injection and encapsulation
  - ✓ Foaming
  - ✓ Films and multilayer films

- Recycling
  - ✓ Recyclability
  - ✓ Additivation and composition
  - ✓ Harmonization and plastic waste
  - ✓ New applications

I.4 Background

In this section, previous work related to nanosilica and PLA in recent years will be presented. Characterization testing performed, authors, the goal to be achieved and other relevant aspects will be discussed.

- **"Thermal properties of Poly(Lactic acid) fumed silica nanocomposites. Experiments and molecular dynamic simulation". 2008**
    - ✓ Author: Jian Zhang, Jianzhong Lou.
    - ✓ **North Carolina A&T University. U.S.A**
    - ✓ Fumed silica nanocomposites were prepared by twin-screw extruder
    - ✓ Characterization Test: DSC; TGA; Molecular dynamic simulation.
    - ✓ Conclusion: PLA degradation at temperatures lower than 300°C. The decomposition of chain-ends occurs at temperature beyond 300°C through random scission of chains. Shear viscosity increases when PLA chains approached the surface of the nanoparticle.

- "**Preparation, characterization and biodegradation of biopolymer nanocomposites based on fumed silica**". **2010**
    - ✓ Author: Fukushima, Tabuani, Abbate, Arena, Rizzarelli.
    - ✓ **Politecnico di Torino, Italy**
    - ✓ Nanocomposites were prepared at 5 wt.% filler loading in Rheomix–Brabender (OHG 47055) with a mixing time of 5 min. After manually extraction from the mixing chamber, films were obtained by compression molding the materials in a hot-plate hydraulic press at 120 °C.
    - ✓ Characterization test: DSC (crystallization level); TGA (degradation); SEM (dispersion); DMTA (Temperature dependence in the storage modulus); SEC (chromatographic analysis); FTIR-ATR (analysis of chemical structure).
    - ✓ Conclusion: High surface area. Good dispersion polymer-filler interaction. Improvement of thermomechanical properties. Protection action of silica towards PLA degradation.

- **"PLA nanocomposites: Effect of filler type on non-isothermal crystallization". 2010**
    - ✓ Author: G.Z Papageorgiou, D.S Achilias, S.Nanaki. T. Beslikas.
    - ✓ **University of Thessaloniki. Greece**
    - ✓ PLA nanocomposites (2.5 wt% nanoparticles) were prepared, by solvent evaporation method.

- ✓ Characterization test: DSC; PLM; Morphological examination (EP, TEM).
- ✓ Conclusion: less than 5% of filler amounts result in an effective enhancement of the nanocomposite.

❖ **"Polylactic Acid and PLA-based nanocompisite Photooxidation". 2010**

- ✓ Author: Sergio Bocchini, Kikko Fukushima, Alessandro di Blasio.
- ✓ **Politecnico di Torino. Italy**
- ✓ Nanocomposites were obtained at 5% filler loading by melt blending using a Microextruder DSM Micro 15CC Twin Screw Compounder. Film were prepared from pellets using a hot-plate hydraulic press.
- ✓ Characterization test: WAXS (x-ray); SEM
- ✓ Conclusion: Nanofillers increase the rate of anhydride formation (biodegradation) when environmental biodegrability is desired, by adding nanofiller PLA decomposition could be accelerated.

❖ **"Study of thermal stabilization mechanism of biodegradable Poly(L-Lactide)/silica nanocomposites". 2010**

- ✓ Author: Xin Wen, Kuny U Zahang, Yan Wang, Lijing Han, Changyu Han.
- ✓ **Society of chemical industry**
- ✓ PLA with 1, 3, 5, 7 and 10 wt% of nanosilica was prepared using a Haake batch intensive mixer (Haake Rheomix 600, Karlsruhe, Germany). The two components were mixed at 175°C for 5 min, with a screw speed of 60 rpm.
- ✓ Characterization test: Spectroscopy and Thermogravimetric test.
- ✓ Conclusion: Hydroxyl groups on SiO_2 and PLA chain-ends reacted during the melt processing. Improvement of thermal stability: mobility of active group hydroxyl end-groups.

❖ **"Effect of silica nanoparticles on the mechanical performances of poly(lactic acid)".2012**

- ✓ Author: A. Dorigato, M. Sebastiani
- ✓ **University of Trento, Italy**
- ✓ The nanofillers and the matrix were melt compounded in PolyLab Rheomix R600 internal mixer. The resulting materials were then pressed through a laboratory press
- ✓ Characterization test: DSC; Impact test
- ✓ Conclusion: Tensile strength of PLLA matrix was greatly improved. Extend the apparent linearity limit of the viscoelastic behavior.

- **“Fracture toughness of epoxy polymer modified with nanosilica particles. Particle size effect”. 2012**
  - ✓ Author: Milad Zananion, Mehrzad Motezaei.
  - ✓ **Amirkabir University. Iran**
  - ✓ Epoxy resin was dissolved in acetone. After full dissolution, different nanosilica contents (wt.%), were added into epoxy solution and then were dispersed through mixing and ultrasonication.
  - ✓ Conclusion: Microstructure suitable dispersion. Glass transition unchanged. By adding more silica the tensile modulus increases but at high contents the formation of agglomerates is promoted. Increase of fracture toughness until a volume specific fraction and with the decrease of particles size. More plastic deformation resistance.

- **“Effect of organosilane coupling agent on microstructure and properties of nanosilica/epoxy composites”. 2012**
  - ✓ Author: Zh-Qiang Yu, Shu-Li You, Horst Baier.
  - ✓ **Fundan University. China**
  - ✓ Surface silica modification: 5 g silane (coupling agent) were added in aqueous ethanol solution prepared according to a volume ratio (1: 9 ethanol/water). The solution was stirred for 5 minutes, the dry nanosilica (50g) was dispersed in the solution with a mechanical stirrer under nitrogen, and in a ultrasound bath.
  - ✓ Epoxy matrix nanocomposites with 4 wt% nanosilica mass fractions were obtained by blending using a ‘‘high shear’’ laboratory-mixing device.
  - ✓ Conclusion: All the obtained systems have high dispersion and inhibition of thermal decomposition. Reaction with resin matrix during curing process. Strong interaction functional epoxy group.

- **“Synthesis and characterization of PLA nanocomposites containing nanosilica modified with different organosilanes”.2012**
  - ✓ Author: Luca Basilissi, Giuseppe Di Silvestro, Hermes Farina.
  - ✓ **Università Degli studi di Milano. Italy**
  - ✓ Polylactide nanocomposites were prepared by employing bulk ring opening polymerization from lactide.
  - ✓ Organosilanes containing amino and epoxy groups.
  - ✓ Characterization tests: Rheological properties, thermal properties (crystallinity).
  - ✓ Conclusion: Pure silica tends to decrease the molecular weight but when silanes are present on surface the molecular weight are similar to industrial PLA. Silanes improve dispersion of material. Melt viscosity increases at zero shear and decreases when shear rate increases.

- ❖ **“Preparation and properties of melt-blended Polylactic Acid/Polyethylene glycol-modified silica nanocomposites”. 2012**
  - ✓ Author: Sun-Mou Lai, Jhong-Ren Chen, Jin-Lin Han.
  - ✓ **I-Lan University. China**
  - ✓ PLA and the modified silica [1, 4, 10 phr (parts per 100 resins)] were mixed using an internal mixer (Brabender). Then was obtained the film with hot-pressed procedure.
  - ✓ Silica with methoxy polyethylene glycol.
  - ✓ Characterization test: FTIR; TEM; TGA; Tensile strength, elongation at break and young’s modulus; Optical transmittance.
  - ✓ Conclusion: increase of thermal stabilization, no significant variation of glass transition temperature. Young’s modulus for modified silica decreases until some value. Elongation break of modified higher than unmodified silica.

- ❖ **“Synthesis of silica nanoparticles by sol-gel: size dependence particle, surface modification and application in silica-polymer nanocomposites”. 2012**
  - ✓ Author: Ismoil Ab Rahman.
  - ✓ **University Sains. Malaysia.**
  - ✓ Methods for dispersing nanosilica: Solution mixing; in-situ polymerization (higher dispersion); melt mixing process (most favorable technique).
  - ✓ Epoxy (10-20 nm): decreases glass transition temperature and increases thermal stability.
  - ✓ Conclusion: the particle size increases with increasing the ammonia concentration. The amount of atoms residing on the surface increases with the decrease of the particle size. Epoxy silanes were more effective in dispersing silica as compared to amino silanes.

- ❖ **“Aluminated mesoporous silica as novel high-effective flame retardant in polylactide”. 2013**
  - ✓ Author: Yon Qian, Ping Wei.
  - ✓ **Shanghai Jiao Tong University. China**
  - ✓ The PLA nanocompisites were prepared in a HAAKE Rheocord 90 internal mixer.
  - ✓ Characterization test: XRD; SEM; FT-IR.
  - ✓ Conclusion: Limiting Oxygen Index of Polylactide composite increases. Decrease of heat peak in the polymer. Less volatile products. Improved hydrolysis resistance and tensile properties

- **“Thermal and mechanical properties of biodegradable polyester/silica nanocomposites”. 2013**
  - ✓ Author: Rattikorn, Sommai Pivsa-Art, Hamada Hiriyuki.
  - ✓ **Silpkorn University, Rajamangala University (Thailand) Kyoto Institute of Technology (Japan)**
  - ✓ PLA, PBS and PHBV with fumed silica nanocomposites were prepared by twin screw extrusion.
  - ✓ Characterization test: TGA; HDT testing; Tensile and impact testing.
  - ✓ Conclusion: At high silica concentration, the elongation break decreases: polar groups on the surface of silica tend to agglomerate.

- ❖ **“Synergistic effect of fumed silica with Ni_2O_3 on improving flame retardancy of Poly(Lactic acid)”. 2014**
  - ✓ Author: Jiang Gong, Nana Tian, Xin Wen.
  - ✓ **University of Chinese Academy of sciences. China**
  - ✓ PLA composites were prepared by mixing PLA pellets with SiO_2 and/or Ni_2O3 in a Brabender mixer.
  - ✓ Conclusion: Silica forms a protective layer acting as a heat insulator and barrier for degradation products. The interaction between two fillers inhibits re-aggregation of the dispersed fillers preventing diffusion of O_2 and reduction of the release of flammable degradation product.

- ❖ **“Sheets of branched poly(lactic acid) obtained by one-step reactive extrusion–calendering process: physical aging and fracture behavior”. 2014**
  - ✓ Author: J. Cailloux, O. O. Santana, E. Franco-Urquiza, J. J. Bou, F. Carrasco, M. Ll. Maspoch.
  - ✓ **Centre Català del Plàstic (CCP), Universitat Politècnica de Catalunya (UPC).**
  - ✓ Linear poly(D,L-Lactide) acid (Ingeo 4032D) modification were induced by a one-step reactive extrusion–calendering process using Joncryl. For such REX-PLA the rate of physical aging at 30 °C was investigated during 1 week in order to simulate industrial storage conditions.
  - ✓ Tensile test and fracture behavior of ‘‘de-aged’’ and ‘‘controlled aged’’ (1 week); DSC; SEM.
  - ✓ Conclusion: Decrease in the crystallization ability for REX-PLA. A higher entanglement network density is therefore a good way to reduce the ability of reorganization toward a more ordered conformational state of the amorphous PD,L-LA biopolymer over time. Aged REX samples subjected to uniaxial loading presented a slight increase in the strain at

break. In REX-PLA samples, crack propagation process was the result of the craze–crack transition phenomenon.

II. EXPERIMENTAL CHAPTER

This chapter will describe the **compounds used**, giving the information provided by the supplier and some properties of interest. On the other hand, the **experimental procedure** developed as well as the amounts of product obtained in each step will be presented. The experimental steps are listed as follows:

- Conditioning of the raw material
- Preparation of REX -PLA nanocomposites
- Characterization step: instruments for the analysis of the materials used in the preparation step will be described, as well as those used in order to compare the materials produced during the experimental activity.

II.1 Raw Material description

II.1.1 Base Material: PLA 4032D

Polylactic acid pellets (PLA) (Ingeo 4032D) were supplied by Arendonk, Belgium as pellets. The PLA grade is that of a semicrystalline material containing 2% of D-lactic acid enantiomers with a melting point in between 155-170°C, its average molecular weight is 180,000 g/mol [21]. Before processing, pellets must be dried at 80°C for 4 hours. The basic structure of the PLA is shown in **Figure 18.**

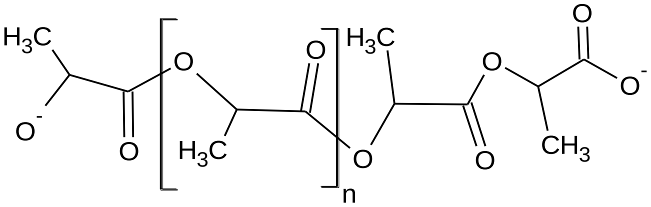


Figure 18. Basic structure of PLA.

II.1.2 Chain extender (Joncryl)

As a chain extender, a multifunctional oligomer of styrene - acrylic - epoxy, also called Joncryl (ADR- 4300F) was supplied by BASF in form of flakes (2.5 - 4.0 mm); its melting temperature is 56°C. To avoid agglomeration in the extrusion process the temperature of the feeding zone must be below 80°C, with a range recommended between 20 and 40°C; the rest of the areas can be changed according to the treated plastic [22].

The reactive extrusion with Joncryl significantly increases the polymer molecular weight (henece an increase in viscosity). Thus, an increase in pressure registered on the machine is observed, ranging from 25 to 100% as a function of the amount of oligomer used [22]. Its structure can be seen in pargraph **5.1.1** of the framework in the introductory chapter of this work.

The Joncryl 4300 -F is approved for contact with food according to European standards and for being provided in solid form of flakes; it is also easy to handle.

II.1.3 Nanosilica: Cab-O-Sil

The amorphous-synthetic nanosilica (Cab-O-Sil EH5) was supplied by CABOT in powder form. It is produced by pyrogenic route, with a surface area of 380 m^2/g, a primary particle size of 0.007 μm. It is dispersible in organic solvents and has a percentage by weight of silanes (SiO_2)>98% [16]. The structure of this type of silica is schematized in section **I-7.1** "**Preparation of Nanocomposites of PLA**" in the introductory chapter.

II.1.4 Nanosilica modified with amino groups

This type of nanosilica (SiO_2 6851HN) has been undergone to a surface modification with amino groups, and was supplied by Skyspring Nanomaterials, Inc. in powder form. It is dispersible in organic solvents (toluene, chloroform, etc.), as well as in polymers bearing reactive epoxy and carboxyl groups. In addition, it has a percentage of silanes (SiO_2) greater than 99.8 % (950°C, 2h) , a particle size of 10-20 nm and a surface area of 90-130 m^2/g [23]

Its structure is simplified in **Figure 19.**

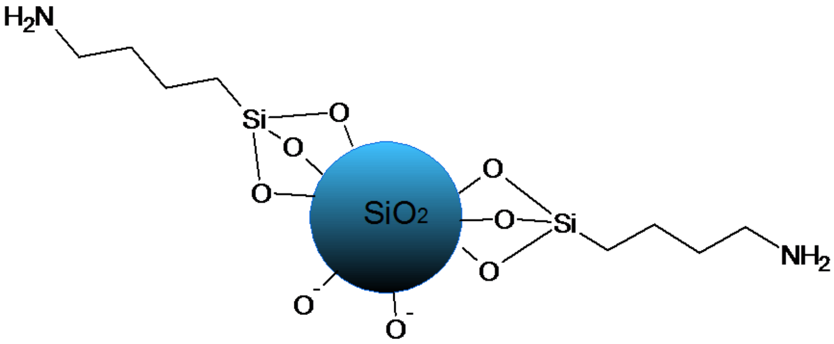


Figure 19. Basic structure of modified Silica with amino group.

II.1.5 Nanosilica modified with epoxy groups

Nanosilica surface-modified with epoxy group (SiO_2) was supplied by Skyspring Nanomaterials Inc. in powder form. It is dispersible in organic solvents such as toluene and chloroform. It can be reacted with epoxy, amino, carboxyl and hydroxyl groups for the production of nanocomposite polymers. The content of silanes (SiO_2) is greater than 99.8 % (950°C, 2h); it has a particle size of 10-20 nm and surface area of 90-130 m^2/g. [23]

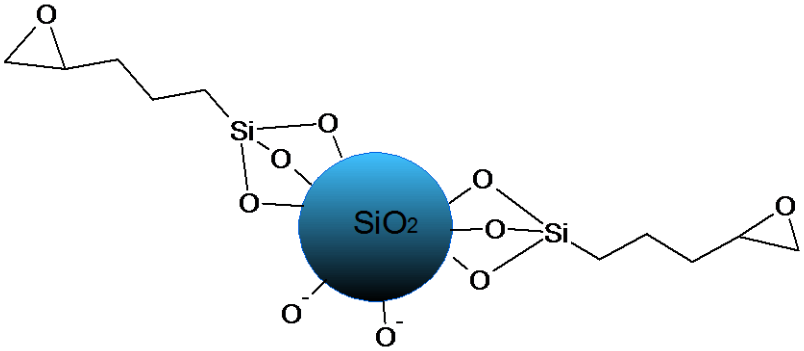


Figure 20. Basic structure of modified Silica with epoxy group.

II.2 Experimental procedure

The experimental step mainly consists of three phases:

II.2.1 Conditioning of the raw material: First reactive extrusion of PLA with Joncryl (REX-PLA), which is obtained in the form of pellets, and encapsulation of nanocomposites in the PLA matrix (masterbatches).

II.2.2 Preparation of nanocomposites REX-PLA: Reactive Extrusion REX - PLA with each masterbatch is obtained. This phase consists of two subphases: the obtainment of pellets (first and second extrusion) and then, the homogenization and preparation of polymer films (third extrusion).

II.2.3 Phase characterization of the obtained films.

A detailed description of these steps is reported as follows:

II.2.1 Conditioning of the raw material

The objective of this phase is to prepare the compound **REX-PLA**, as well as of a concentrate of nanofiller material encapsulated in the PLA matrix, hereinafter called **masterbatch**, referring to the polymer with a high concentration of nanoparticles. This masterbatch is designed to make the nanoparticle suitable for the reactive extrusion process with REX-PLA. This stage is considered very important as a good preparation of the raw material guarantees reliable results; the following characteristics have to be fulfilled: clean work site and organization in the work area, properly clean instruments, correct use of instrumentation, and respect of safety rules in the laboratory.

II-2.1.1 Preparation of REX -PLA

The first step is to grind the JONCRYL: to this aim, a coffee grinder (FIORENZATO F 5G/A) was used. Once grinded, we proceeded to the homogenization of particle size, using a metal kitchen filter/strainer as sieve.

For obtaining REX–PLA, reactive extrusion of PLA with JONCRYL chain extender (crushed and sieved) was perfomed. A twin-screw extruder "COLLIN Kneter 25x24 D " was used for this purpose. Before extrusion, the PLA must be dried at 80°C for 4 hours in the PIOVAN (DSN506HE, Venice, Italy) (dew point= -40°C) due to its tendency to hydrolyze. The Joncryl must be stored under vacuum in a laboratory vacuum desiccator to prevent moisture contact. Then the production process is illustrated as follows:

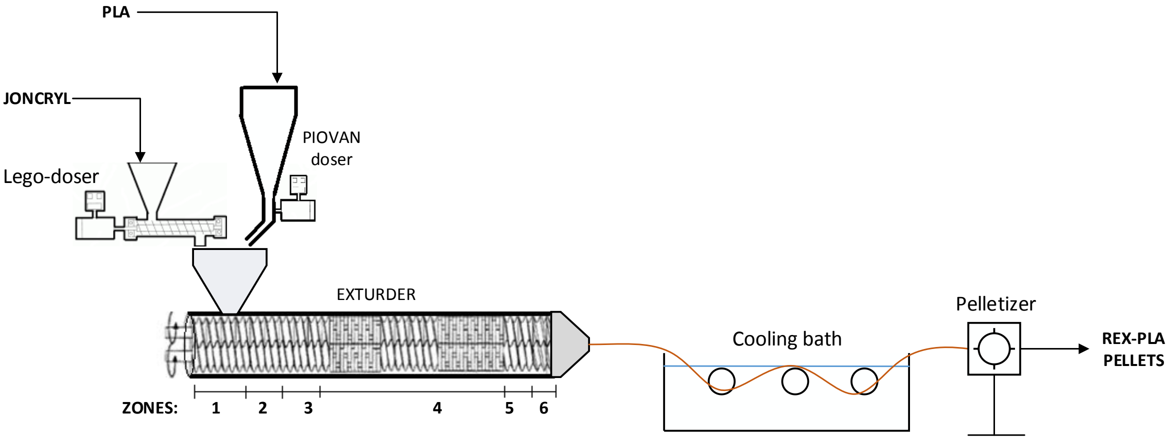


Figure 21. REX-PLA production scheme.

It is important to mention that the percentage of Joncryl should be 1% in the polymer, as previous studies have shown a high degree of branching and cross-linking when that percentage was exceeded; as a consequence, this may cause further degradation of the material during its processing [10].

For the dosage of **JONCRYL (0.5-0.6 g/min)**, a Lego-doser was used. This instrument was designed especially for this process, as it allows obtaining a sufficiently low mass flow consistent with the recommended percentage. Furthermore, the **PLA** feeding is performed at 420 RPM in a PIOVAN dispenser. This equals to a mass flow of **44.6 g/min** according to the calibration curve made (**Figure 22**). These dosage values were set to obtain a percentage of Joncryl close to 1%, taking into account losses in Lego-doser, as well as the subsequent introduction of PLA, with the nanosilica encapsulated, which can further react with the remaining Joncryl.

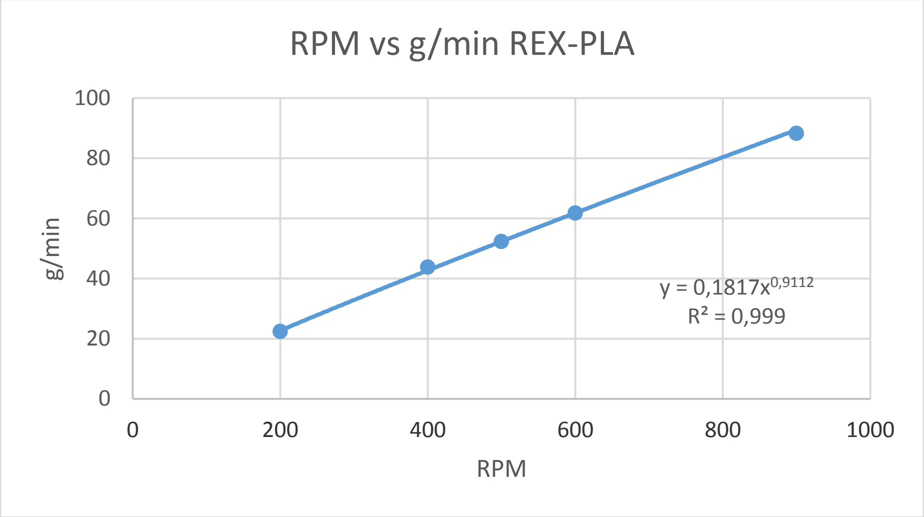


Figure 22. Calibration curve of PIOVAN dosification.

With respect to extruder conditions, 35 RPM were selected for rotating the screws. At the feeding zone, a constant flow of nitrogen was applied at 2.5 bar, in order to avoid the presence of moisture in the process and thus PLA degradation. During extrusion, an inert tracer was introduced to measure the approximate time in which the faster component leaves the reactor, which was 4 min. The temperature profile for each zone is schematized as follows:

Table 3: Extruder zones. Production of REX-PLA.

Zone	**Funtion**	**Temperature (°C)**
1	Feed under N_2	45
2	Melting	165
3	Ventilation (remove volatile compounds)	165
4	Mixing	170
5	Vacuum applied (remove volatile compound)	180
6	Overcoming the die pressure of the Outlet	190

The extruded polymer was immediately cooled in a water bath at room temperature (≈25 ° C) and REX–PLA pellets were produced. 48 kg of REX-PLA were produced in this experimental stage after 5 days of extrusion (about 10 kg/day), suitable for all the subsequent experimental activity.

All the material obtained (pellets) was subjected to a thermal treatment for 4 hours at 90 ° C in DRY-BIG oven, manually stirring every 30 minutes.

II-2.1.2 First encapsulation of nanofiller in PLA

For the production of nanocomposites at laboratory scale, the so-called **Dispersion in solution** technique has been exploited. It involves the use of a solvent compatible with the polymer and the nanocomposite has been mechanically stirred [24]. Then, for better dispersion, ultrasound was applied to the resulting solution. Subsequently, the solvent was removed by evaporation. This encapsulation technique was applied in order to obtain nanosilica masterbatches suitable for extrusion with the prepared REX-PLA.

In order to obtain an approximate 30% of nanofiller in the polymer matrix of PLA, in the first encapsulation, the following amounts of material were used for each batch:

Table 4: Raw material quantities in the first nanofiller encapsulation.

Material	Quantity
PLA	25 ± 0,01 g
Chloroform	500 ± 10 mL
Nanofiller	10,7 ± 0,01 g

Three different batches were prepared with different nanoparticles: unmodified nanosilica, nanosilica modified with amino groups and nanosilica modified with epoxy groups. For this purpose, the following procedure was followed.

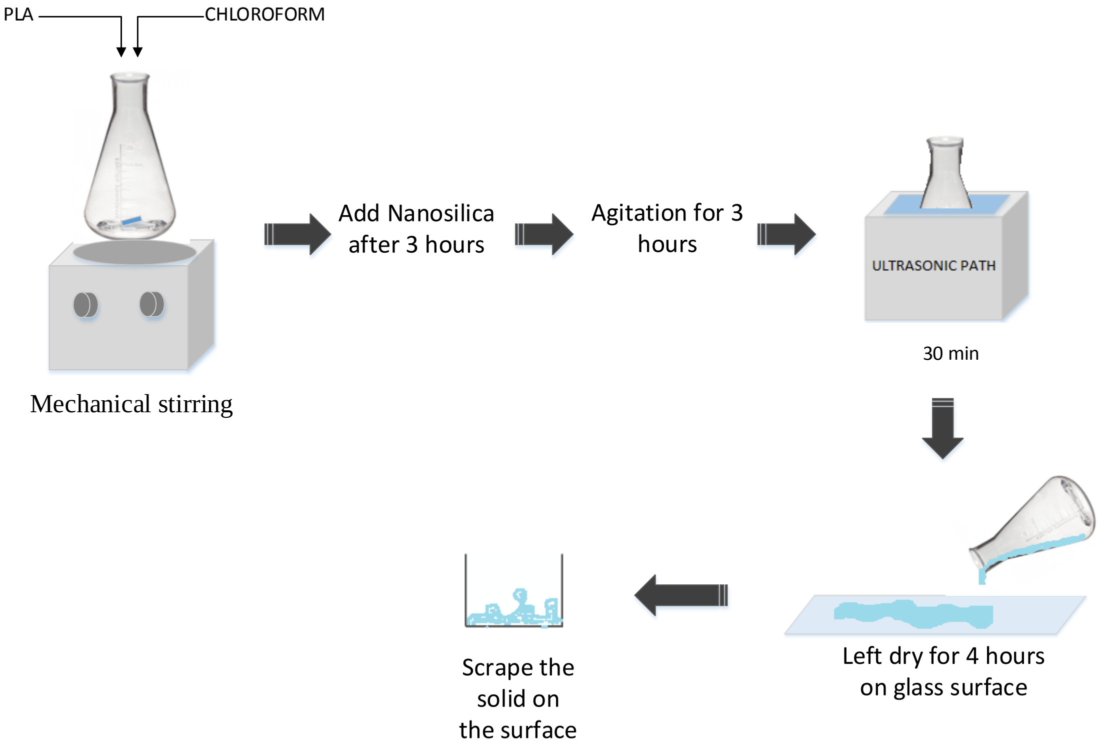


Figure 23. Scheme of nanosilica encapsulation.

By repeating this procedure several times, amounts nearby 200g were reached for each nanofiller. Then each batch was crystallized at 100 ° C for 2 hours in the oven (DRY-BIG 2003740) to facilitate the subsequent grinding. A Crusher kitchen was used for this purpose. The grain size was then homogenized with a metal kitchen Filter resulting in the production of the following amounts, taking into account lost due to human error and efficiency of the instruments used.

Table 5: Quantity of each masterbatch obtained. First encapsulation.

Masterbatch	Mass (± 0,01 g)
PLA/SiO_2	183
PLA/Am.SiO_2	211,4
PLA/Ep.SiO_2	190,3

Then, thermogravimetric analysis (TGA) was performed in order to verify the correct encapsulation because it is not a standardized procedure: the operational method is detailed in **Technical analysis** chapter. For each material, 10 g of sample were taken and temperature gradually was increased from 30 to 1000 ° C at 10 °C/min. The portion of the inorganic part was thus obtained and the the organic percentage (loss on drying) present in nanosilica was added (provided by the supplier) (**Table 6**).

Table 6: Nanosilica Percentage in PLA in first encapsulation.

	%Inorganic	% Organic	**% Final Nanosilica**
PLA/SiO_2	27,97	2,5	28,67
PLA/Am.SiO_2	26,2	10	28,82
PLA/Ep.SiO_2	25,1	12	28,11

II.2.2 Preparation of REX-PLA nanocomposites

At this stage, the reactive extrusion of REX-PLA with each prepared masterbatch was carried out. Prior to extrusion, the masterbatch of nanosilica with PLA grinded were dried at 90 ° C for 4 hours in a laboratory vacuum desiccator. Similarly, REX-PLA produced above was placed in PIOVAN 80 ° C for 4 hours in order to eliminate possible moisture during extrusion.

II.2.2.1 Pellets preparation

II.2.2.1.1 First extrusion

Before proceeding with the extrusion, rheology tests were performed on a Brabender Plasti- Corder internal mixer, whose operation will be explained in **Technical analysis** chapter**.** This was done in order to observe the behavior of the torque as a function of time at a given temperature and check whether they are suitable for extrusion. The conditions for this test are as follows: Total mass of 40g with approximately 2,4% of nanosilica, temperature of 200°C for 30 min and 50 RPM applied. All the results showed stability below 20 Nm and therefore the masterbatches were found to be suitable for extrusion based on other experiments done in the research center CCP, this can be seen in **Figure 24**. This result give us an idea of how much has to be the RPM of the shafts in the extruder.

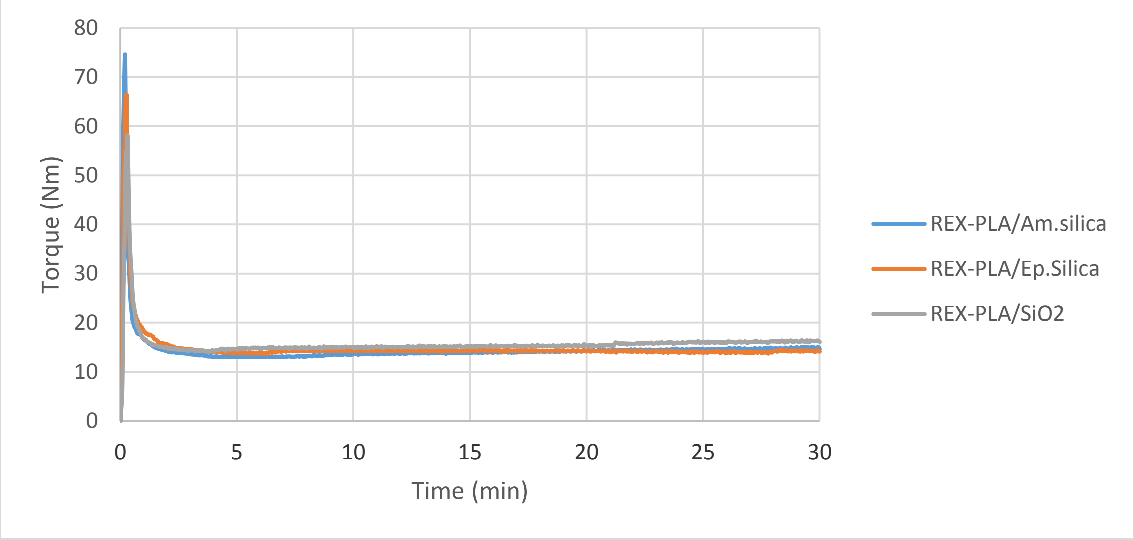


Figure 24. Torque versus time of each REX-PLA/Nanosilica mixure.

Then, the extrusion was performed in a twin screw extruder COLLIN Kneter 25x24 D. The dosage of the encapsulated nanofiller was held in the twin screw doser (ATB-LOHER FLENDER VDE 0530/84) after calibrating and checking that the lego-doser did not reached the required mass flow. The REX-PLA was dosed with a PIOVAN apparatus (DSN506HE, Venice).

It is noteworthy that the first extrusion of REX-PLA/SiO_2, with a continuous dosage rate of PLA/SiO_2 equal to 17 g/min (lowest speed of the twin-screw doser) and 43 g/min of REX-PLA, brought problems of aggregation of the nanofiller, leading to loose 123 g of masterbatch PLA/SiO_2. As a consequence, the process of encapsulation and extrusion had to be repeated.

Thus, the dosing rate of the nanosilica was reduced, making discontinuous downloads of masterbatch during extrusion, thereby avoiding excessive agglomeration.

Extruding process of each mixture shown below in **Figure 24.**

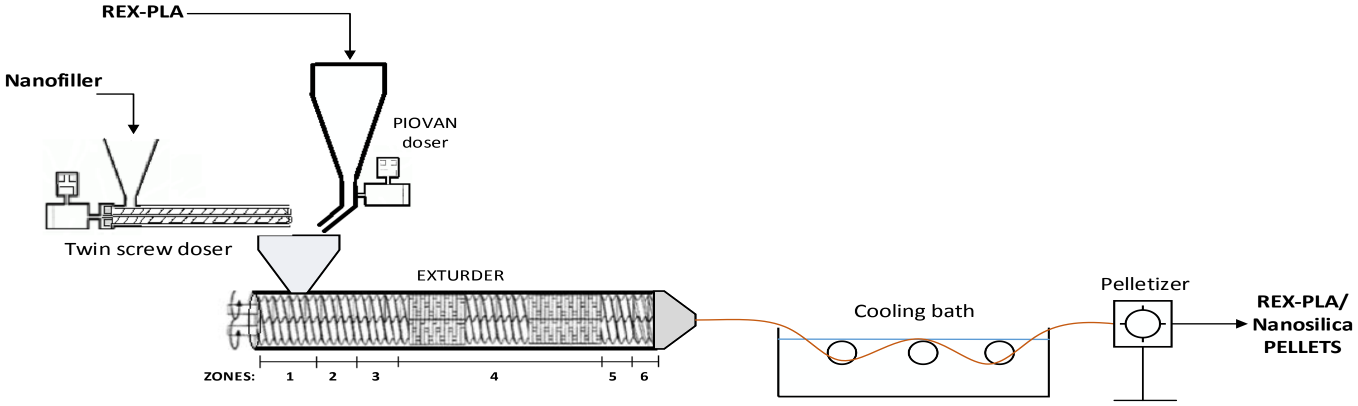


Figure 25. REX-PLA/Nanosilica pellets production scheme.

For this process 45 RPM was set in the extruder, the feed zone worked under 2.5 bar of nitrogen pressure, to avoid moisture in that area and also was connected to a vacuum pump in zone 6 for removing the volatiles formed. The inert tracer was exploited for measuring the residence time of the faster component for leaving the reactor, being in this case approximately 4 minutes 30 seconds. The temperature profile in the extruder is shown in the following table:

Table 7: Extruder zones. Production of REX-PLA/Nanosilica.

Zone	Funtion	Temperature(°C)
1	Feed under N_2	150
2	Melting	170
3	Ventilation (remove volatile compounds)	180
4	Mixing	190
5	Vacuum applied (remove volatile compound)	195
6	Overcoming the die pressure of the Outlet	200

In each case, the dosage of marterbatch with nanofiller was gradually increased as the nanosilica desired in the resulting material percentage is about 2%, this composition was fixed as a tolerable range respect to the limit of 5% for an effective improvement of the properties[12]. In the second case, after validating the correct operation, the amount of REX–PLA was decreased. In **Table 8,** different cases are presented: furthermore, it can be noted that in the column of dosage of nanofiller, which is discontinuous, the discharge time (d) and timeouts for the next supply nanosilica (w) are indicated.

Table 8: REX-PLA and Nanocharge Dosification in the first extrusion.

Material to obtain	**Masterbatch to extrude (**± 0,01 g**)**	**Nanofiller dosing (g/min)**	**REX-PLA dosing (g/min)**
REX-PLA/SiO_2	60	1,8 (t:30s; w:270s)	47 (440 RPM)
REX-PLA/Am.SiO_2	211,4	1,8 (t:30s ; w: 270s)	35 (320 RPM)
REX-PLA/Ep.SiO_2	190,3	2,2 (t:35s ; w:270s)	35 (320 RPM)

At the end of this step we obtained:

Table 9: Amount of Pellets obtained in the first extrusion.

Material	**Time of extrusion (min)**	**Total mass (**± 0,1 g**)**
REX-PLA/SiO_2	35	1862
REX-PLA/Am.SiO_2	130	3256
REX-PLA/Ep.SiO_2	70	2122

The following equation allows calculating the theoretical percentage of nanosilica expected in the material produced.

$$\boldsymbol{theoretical}\,\%\,\boldsymbol{Nanosilica} = \frac{\boldsymbol{Nanosilica\ content * 100}}{\boldsymbol{Total\ mass}}$$

(II.1)

According to the results in **Table 6**, a percentage of approximately 28 % of nanosilica is assumed in the masterbatch, having the following theoretical percentages.

Table 10: Theoretical percentage of Nanosilica in the first extrusion.

Material	**Nanosilica content (28%)**	**Theoretical % Nanosilica content**
REX-PLA/SiO_2	16,8	0,90
REX-PLA/Am.SiO_2	57,1	1,75
REX-PLA/Ep.SiO_2	53,3	2,51

As can be seen, only the nanosilica modified with epoxy groups reached the desired value, so that we proceeded to a further encapsulation and extrusion in order to increase the percentages of nanosilica REX-PLA unmodified and modified with amino groups respectively.

II.2.2.1.2 Second encapsulation of Nanosilica in PLA matrix

It was decided to make a second encapsulation in order to concentrate in nanofiller REX-PLA/SiO_2 and REX-PLA/Am.SiO_2 extruded. PLA masterbatches were prepared with 40% of respective nanocomposite; the suitable amounts are collected in **Table 11.**

Table 11: Raw material quantities in the second nanocharge encapsulation.

Material	**Quantity**
PLA	25 ± 0,01 g
Chloroform	500 ± 10 mL
Nanofiller	16,7 ± 0,01 g

Following the procedure described in **Figure 23**, amounts up to 80 g were reached for each nanofiller. Each batch was also thermally treated at 100 ° C for 2 hours in the oven (DRY- BIG 2003740). Then the grinding was performed with a grinder cooking. The grain size was then homogenized with a metallic cooking filter, providing the amounts listed in **Table 12**.

Table 12: Quantity of each masterbatch obtained. Second encapsulation.

Masterbatch	Mass (± 0,01 g)
PLA/SiO_2	76,2
PLA/Am.SiO_2	76,6

II.2.2.1.3 Second extrusion

Once grinded, the masterbatches of PLA with 40% of nanosilica were dried at 90 ° C for 4 hours in a laboratory vacuum desiccator. The REX-PLA was subjected to 80°C for 4 hours in a PIOVAN apparatus (DSN506HE, Venice, Italy) in order to eliminate possible moisture during extrusion.

The dosage of the encapsulated nanofiller was performed in the twin screw doser (ATB-LOHER FLENDER VDE 0530/84). The REX-PLA was dosed with a PIOVAN (DSN506HE, Venice) apparatus.

In the extruder (twin screw COLLIN Kneter 25x24 D), 45 RPM were set for this process; the feed zone worked under nitrogen atmosphere at 2.5 bar constantly to prevent moisture in that area and a vacuum pump was connected in zone 6 to remove volatile comounds formed. The time took by the inert tracer to leave the extruder was around 4 min and 3 s. The temperature profile in the extruder can be seen in the **Table 8**. In addition, the process performed is schematized in **Figure 25**.

The feed flow conditions in this case are seen below in **Table 13**. The dosage nanofiller, which is discontinuous, the discharge time (d) and timeouts for the next supply nanosilica (w) are presented.

Table 13: REX-PLA and Nanocharge Dosification in the first extrusion.

Material to obtain	Nanocharge masterbatch (± 0,01 g)	Nanocharge dosification (g/min)	REX-PLA dosification (g/min)
REX-PLA/SiO_2	76,2	9,2 (t:35s; w:270s)	32 (320 RPM)
REX-PLA/Am.SiO_2	76,6	9,2 (t:35s ; w: 270s)	32 (320 RPM)

The result of this extrusion is presented in **Table 14**:

Table 14: Material obtained in the second extrusion.

Material	Time of extrusion (min)	Total mass (± 0,1 g)
REX-PLA/SiO_2	16	494
REX-PLA/Am.SiO_2	16	489

Subsequently, the pellets of each material were mixed manually resulting the following theoretical percentages applying equation **(II.2)**:

Table 15: Theoretical percentage of Nanosilica after the second extrusion.

Material	**Nanosilica content (g)**	**Total Masterbatch extruded (g) [± 0,1 g]**	**Theoretical Nanosilica content (%)**
REX-PLA/SiO_2	47,3	2356	2,0
REX-PLA/Am.SiO_2	87,7	3745	2,3

At this stage, also about 600 g of REX-PLA without any nanoparticle were extruded, in order to compare their properties with the nanocomposites, thermal history.

Immediately, the material obtained was recrystallized at 90°C for 5 hours, manually stirring every 30 min, aiming at avoiding unwanted casting before processing by increasing the melting temperature.

II.2.2.2 Homogenization and preparation of the films: Third extrusion

A twin-screw extruder "COLLIN Kneter 25x24 D" with a flat head extrusion adjusted to 0,6-0,7 mm of thickness was used for obtaining polymer films. Before this process, the material was dried at 80°C for 4 hours in a PIOVAN (DSN506HE, Venice) (dew point =-40°C) apparatus. The process is schematized in **Figure 26**.

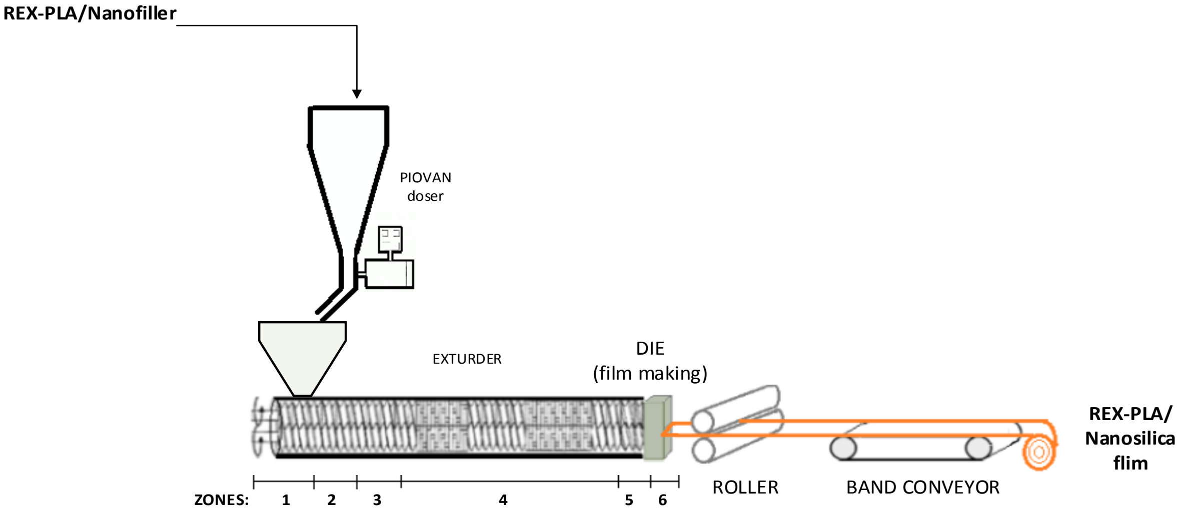


Figure 26. REX-PLA/Nanosilica film production scheme.

After the extruder Rollers (Chill-Roll Collin GMBH CR 72-T) for cooling the material were placed, following was a band conveyor (Brabender Conveyor belt) and all the material was rolled at the end of the line.

The extruder worked with 60 RPM of the screws. In the feed zone a constant flow of nitrogen was applied at 2.5 bar in order to avoid moisture in the process. The temperature profile for each zone is the following:

Table 16: Extruder zones. Films Production of REX-PLA/Nanocharge.

Zone	**Function**	**Temperature (°C)**
1	Feed under N_2	150
2	Melting	170
3	Ventilation (remove volatile compounds)	180
4	Mixing	190
5	Vacuum applied (remove volatile compound)	195
6	Overcoming the die pressure of the Outlet	200

Dosing conditions and film of polymer obtained are listed as follows:

Table 17: Film production results

Film	Pellets Dosing (g/min)	Time of extrusion (min)	Film obtained (m)
REX-PLA/SiO_2	44,6 (420 RPM)	60	31
REX-PLA/Am.SiO_2	44,6 (420 RPM)	90	51
REX-PLA/Ep.SiO_2	44,6 (420 RPM)	40	16
Net REX-PLA	67,4 (660 RPM)	30	7

II.3 Characterization phase

The nanosilica content in each film was assessed at this stage by thermogravimetric analysis (**TGA**). Once completed, it was compared with the theoretical values. In addition, the results of thermogravimetric analysis allowed to get some information about the thermal stability of the REX-PLA matrix, as well as of its nanocomposites.

Then, Differential Scanning Calorimetry (**DSC**) analyses were performed, contributing to complete the information provided by TGA.

Furthermore, the mechanical properties of the materials were evaluated by means of **tensile tests** that allowed assessing the aging effect of the obtained films.

All mentioned analysis techniques will be explained in detail in the next chapter.

III. TECHNICAL ANALYSIS

III.1 ANALYSIS RHEOLOGICAL

Rheology is the branch of physics that studies the deformation and flow of matter under the influence of stress [25]. In the characterization of materials such as polymers, inks, foods and oils is widely applied, since the comprehension of the rheological behavior of them is essential for processing information. One of the instruments most used in the characterization of polymers is the torque rheometer (BRABENDER).

Heat and shear stability (BRABENDER)

The torque rheometer is one of the most complete and used in the characterization of polymeric materials and instruments. It allows knowing, with anticipation, the behavior of the polymers in such processing equipment as an extruder or injection molding machine. This makes it an ideal instrument to research, development, quality control, fault detection and formulation process.[26] In figure 27, a picture of BRABENDER Plasti-Lab-Station Corder® used is depicted.

Figure 27. BRABENDER Plasti-Lab-Station Corder.

The torque rheometer is basically a batch mixer that measures the twisting force required to rotate the blades located within the enclosure, indicated in **Figure 27** with molten material, at a speed and temperature fixed. The material resistance to shearing action produces the torque.

The speed, temperature and time parameters of the test are fixed by a graphical interface on the computer, which also collects the resulting data from the experiment. A typical graph is shown in **Figure 28**:

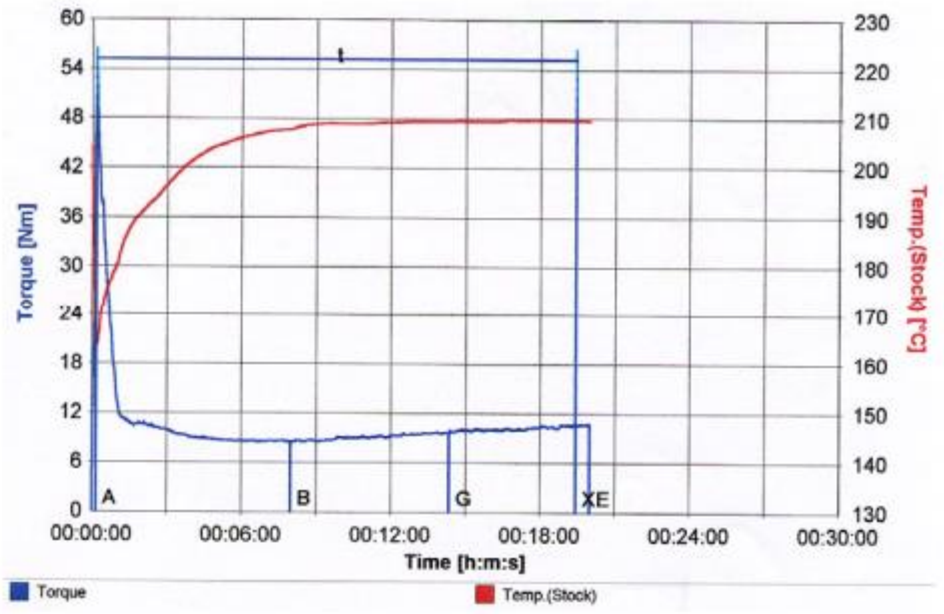


Figure 28. BRABENDER plot of torque vs. time.

The maximum torque in the curve (point A) represents the loading time of the mixer, the curve is decreasing as the crystalline material is melted. The smaller peaks (zone A-B) arising during the melting process of the crystals, that remain unmelted in the batch, are observed about one minute after the mixing starts. For reactions of generated compounds, the torque trend changes. When the viscosity of the mixture increases, the torque will rise accordingly. If degradation of the material takes place, it will be reflected as a drop in the torque due to the decrease of the material viscosity. During this process, the melting temperature increases to a constant value.

When the torque and temperature of the mixture is stabilized, it means that the balance has been reached.

III.2 THERMAL ANALYSIS

In this type of analysis, the physical or chemical properties are recorded versus time or temperature under a controlled heating rate and a specified atmosphere. Among these, it is worthy to mention Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA), Differential thermal analysis (DTA), Thermo-mechanical Analysis (TMA) and others. In particular, the first two thermal techniques have been exploited in this work.

III.2.1 Thermogravimetric analysis (TGA)

In the thermogravimetric analysis, the weight loss of the sample is registered while the temperature is controllably increasing under a specific selected atmosphere, thus obtaining the so-called thermograms. The atmosphere is maintained by a predetermined flow rate of gases such as nitrogen or air. [27]

One of the main function of this type of test is to determine the percentage of inorganic material, as well as to evaluate its degradability during the process. Centro Catalan del Plastico has a TGA/DSC 1 STAR System, which can give information about the transitional phenomena of the material, but without a sufficient precision.

The used equipment consists of five main parts:

1. An electronic microbalance and its control equipment.

2. An oven and temperature sensors near the sample.

3. A temperature control system.

4. An atmosphere control system (gas type and flow)

5. Device for storing weight data and fundamentally T.

These parts are illustrated in **Figure 29.**

Figure 29. Parts of a TGA equipment.

III.2.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is a very powerful tool in terms of polymers characterization. It is very useful in quality control, materials selection process and adequate to behavior prediction. Also, it gives information about such phenomena as glass transition, cold crystallization, melting and non-isothermal crystallization from melting state, as well as degree of crystallinity and structural relaxations taking place in the material. The main advantages of calorimetry are the speed and automation that allow an accurate control of the thermal history by heating programmed cycles.

The operation of the DSC is based on the phenomenon of compensation ("temperature compensation"). It has an oven (**Figure 32**) where two crucibles are placed, one containing the sample to be evaluated and the other the reference material whose phase transition temperature and heats of fusion are known (Indium or lead). During each thermal cycle, a delta of temperature between individual crucibles is registered by thermocouples. To evaluate the transition of heat decomposition, a linear variation of the temperature is required. Using a computerized data acquisition and processing, it is possible to obtain the following heat flow chart at constant pressure (dH/dt) vs. temperature called thermogram (**Figure 32)**. This corresponds to a heating cycle.

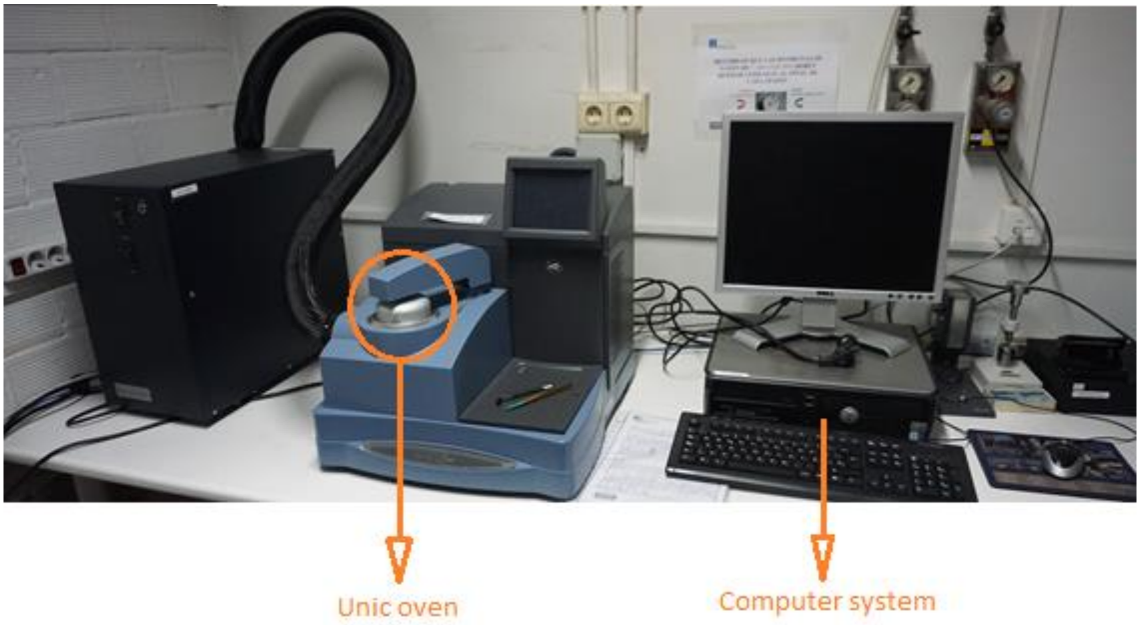


Figure 30. DSC Q2000.

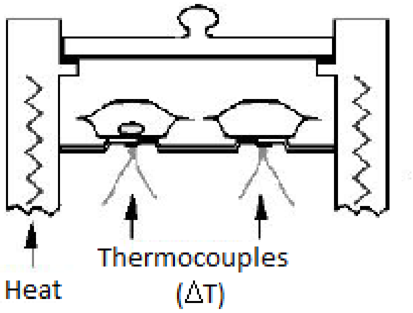


Figure 31. Scheme of DSC by temperature compensation.

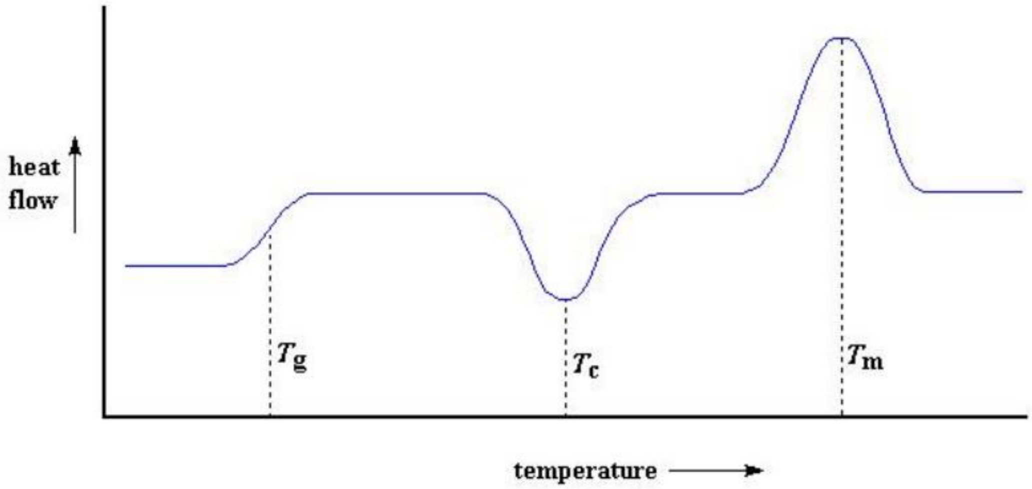


Figure 32. Thermogram from DSC result.

In the thermogram, we can observe the glass transition (Tg), which is indicated by an increase in the heat capacity of the material. The abrupt change of specific heat can be explained more clearly during cooling, during which the macromolecules move so slowly that decrease their mobility and in the glass transition range they do not have the opportunity to significantly rearrange [28]. At this point, below the glass transition temperature range, the characteristic times of motion of the macromolecules become so slow for practical purposes that the material is considered glassy.

In the heating process, beyond Tg, the macromolecules acquire a great mobility; as a consequence, the chain diffusion takes place and the formation of crystalline structures that are more thermodynamically stable than the amorphous material is observed: this process is called "cold crystallization ". Consequently, an endothermic peak is observed, in which the melting of crystals already present in the polymer and of those formed in the cold crystallization occurs.

III.3 MECHANICAL ANALYSIS

The experimental characterization of the mechanical properties is extremely useful for the evaluation of improvements of a given material. More specifically, properties are determined in the laboratory and real performance of the material is analyzed for different types of stresses. One of the most applied tests for the characterization of polymer films is the **tensile test**.

III.1.4 Standard Mechanical Characterization (Tensile test)

The tensile test is a low speed mechanical test perfomed for obtaining the stress-strain curve until the maximum load is achieved. This test gives a number of parameters that define the behavior of the material under tensile stresses; a valuable information regarding the strength and elongation of the polymer can be obtained.

The experiment is performed in a testing machine with uniaxial stress at constant speed and uniform initial tension along the whole section of the sample distribution. It has a control computer (software) and data recording. For measuring the deformation of the specimen, it has a video-extensometer.

Figure 33. Tensile test equipment.

To carry out this test, a specimen with a geometry and size according to ASTM D638 is needed; depending on the thickness of the film a specific section has to be applied (Type I, II, III, IV and V). An example is shown in **Figure 34**. The dimensions indicated in Figure change according to specific standard.

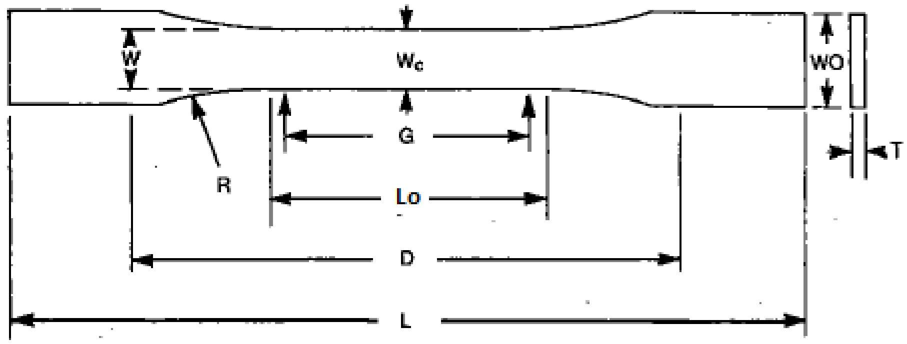


Figure 34. Tensile test sample.

The output of this test is shown in **Figure 35.**

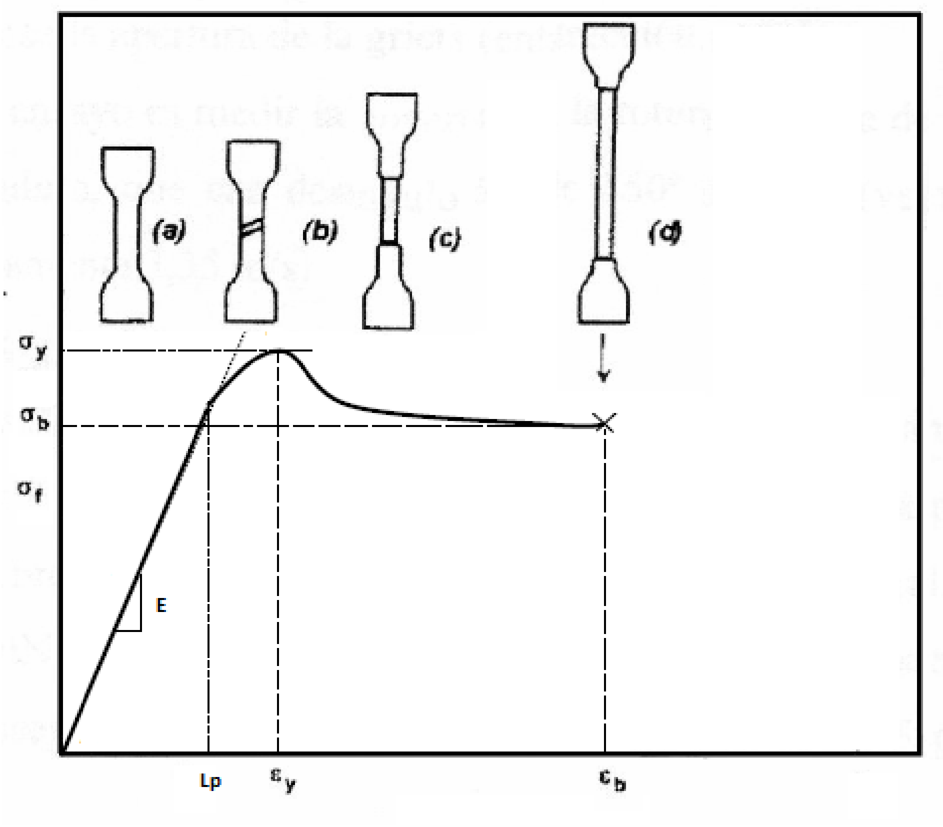


Figure 35. Tensile test result example.

The parameters of interest are listed as follows:

- Elastic or Young's Modulus: It is the relation between mechanical stress and strain suffered by the material. This coefficient characterizes the polymer stiffness, i.e. the resistance to deformation when is subjected to stresses. The strain of the material is proportional to the force applied until the limit of elasticity (Hooke's law), the value of the initial linear slope of this area is known as Young's Modulus [29]

$$\boldsymbol{E} = \frac{\Delta\sigma}{\Delta\varepsilon} \qquad (\boldsymbol{III.1})$$

In which,
E: Young's modulus [N/m^2]
σ: Engineering stress (Force/transverse area) [N/m^2]
ε: Engineering Strain of the specimen (L/Lo*100)

- Stress at yield (σy): It is the stress measured at the yield point that is located after the limit of proportionality (Lp) and is related to the maximum tensile stress that a material can withstand before its deformation becomes irreversible (plastic deformation). [30]

$$\boldsymbol{\sigma y = \frac{Fy}{So}} \qquad (\boldsymbol{III.2})$$

where:
σy: Yield stress [N/m^2]
Fy is the load associated with the stress [N].
So is the initial cross-section of the specimen [m^2].

- Strain at Yield Point (ε_y): it represents the corresponding elongation at yield.

$$\boldsymbol{\varepsilon y = \frac{Lr-Lo}{Lo} * 100} \qquad (\mathbf{III.3})$$

where:
εy: Yield strain (%)
Lr is length measured at the point [cm].
L_0 is the initial distance [cm].

- Strain at break (ε_b): it is the corresponding elongation at break.

$$\boldsymbol{\varepsilon b = \frac{Lr-Lo}{Lo} * 100} \qquad (\mathbf{III.4})$$

- Tensile Strength at Break (σ_b): Stress, at which fracture occurs.

$$\boldsymbol{\sigma b = \frac{Fb}{So} * 100} \qquad (\boldsymbol{III.5})$$

When a tough material is considered, a high stress has to be applied in order to break it, whereas a ductile material is one that is deformed considerably without breaking. The trend of the resulting curve can be a method for classifying the materials from a mechanical point of view. **Figure 36** shows the different cases:

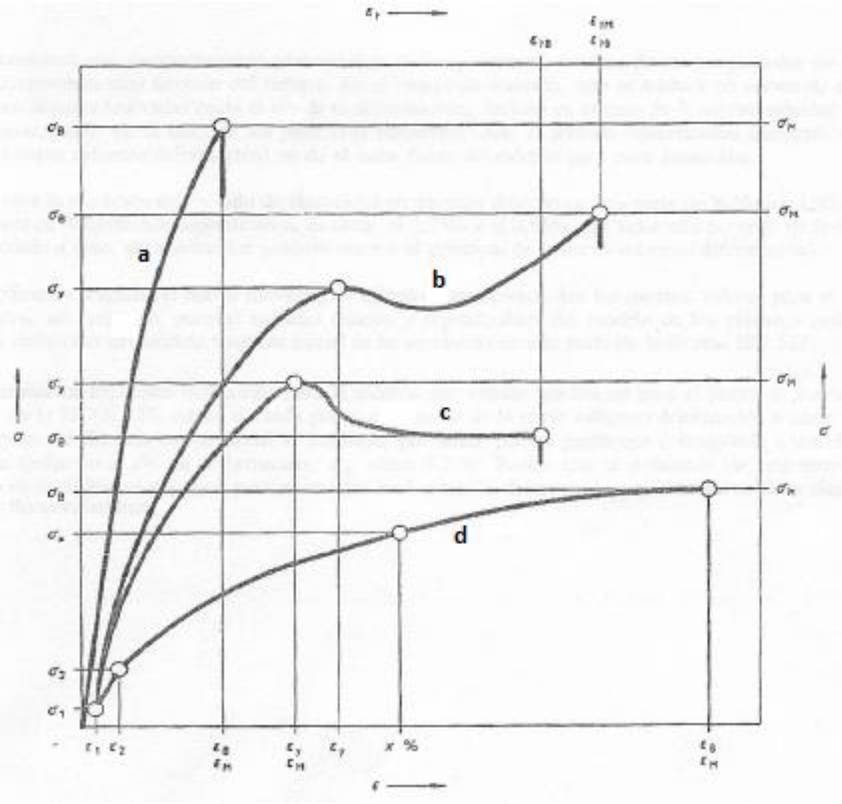


Figure 36. Polymer behavior in tensile tests. [29]

where:

a. refers to tough and brittle materials (polymer glassy state).

b. refers to ductile materials with yield point (tough and ductile semicrystalline polymer).

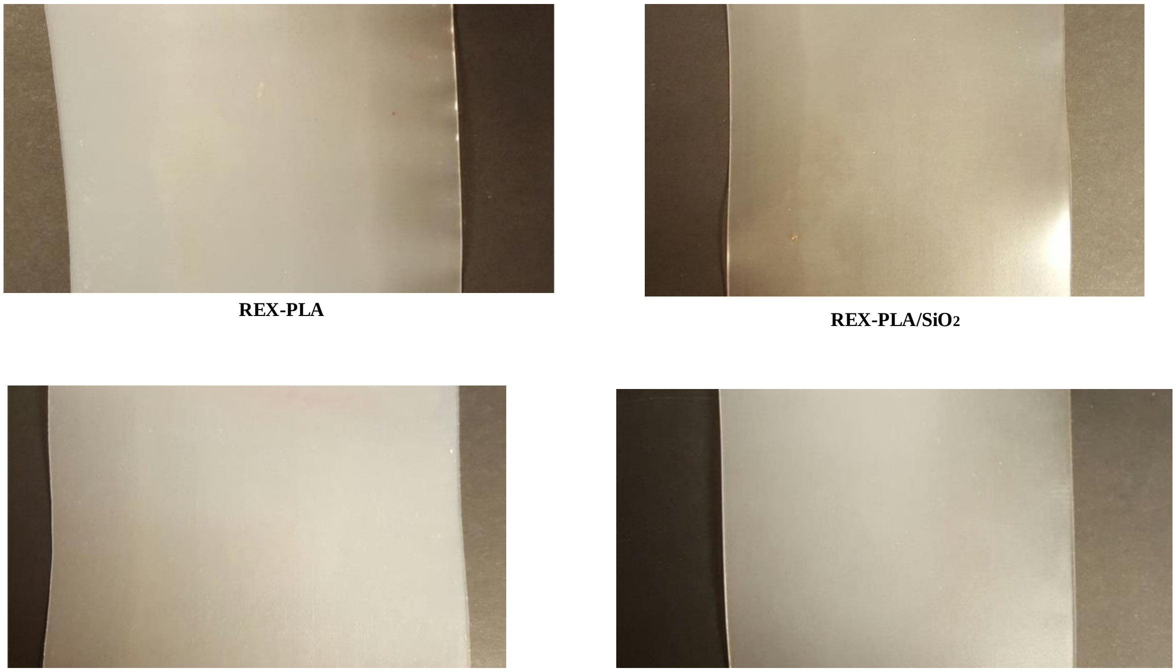
c. refers to ductile materials with yield point (less resistant and ductile).

d. refers to ductile materials without yield point (rubbers).

IV. RESULTS AND DISCUSSION

IV.1 Sensorial inspection

By using the following pictures (**Figure 37**), according to the experimental procedure described below the following conclusions can be summarized:



REX-PLA

REX-PLA/SiO$_2$

REX-PLA/Am.SiO$_2$

REX-PLA/Ep.SiO$_2$

Figure 37. Films obtained.

- The color of the film is very similar, if observed in detail in the REX-PLA/SiO$_2$ agglomeration nuclei are evident.
- All polymers are odorless.
- It can be appreciated differences in texture; REX- PLA/Am.SiO$_2$ and REX-PLA have a smooth surface; the REX-PLA/SiO$_2$ and REX-PLA/Ep.SiO$_2$ have a corrugated surface.

- The thickness of each type of polymer produced ranges from 0,06 to 0,07 mm.

- The width of all the films was about 15 cm.

IV.2 Thermal analysis of the films

IV.2.1 Thermogravimetric analysis (TGA)

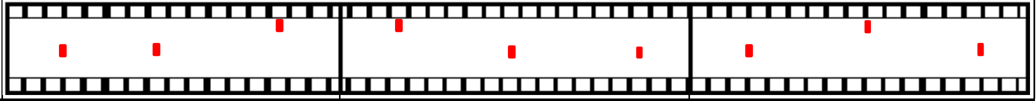
IV.2.1.1 Films Composition

The thermogravimetric analysis was performed with samples of an approximate mass of 10 mg in a TGA 1 STAR System. The temperature was varied from 0 ° C to 1000 ° C at a rate of 10 °C /min under nitrogen atmosphere.

First, the mass fraction of nanofiller on each polymer prepared was determined using the residues at 1000 ° C, which correspond to the inorganic portion in the polymer (nanosilica). To this percentage the organic part of each nanosilica was added (given by the supplier), which was degraded in the test.

In the case of unmodified nanosilica, 9 tests were made in total. Two pairs of 3 performed on each section, 2 correspond to the middle of the film and 1 on the side thereof. Then an average to obtain the final percentage was calculated.

Table 18: Percentage of nanofiller in REX-PLA/SiO_2.

	REX-PLA/SiO2								
	t=0 min; 0 m								t=60min; 30 m
	BEGINNING (start extrusion)			MIDDLE			END (end extrusion)		
Flim from extruder									
Time [min]; Position in film [m]	8 min; 4 m	14 min; 7 m	20 min; 10 m	28 min; 14 m	30 min;15 m	32 min;16 m	42 min;21 m	46 min;23 m	54 min;27 m
% TGA (inorganic part)	2,05	1,44	1,67	1,75	2,38	1,71	1,65	1,83	2,10
%Final (+2,5% : organic part)	2,10	1,48	1,71	1,79	2,44	1,75	1,69	1,88	2,16
Average of each part	1,76			2,00			1,91		
Total Film %	**1,89**								
Standard deviation	0,29								

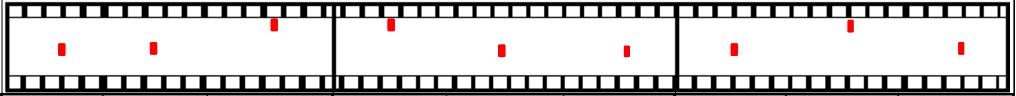
▨ Part excluded of the film

🟥 sample place

The percentage of unmodified nanosilica in the REX-PLA was **1.89 ± 0.29 %**, which is an acceptable result in relation to the theoretical one (2%). As can be seen, there is a slightly higher percentage of nanosilica in the middle of the film. This may be due to the co-rotating sense of the screws in the extruder, where the higher concentration tends to be in the center of the device.

Regarding the nanosilica modified with amino groups, 9 tests were made as well, using the same methodology followed with unmodified nanosilica.

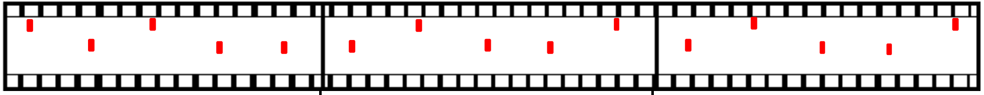
Table 19: Percentage of nanocharge in REX-PLA/Am.SiO$_2$.

	REX-PLA/Am.SiO2								
	t=0 min; 0 m								t=90min; 50 m
	BEGINNING (start extrusion)			MIDDLE			END (end extrusion)		
Flim from extruder									
Time [min]; Position in film [m]	7 min; 4 m	9 min; 5 m	22 min; 12 m	36 min; 20 m	54 min;30 m	68 min;38 m	72 min;40 m	86 min;48 m	86 min; 48 m
% TGA (inorganic part)	2,26	2,08	2,05	2,04	1,88	2,11	1,80	1,90	1,86
%Final (+10% : organic part)	2,49	2,29	2,26	2,24	2,07	2,32	1,98	2,09	2,05
Average of each part	2,34			2,21			2,04		
Total Film %	**2,20**								
Standard deviation	0,16								

In this case, The REX –PLA contains **2.20 ± 0.16 %** of nanosilica modified with amino groups. Once again, it is an acceptable result in relation to the theoretically expected (**2.34 %**).

For REX-loaded PLA nanosilica modified with epoxy groups, 15 tests in total were performed due to the high standard deviation recorded. The results are shown in **Table 20**.

Table 20: Percentage of nanofiller in REX-PLA/Ep.SiO$_2$.

	REX-PLA/Ep.SiO2														
	t=0 min; 0 m														t=40min;
	BEGINNING (start extrusion)					MIDDLE					END (end extrusion)				
Flim from extruder															
Time [min]; Position in film [m]	8 min; 3 m	11 min; 4 m	11 min; 4 m	13 min; 5 m	13 min; 5 m	19 min; 7 m	19 min; 7 m	21 min; 8 m	21 min; 8 m	24 min; 9 m	29 min; 11 m	29 min; 11 m	32 min; 12 m	32 min; 12 m	35 min; 13 m
% TGA (inorganic part)	2,04	1,68	1,94	2,83	2,57	1,98	1,72	2,48	2,79	2,10	2,14	2,26	2,54	2,65	2,22
%Final (+12% : organic part)	2,28	1,88	2,17	3,17	2,88	2,22	1,93	2,78	3,12	2,35	2,40	2,53	2,84	2,97	2,49
Average of each part	2,48					2,48					2,65				
Total Film %	**2,53**														
Standard deviation	0,41														

It is clear that the sample has a high standard deviation, so that it was decided to exclude some data using a box plot (**Figure 38**). The most distant from the median calculated values were discarded. This diagram also distinguishes the samples corresponding to the central and sides of the polymer film.

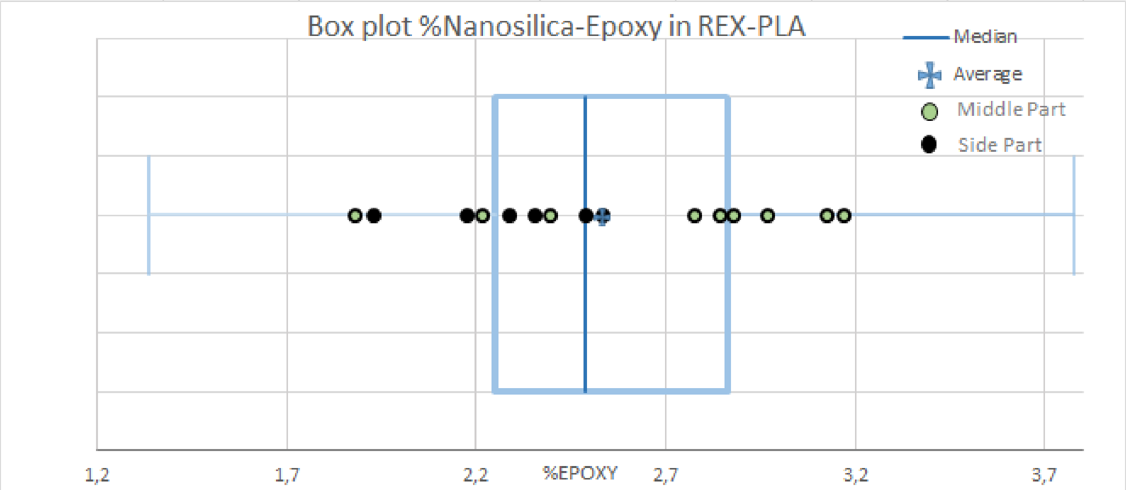


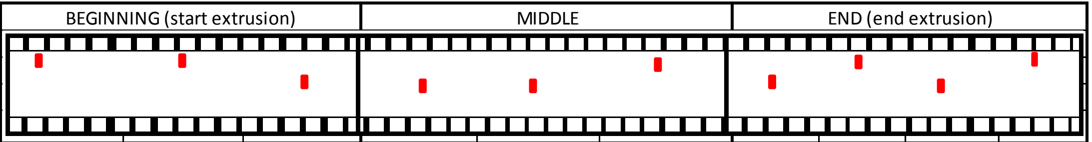
Figure 38. Box plot of REX-PLA/Ep.SiO$_2$ TGA data.

After this process the resulting percentage was **2.49±0.26%** (**Table 21**), which approximates to the ideal value calculated (2.5%). The values were found slightly greater at the center of film as compared to the sides.

Table 21: Percentage of nanocharge in REX-PLA/Ep.SiO$_2$.

REXPLA/EP.SiO2 (EXCLUDING HIGH DEVIATION VALUES)

t=0 min; 0 m t=40min; 1

	BEGINNING (start extrusion)			MIDDLE			END (end extrusion)			
Flim from extruder										
Time [min]; Position in film [m]	8 min; 3 m	11 min; 4 m	13 min; 5 m	19 min; 7 m	21 min; 8 m	24 min; 9 m	29 min; 11 m	29 min; 11 m	32 min; 12 m	35 min; 13 m
% TGA (inorganic part)	2,04	1,94	2,57	1,98	2,48	2,10	2,14	2,26	2,54	2,22
%Final (+12% : organic part)	2,28	2,17	2,88	2,22	2,78	2,35	2,40	2,53	2,84	2,49
Average of each part	2,45			2,45			2,56			
Total Film %	**2,49**									
Standard deviation	0,26									

IV.2.1.2 Thermal stability

The Thermogravimetric assay allows obtaining information about the thermal stability of the materials produced. **Figure 39** shows the behavior of the mass fraction of each material (by selecting the samples less deviated to the average value) as a function of the temperature increase. In the graphic, the temperature scale was reduced (from 1000°C to 500°C) in order to see easily the different curves.

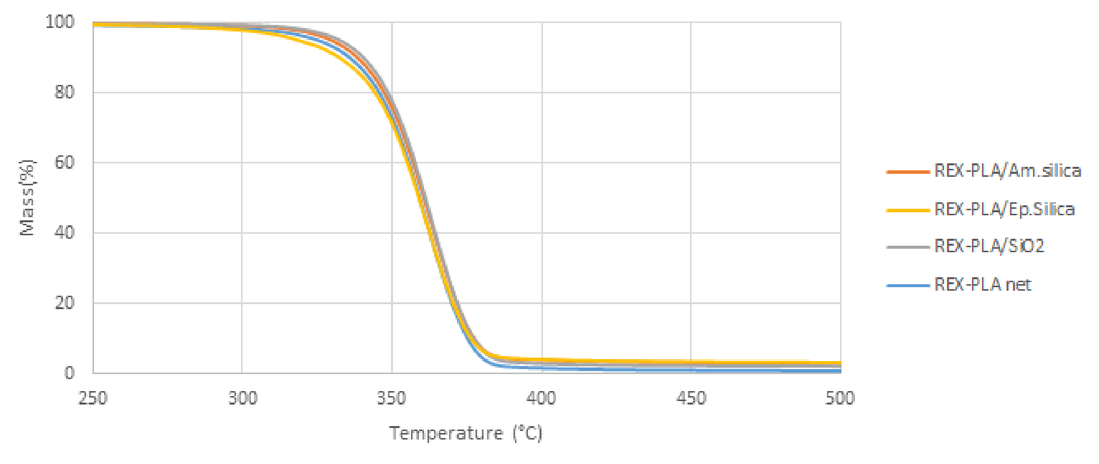


Figure 39. TGA graphic result.

In the case of PLA the degradation occurs at approximately 200°C [4]. As shown in **Figure 40**, the H-bond interaction between the PLA and unmodified nanosilica is similar to that of REX-PLA and the nanoparticles. With the addition of JONCRYL, the epoxy groups remaining can represent an alternative of interaction between polymeric matrix and nanosilica reactive groups.

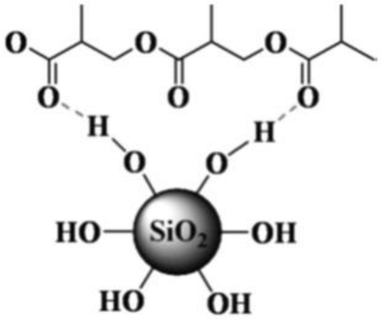


Figure 40. Hydrogen bonding interaction between PLA and nanosilica.[17]

The temperature at which the polymer loses 5% of its mass ($T_{95\,\%}$) is used to compare the thermal stability of each material. It can be noted that the REX-PLA/Ep.SiO_2 has the lowest $T_{95\,\%}$ with an approximate value of 325°C; unmodified REX-PLA shows a value close to 330 ° C. In other words, the nanosilica modified with epoxy groups may represent a negative contribution to the thermal stability of the polymer: this means that its degradation temperature could be reached easily by adding this kind of nanofiller. This behavior could be ascribed to the difficulty of packaging of the chains, because of the size of the nanosilica bearing epoxy group on its surface.

The $T_{95\%}$ values of nanosilica unmodified and modified with amino groups are slightly higher than that recorded for REX-PLA without nanofiller, at about 335 and 332°C respectively. This means that the addition of such nanoparticles can improve the thermal properties of the polymer matrix that starts to degrade at higher temperatures. This rise on degradation temperature can be due to reactions occurring between the functional groups of nanosilica modified with carboxylic groups and epoxy (remaining Joncryl) in the polymeric matrix, strengthening the structure of the polymer. However, this rise is not as high to increase significantly the processing temperature of the REX-PLA.

IV.2.2 Differential Scanning Calorimetry (DSC)

Three samples of approximately 5mg for each material were prepared, sealed in aluminum crucibles by using a "Perkin Elmer" press. The samples were taken from the films, at the beginning, middle and end of the extrusion respectively. A DSC Q2000 apparatus was used, following the procedure described in **Table 22**. It is important to mention that all the tests were carried out under inert atmosphere with nitrogen and 10°C/min.

Table 22: DSC cycles.

Cycle	**Temperature**
Cycle 1	Stabilization to 30°C
Cycle 2 (1° heating)	30°C to 200°C
Cycle 3	Isothermal in 200°C/2min
Cycle 4 (Cooling)	200°C to 30°C
Cycle 5	Isothermal in 30°C/2min
Cycle 6 (2° heating)	30°C to 200°C

The software tool TRIOS TA Instruments v3.3.1.40055 was utilized for analyzing results. The real behavior of each material is shown in the first heat (directly from processing). For simplicity only those thermograms of the films taken from the half of the extrusion are presented, notwithstanding that experiments at the beginning and at the end of the extrusion were perfomed as well. Each sample was taken in the central part of the extruded film, because it is the region where the highest concentration of nanoparticles is expected.

IV.2.2.1 First heating scan (sample as received)

From previous experimentations with PLA, it is known the thermal properties of PLA 4032D as derived from the first heating scan.

Table 23. PLA 4302D thermal properties. [31]

Property	PLA 4032D
Tg (°C)	61,3±0,5
Tm (°C)	164,1±0,1
ΔHcc (J/g)	29,2±1,4
ΔHm (J/g)	31,2±0,4
Xc (%)	2,2±1,1

The result of the first heating in each material shown in **Figure 41**.

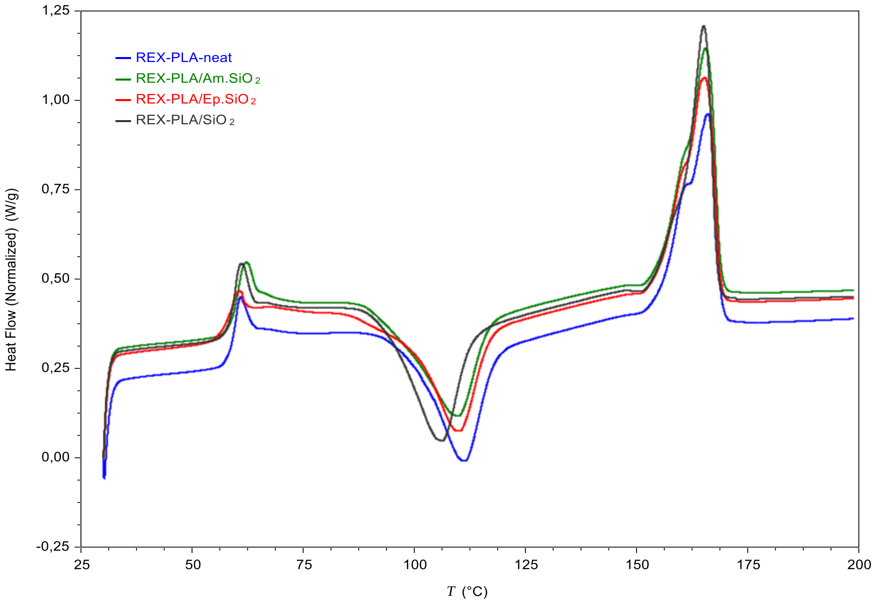


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Figure 41. Comparison of the first heating scan of each material.

In order to clearly observe every change in the curves separately and compare relevant aspects with a high interpretative level, the results are plotted in the following figure:

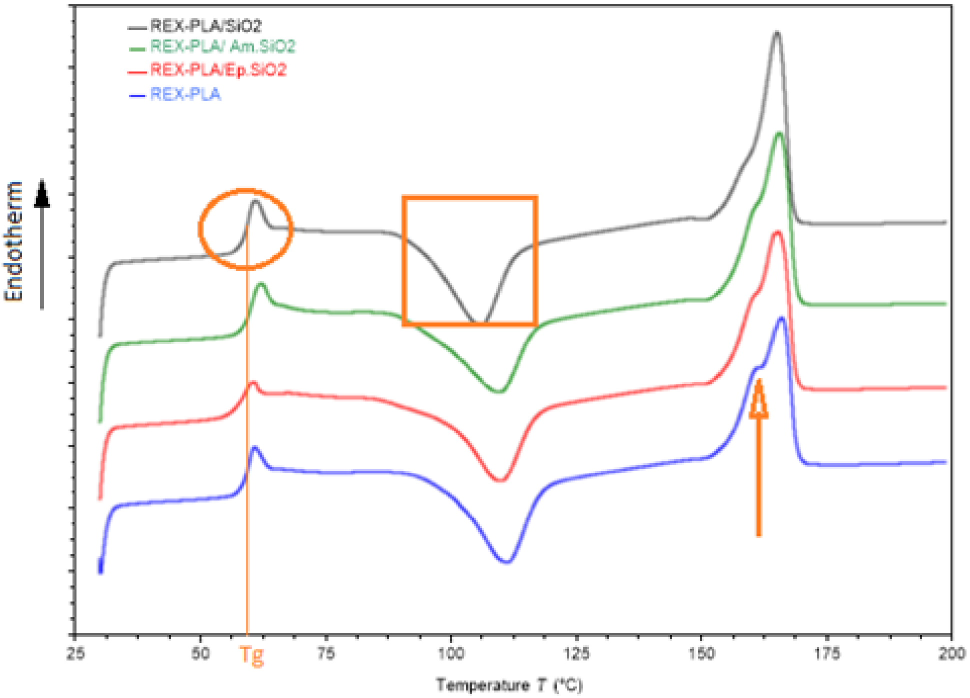

Figure 42. Comparison of the first heating scan of each material (Y-axis modified).

Table 24 and **25** collect the numerical values of interest for each material in the first heating scan.

Table 24: Average DSC results of the first control heating (Cold Crystallization).

		Cold Crystallization		
Material	Tg(°C)	Tc-peak(°C)	Tc-o (°C)	ΔHcc (J/g)
Net REX-PLA	59,44±1,3	111,31±0,33	92,78±0,65	31,60±1,34
REX-PLA/SiO_2	58,04±0,4	107,37±1,06	87,31±2,00	32,61±0,99
REX-PLA/Am. SiO_2	58,74±0,8	109,87±0,06	89,19±0,70	31,40±0,71
REX-PLA/Ep.SiO_2	57,83±0,1	110,30±0,42	87,66±2,05	31,10±1,15

Table 25: Average DSC results of the first control heating (Melting).

	Melting			
Material	Tm-o (°C)	Tsm(°C)	Tm-peak(°C)	ΔHm (J/g)
Net REX-PLA	170,11±0,49	160,16±0,32	165,96±0,15	34,92±1,68
REX-PLA/SiO_2	169,24±0,20	159,45±0,45	165,17±0,23	35,08±1,09
REX-PLA/Am.SiO_2	170,11±0,22	160,24±0,42	165,85±0,32	35,46±0,79
REX-PLA/Ep.SiO_2	170,14±0,74	160,18±0,18	165,49±0,32	34,71±1,26

Figure 42 shows the glass transition region (Tg), which is characterized by the occurrence of a sharp increase in the heat capacity of the material. This temperature was calculated by extrapolation of the trend lines of the glassy state and the elastic behavior towards glass. The (central) straight line that corresponds to the percentage of these two extrapolations is assumed as Tg [28]. As shown in **Table 24,** the Tg is not significantly affected by the presence of nanoparticles, hanging around 58°C, which is very close to that of PLA (61°C).

Immediately after the Tg, an endothermic signal (orange circle) is observed: this the so-called enthalpic or structural relaxation of the material. This term refers to the process of approaching to a steady state in the glassy material maintained at constant environmental conditions (aging), the relaxation phenomenon is extremely complex and depends not only on the state of the material, but also on how it reached that state (i.e. on its thermal history) [28].

All the materials show a process of "cold crystallization" (orange box); the temperature of maximum speed thereof (Tc-peak) in each one is approximately equal to 110°C. The enthalpy of the process, which corresponds to the integral under the curve, turns out to increase in the case of unmodified nanosilica (32,61±0,99 J/g) in comparison to the REX-PLA (31,60±1,34 J/g) and to decrease in the case of the nanofiller modified with amino (31,40±0,71 J/g) or epoxy groups (31,10±1,15 J/g). This finding may be due to the steric effect exerted by the substituent groups, hindering the mobility of the macromolecules and thus the crystallization during heating.

Before reaching the maximum peak of the melting process, all the materials show a "shoulder" (Tsm) around 160°C (orange arrow), which may be the result of polymorphism, that is to say, the presence of different crystalline populations.

It is possible to calculate the degree of crystallinity of the material directly after processing using the following equation, where the contribution of Joncryl is negligible as it forms a single phase with PLA.

$$\boldsymbol{Xc}(\%) = \left(\frac{\boldsymbol{\Delta Hm - \Delta Hcc}}{\boldsymbol{\Delta Hm}^{\circ} * \left(\frac{\boldsymbol{\%PLA}}{\boldsymbol{100}}\right)}\right) * \boldsymbol{100} \qquad \textbf{(IV.2)}$$

where:

ΔHm: Melting enthalpy (J/g).

ΔHcc: Cold crystallization enthalpy (J/g).

ΔHm°: Melting enthalpy of 100 % crystalline PLA (J/g): 93,6 J/g[11].

%PLA: Percentage of pure PLA in the material.

Table 26: Lists the results using the equation **(9)** for each polymer (%Crystallinity)**.**

Material	%Crystallinity
Net REX-PLA	3,54
REX-PLA/SiO_2	2,68
REX-PLA/Am.SiO_2	4,43
REX-PLA/Ep.SiO_2	3,96

According to the obtained values, it can be said that all materials are almost amorphous. The crystallinity of the REX-PLA with unmodified nanosilica decreased to 2.68% compared to the material without nanofiller (3.54%). The nanofiller-polymeric matrix interaction is not sufficient to counteract the steric effect caused by the nanoparticle, preventing an efficient organization of the structure. In addition, a slight increase in the crystallinity degree is observed in the case of REX-PLA/Am.SiO_2 (4.43%) and REX-PLA/Ep.SiO_2 (3.96 %) thus supporting that the effect of modified nanosilica increase the crystallization rate due to the greater interaction occurring within the organic-inorganic interface.

IV.2.2.2 Cooling step

This process promotes the crystallization starting at liquid state. This process is thermodynamically unfavorable and thus there are supercooling effects. **Figure 43** and **44** show the curves obtained.

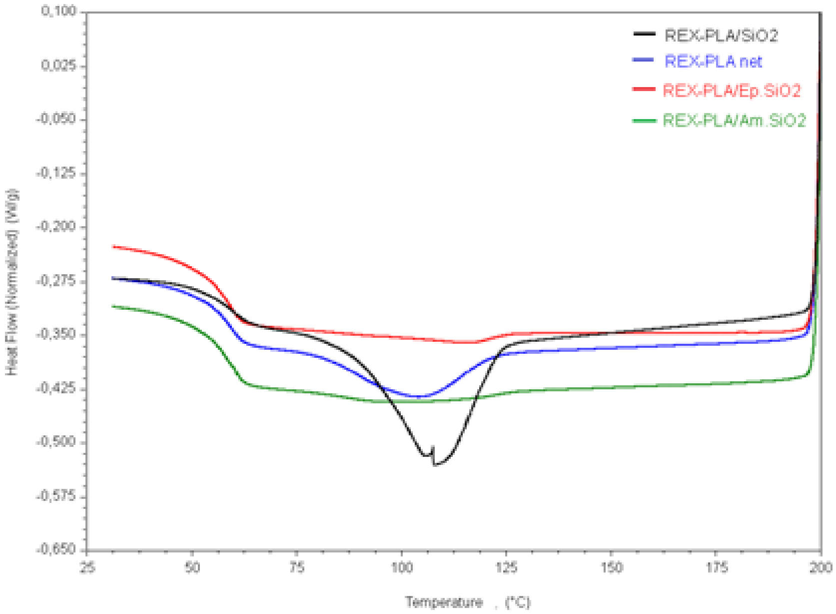

Figure 43. Comparison of the cooling step of each material.

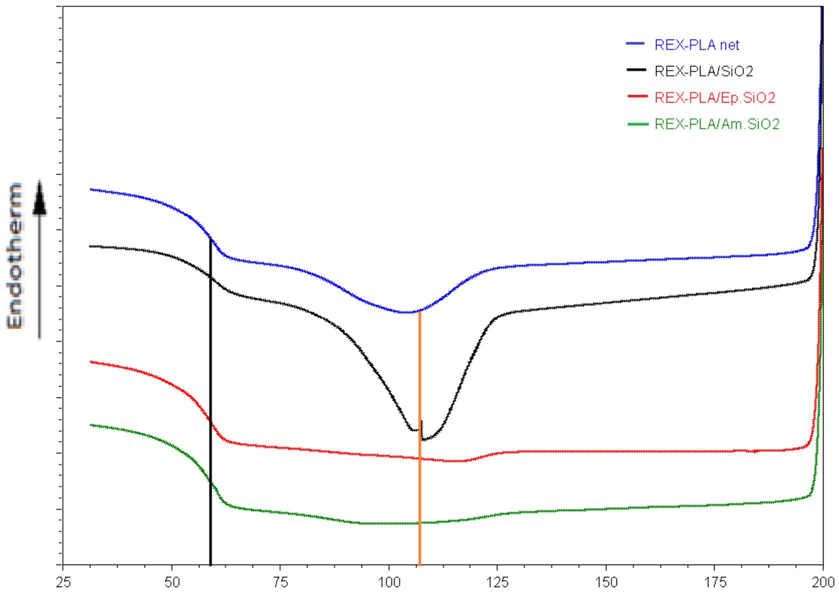

Figure 44. Comparison of the cooling step of each material. (Y-axis modified).

The crystallization process (orange line) occurs at temperatures below the melting point due to the necessity of forming the surface at the interface of glass/melting. Similarly, the glass transition (black line) is observed, however this parameter is more evident in the second heating scan. **Table 27** collects the values of crystallization enthalpy (Hc) and peak crystallization temperature (Tc).

Table 27: Average DSC results of the cooling scan.

Material	ΔHc (J/g)	Tc (°C)
Net REX-PLA	11,36±0,73	103,68±0,45
REX-PLA/SiO_2	26,34±2,19	107,97±0,76
REX-PLA/Am.SiO_2	ND	ND
REX-PLA/Ep.SiO_2	ND	ND

The only material able to crystallize under these cooling conditions is REX-PLA , which reaches about 12% of crystallinity, and the REX-PLA/SiO_2, which in turn reaches approximately 28% crystallinity. This difference in crystallinity evidences the nucleating effect exerted by the unmodified nanosilica that promotes the crystallization speed[32].

When nanosilica is surface-modified, apparently crystallization does not occur during cooling, indicating that the REX-PLA with modified nanofillers requires less subcooling in the vitrification process. This reduced demand for subcooling may be due to the decreased of mobility of nanosilica, because of the increase in size after the addition of functional groups.

IV.2.2.3 Second heating scan (after controlled cooling)

After a controlled cooling, in which the removal of the thermal history is sought, the behavior of the material itself can be examined. In the second heating, the material structure is completely different from the first scan: indeed, at this point the material contains a much lower amorphous because it the regions are likely to be constrained between crystalline lamellae becoming, after the controlled cooling, spherulitic superstructures.[28]. **Figures 45** and **46** show the resulting DSC thermograms.

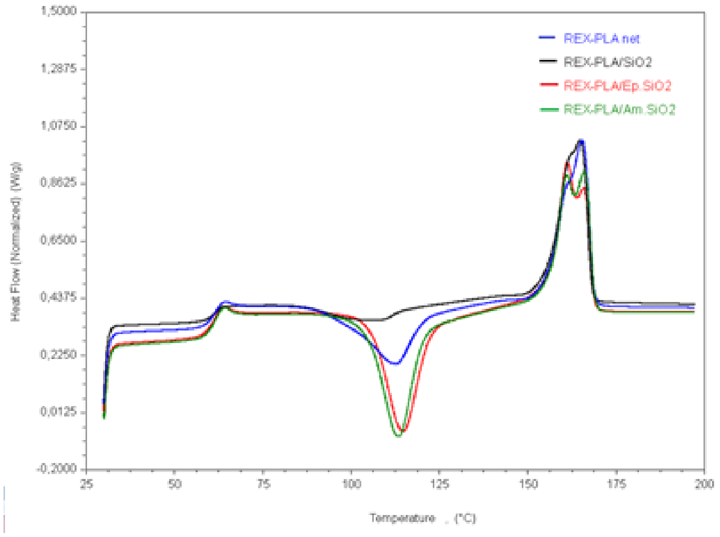

Figure 45. Comparison of the second heating scan of each material.

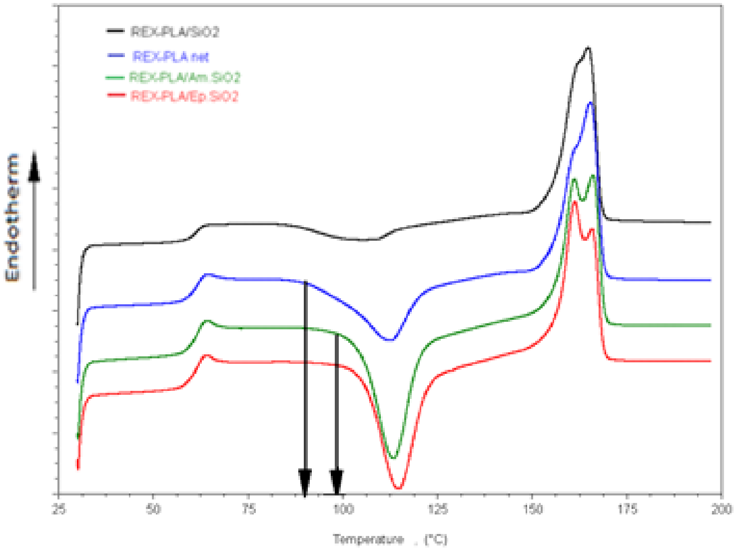

Figure 46. Comparison of the second heating scan of each material. (Y-axis modified).

The numerical values presented in **Table 28** and **29** were obtained by averaging those for the beginning, middle and end of the film.

Table 28: Average DSC results of the second control heating (Cold crystallization).

		Cold Crystallization		
Material	Tg(°C)	Tc-peak(°C)	Tc-o (°C)	ΔHcc (J/g)
Net REX-PLA	61,14±0,32	112,80±0,07	87,56±0,66	20,69±1,23
REX-PLA/SiO_2	61,12±0,09	106,14±3,94	86,18±1,14	6,76±2,34
REX-PLA/Am.SiO_2	60,87±0,13	113,32±0,72	92,43±0,70	32,67±0,51
REX-PLA/Ep.SiO_2	60,48±0,12	114,39±0,35	95,32±1,32	32,14±0,47

Table 29: Average DSC results of the second control heating (Melting).

	Melting			
Material	Tm-o (°C)	Tsm(°C)	Tm-peak(°C)	ΔHm (J/g)
Net REX-PLA	170,4±0,62	161,13±0,73	165,51±0,17	34,53±1,24
REX-PLA/SiO_2	169,66±0,80	161,70±0,17	164,84±0,10	38,72±1,10
REX-PLA/Am.SiO_2	169,94±0,61	160,67±0,29	166,03±0,20	35,80±1,22
REX-PLA/Ep.SiO_2	169,82±0,36	165,59±0,33	161,2±0,10	35,42±1,54

In the second heating scan, glass transition temperatures (Tg) are around 61°C, showing no significant change compared to the first scan.

Except for the REX–PLA/SiO_2, all the materials exhibit a significant cold crystallization, showing a “lag” in the temperature of beginning of this process (Tc-o). The crystal structure in this case is entirely conditioned by vitrification of modified nanosilica phase, being the cause of the “delay”. The unmodified nanosilica has low cold crystallization because during the cooling phase much of the polymer structure has crystallized, having a smaller amorphous phase at this point.

The degree of crystallinity without the influence of the thermomechanical history of the material, after applying equation **(IV.8)**, are collected in **Table 30**.

Table 30: Percentage of crystallinity of each material – second heating scan.

Material	% Crystallinity
Net REX-PLA	14,79
REX-PLA/SiO_2	34,80
REX-PLA/Am.SiO_2	3,41
REX-PLA/Ep.SiO_2	3,60

The unmodified nanosilica has a nucleating effect doubling the percentage of the REX-PLA crystallinity without nanofiller. In addition, it is observed that the modified nanosilica markedly decreases the percentage of crystallinity because the bulky substituents limit the mobility in the polymeric structure avoiding its effective packaging.

IV.3 Evaluation of the mechanical properties

Standard Mechanical Characterization (tensile test)

The test was performed following the standard specifications of ASTM D638-02. The test instrumentation consists of Milling Machine (CEAST) for the fabrication of the specimens, universal testing machine GALDABINI model SUN 2500, the computer software control and registration of test data and computer related with the video-extensometer. The testing machine has a servomechanism to keep constant the speed and it was equipped with a 5kN cell. The tests were conducted at room temperature (25°C) with a deformation rate of 10 mm/min.

Specimens with a thickness between 0,06 and 0,07 mm, Type I according to ASTMD638-02 standard and having the dimensions shown in **Figure 47** have been prepared.

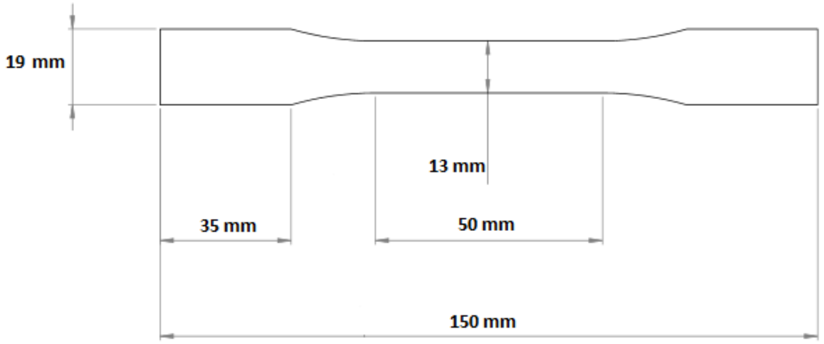

Figure 47. Tensile sample measures.

About 10 specimens were made for each type of material investigated. The cutting position along the film was performed in order to have a uniform thickness distribution; the sides and center of the cut were used for milling the sample as shown in **Figure 48.**

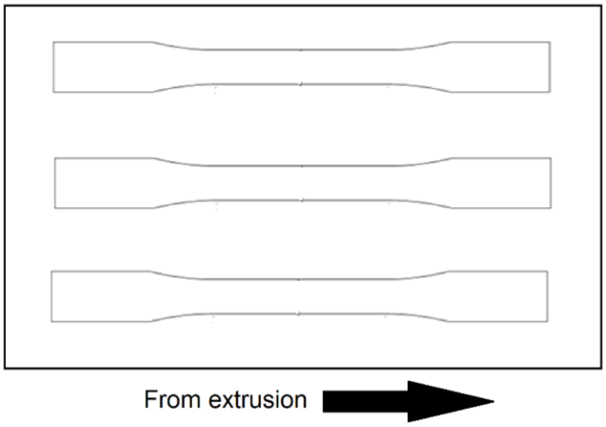

Figure 48. Place of sample. Film from extrusion

The **method of selecting** the samples to be analyzed (between 4 and 5 for each material) was according to breaking point thereof, which should be between the boundaries lines (blue) set by the standard ASTMD638-02. These blue lines play the role of video-extensometer signal to properly determinate the true strain of the sample. **Figure 49** shows an example of a sample properly tested where the boundaries are represented by a blue line.

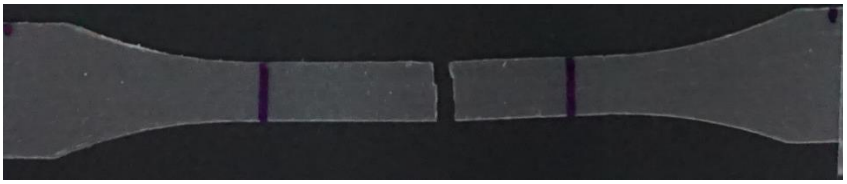

Figure 49. Selection method of tensile samples**.**

In this analysis the mechanical properties of each material and the effect of aging on such properties of the polymer have been investigated. This experiment is divided into two types of tested specimens: de-aged samples and aged samples.

Physical aging of the material occurs due to the tendency toward equilibrium, causing structural relaxation phenomena: in this process, segmental arrangements cause a significant decrease in free volume, as well as an increase in “entanglements” and links in the polymer matrix [33]. These factors limit the molecular mobility negatively affecting its mechanical properties and fracture since they promote the transition from a ductile to a brittle material.

As it is known, the physical aging of polymers is reversible by applying a heat treatment near its glass transition range, increasing the molecular mobility of polymer chains thereby eliminating the more organized areas generated during the aging and its free volume increases [31]. Then it is rapidly cooled to prevent that the structure chains have time to reorder. This treatment promotes the reduction of chains “entangled “ favoring its ductile behavior [33].

The heat treatment applied to the film samples was the following:
1. The film was placed between two metal plates adjusted (preheated to 60°C)
2. Then it was held for 40 min at 60°C in an oven (DRY-BIG 2003740).
3. Finally it was chilled in a cold-water bath for 15 min.

This methodology was chosen for comparative purposes with the previous work done on the Centre Catalan of Plastic[11].

Immediately after this procedure, each sample was cut in the milling machine (CEAST) and directly subjected to tensile tests specimens for de-aged samples. The aged specimens, on the other side, were stored for 1 week after the heat treatment.

It is important to remark that, before each test, thickness, width and length of the real blue boundary lines indicated in **Figure 49** were measured.

IV.3.1 De-aged samples

For each material, five specimens were selected according to the mentioned method and mechanical properties averaged; they are collected in **Table 31**.

Table 31: Average of mechanical properties of the de-aged samples**.**

Material	σ_y (MPa)	ε_y (%)	E (GPa)	ε_b (%)
Net REX-PLA	53±2	2,30±0,07	2,68±0,08	146±24
REX-PLA/SiO_2	51,6±1,9	2,19±0,16	2,56±0,19	43±28
REX-PLA/Am.SiO_2	58,3±4,5	2,24±0,06	2,94±0,25	125±16
REX-PLA/Ep.SiO_2	51,4±1,9	2,2±0,1	2,6±0,07	69,6±43

For simplicity, a sample of each material with a low deviation was selected and plotted in **Figure 50**. As can be noticed, the samples show the expected ductile behavior after the heat treatment performed.

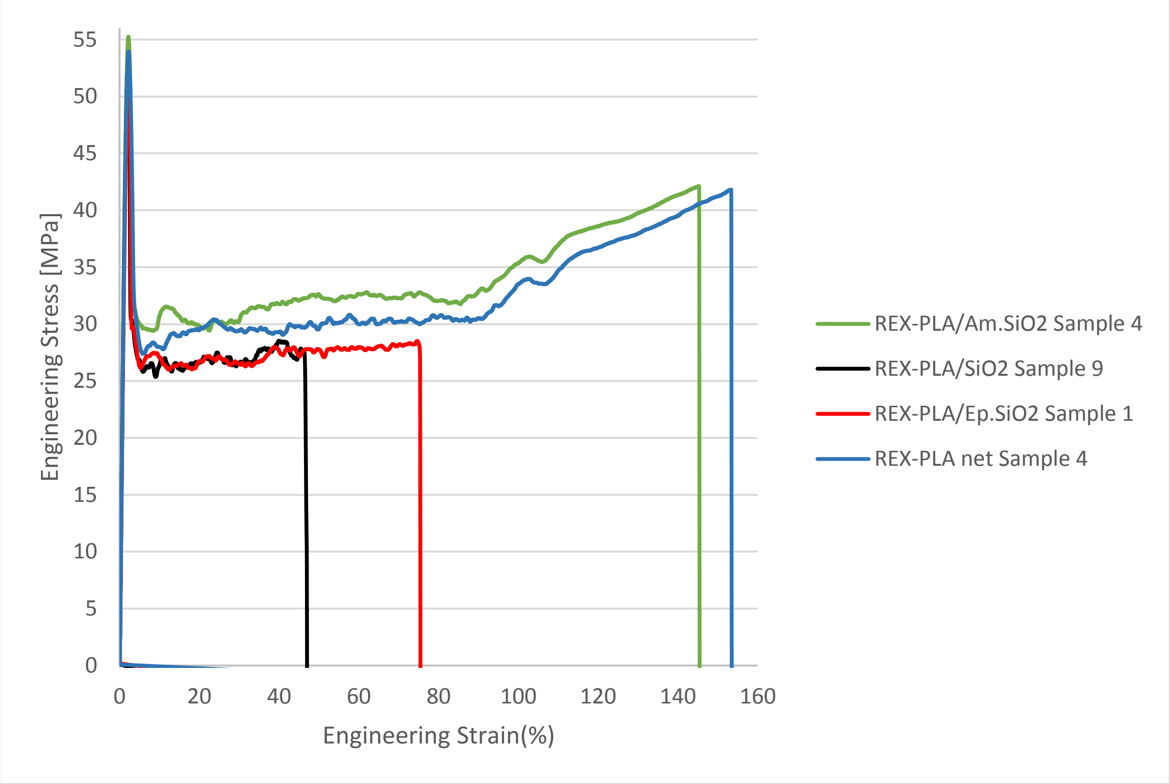

Figure 50. Results of tensile test performed on de-aged samples.

As shown in **Table 31**, REX –PLA/Am.SiO$_2$ shows the highest resistance (58.3±4,5 MPa) to the maximum stress before its plastic deformation (yield point). Regarding the yield point corresponding to the deformation, neat REX-PLA has a slightly higher percentage of strain (2.30 ± 0.04%). However, REX- PLA/Am.SiO$_2$ is the material with the highest relationship between the applied stress and strain (Young's Modulus, 2.94 ± 0.25 GPa) making it the candidate with the most resistance deformation when subjected to mechanical stresses. This means that the interaction between the amino group and the polymer chain is sufficient to achieve a more rigid material.

The elongation at break values were obtained with significant deviations in the polymer with nanofillers probably because, in some cases, the nanoparticles play the role of nuclei of breakage, promoting the cavitation behavior[2]. This is confirmed by the tendency of most of the samples coming from the central part of the film, where the percentage of nanosilica was slightly higher as a result of the TGA; they broke out of limits established without presenting a pattern behavior. In order to further confirm this finding, Scanning Electron Microscopy (SEM) analysis should be performed and the distribution of nanosilica in each case should be assessed.

Unfilled REX-PLA seems to have higher elongation before break (146 ± 32%), but considering the deviation, REX-PLA/Am.SiO$_2$ reaches a similar value (125 ± 16%).

REX-PLA/Ep.SiO_2 shows yield point and Young's Modulus values similar to REX-PLA/SiO_2. It reaches higher elongation values (69.6 ± 43%) compared with unmodified nanosilica (43 ± 28%): however, both of them have a high standard deviation based on the average.

As can be seen, it was obtained a high elongation to break deviation values representing important errors (more than 10%); this is why has to be perform an accurate analysis of the nanofiller distribution with, for example, Transmission electron microscopy (TEM).

In previous studies has been studied the mechanical properties of PLA 4032D with the same thermal treatment used on this project, resulting the following:

Table 32. De-aged PLA4302 mechanical properties.[11]

Material	**σ_y (MPa)**	**ε_y (%)**	**E (GPa)**	**ε_b (%)**
PLA 4032D	58,7 ± 0,5	2,29±0,02	3,2±0,2	165±10

As can be noticed, the behavior of REX-PLA/Am.SiO_2 is similar to the PLA maintaining the resistance despite the change on the molecular structure.

IV.3.2 Aged samples

After a week of storage at room temperature (25°C) the prepared samples were tested: the obtained results are collected in **Table 33.**

Table 33: Average of mechanical properties of the aged samples.

Material	**σ_y (MPa)**	**ε_y (%)**	**E (GPa)**	**ε_b (%)**
Net REX-PLA	66,91±0,6	2,15±0,05	3,11±0,08	3±0,3
REX-PLA/SiO_2	62,6±1,3	2,05±0,05	2,94±0,05	2,3±0,1
REX-PLA/Am.SiO_2	67,9±1	2,24±0,07	2,88±0,18	2,6±0,2
REX-PLA/Ep.SiO_2	64,9±0,8	2,12±0,02	3,09±0,18	2,2±0,1

Samples with lower deviation from the average value were selected and plotted in **Figure 51.**

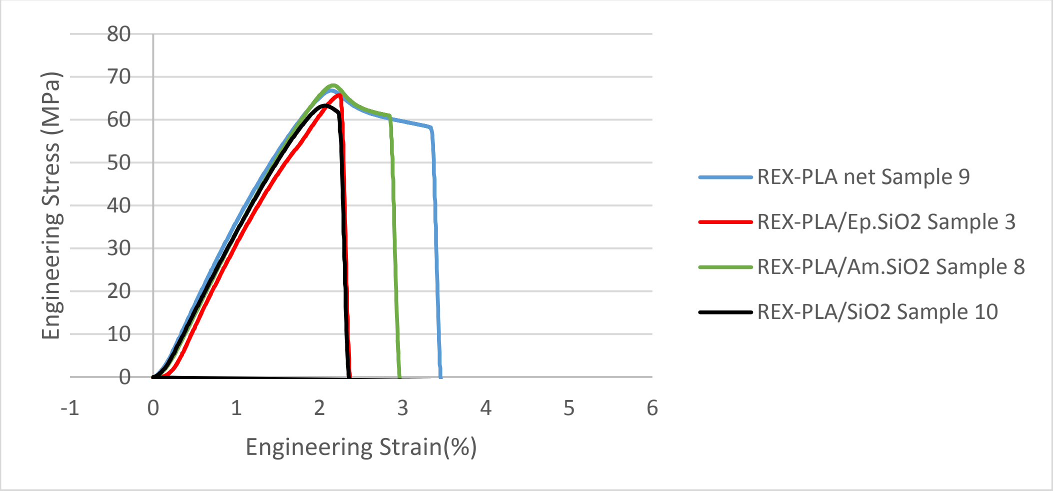

Figure 51. Results of tensile test of aged samples.

A brittle behavior is clearly found when the material is aged: this brings to a quick and unstable crack propagation under the influence of uniaxial stresses [11].

REX-PLA/Am.SiO_2 shows the highest stress at the yield point with 67.9±1 MPa. REX-PLA has a slightly higher Young's modulus (3.11±0.08 GPa) compared with the modified amino group (2.88 ± 0.18 MPa). This means that with the past of the time the REX-PLA become quickly more brittle than the REX-PLA/Am.SiO_2.

REX-PLA/Ep.SiO_2 shows a higher Young's Modulus with respect to PLA-REX/SiO_2, demonstrating an increase in polymer stiffness, despite similar elongation to break.

With respect to pristine PLA, after one week storage at room temperature, it is significantly more brittle than all the other samples tested in this project (**Table 34**).

Table 34. Aged PLA4302 mechanical properties.[11]

Material	σ_y **(MPa)**	ε_y **(%)**	**E (GPa)**	ε_b **(%)**
PLA 4032D	74 ± 2	2,2±0,01	3,5±0,1	2,2±0,1

IV.3.3 Aging factor

Aging factor affects all the materials. The rate of change due to aging has been assessed. **Table 35** shows the percentage of change between aged and de-aged polymers.

Table 35: Mechanical properties percentage of change due to aging.

Material	**%σ_y**	**%ε_y**	**%E**
Net REX-PLA	0,27	0,065	0,16
REX-PLA/SiO_2	0,21	0,062	0,15
REX-PLA/Am.SiO_2	0,17	0,0031	0,020
REX-PLA/Ep.SiO_2	0,26	0,038	0,20

From an overall point of view, REX- PLA/Am.SiO_2 is the systems that behaves in the best way (in other words, it is not very affected by aging). This means that it is likely that the nanofiller delays the aging of the material while maintaining its properties during storage at room temperature. However, further aging tests should be performed in order to corroborate such behavior.

V. CONCLUSION CHAPTER

The overall objective of this research work was to improve the thermal and physical properties of polylactic acid, PLA; this was achieved by preparing and characterizing REX-PLA nanocomposites by reactive extrusion with three types of nanosilica: untreated nanosilica, nanosilica modified with amino groups, nanosilica modified with epoxy groups.

Once produced the REX -PLA as base material for the nanocomposite and encapsulation of the nanoparticles in the polymer matrix of PLA, rheological tests were performed in order to check whether its extrusion was feasible.

Four types of materials were produced in form of film:

- REX -PLA extruded 3 times for comparison.
- REX-PLA with unmodified nanosilica.
- REX-PLA with nanosilica modified with epoxy group
- REX-PLA with nanosilica modified with amino group.

All the obtained films were subjected to a thermal and mechanical characterization.

In the following, the most significant results obtained will be summarized.

A. Thermal analysis

In order to assess the thermal behavior of the different composites, Thermogravimetric and Differential Scanning Calorimetry analyses were performed. From this analysis we can conclude the following:

1. Thermogravimetric Analysis (TGA):

- REX-PLA/Am.SiO_2 and REX-PLA/Ep.SiO_2 exhibit the highest degradation temperature (335°C and 332°C respectively). This finding, compared with the REX-PLA without nanoparticles (330°C) does not represent a significant change in this property. In other words, the added nanoparticles do not exert an important protection against degradation for REX-PLA.

2. Differential Scanning Calorimetry (DSC):

2.1 First heating: material as received from extrusion.

- The crystallinity of the material as received from processing increases in the presence of the modified nanoparticles, being REX-PLA/Am.SiO_2 the polymer with the highest value (4.43%).

2.2 Cooling step

- Polymers with modified nanoparticles showed no crystallization during cooling due to their increased size that affects chain mobility. However, the nucleating effect of the unmodified nanosilica allows achieving a crystallization of 28 %.

2.3 Second heating scan.

- The polymer containing unmodified nanosilica shows a crystallinity of 34.8% demonstrating the nucleating effect of this latter. Furthermore, those containing modified nanosilica showed a low crystallinity values (less than 4%) due to the limitation of chain mobility.

In short, it can be concluded from the thermal analysis that with the addition of 2% w/w of nanoparticles in the REX–PLA, the degradation temperature is not significantly changed. However, an increase of the crystallinity of the material directly from processing is observed, which can enhance the mechanical properties.

B. Mecanichal analysis.

A heat treatment was applied to the samples of each material in order to evaluate the effect of aging at room temperature.

1. De-aged samples

- The REX-PLA/Am.SiO_2 had the highest value of Young's modulus (2.94 ± 0.25 GPa) being the most mechanical performing system.

- The values of elongation at break of the nanofilled polymers show significant deviations. From this, it can be concluded that the nanoparticles act as breaking nuclei.

2. **Aged samples:** 1 week storage at room temperature

- REX-PLA/Am.SiO_2 proved to be the stronger and less brittle material with a Young's modulus of 2.88 ± 0.18 GPa and a yield strength of 67.9 ±1 MPa, being the best nanocomposite option to improve the mechanical properties of REX–PLA.

3. Aging factor

- REX-PLA/Am.SiO_2 is the most stable system, which provides anti-aging features to REX- PLA.

The mechanical tests show that the nanosilica modified with amino groups is able to enhance the tensile strength of the polymer matrix and to reduce the aging.

From an overall point of view, the use of silica nanoparticles modified with amino groups seems to be the best way for improving the thermal and mechanical properties of REX-PLA: indeed, the nanofiller increases the crystallinity and tensile strength of the polymer, hence widening its industrial applicability. It also facilitates handling and storage by reducing the effect of aging on its physical properties.

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Recommendations

It is important to note that this research is part of a larger one, from that perspective it is recommended that in future research be conducted the following tests:

- Testing of Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM) for information about the dispersion of the nanoparticles in the REX-PLA matrix.

- Testing of biodegradation of polymers as it is supreme interest in environmental matters.

- Testing of rheology that have not been carried out as part of this project.

- Expanding the thermal and mechanical characterization of the materials.

APPENDIX

A. Equipment used and its Characteristics

A.1 Mill FIORENZATO (Joncryll milling)

Table 1. Mill FIORENZATO characteristics.[34]

Mill	Characteristics
Power	350 W- 1350 RPM
Weight	14 Kg
Dimensions (length, width and height)	615 x 230 x 270 mm
Cutter blade dimeter	64 mm

Figure 1. Mill FIORENZATO for grinding Joncryl.

A.2 Lego-doser (Joncryll dispenser)

Table 2. Powder low mass flow Dispenser (Lego-doser) characteristics.[35]

Powder doser	Characteristics
hopper volume	82,99 cm^3
Working voltages	3V; 4,5 V; 5 V; 6V; 7,5V; 9V and 12 V
Number of speeds remote control by voltage	7
Maximum dosing speed	144,5 RPM (9V)
Lower dosing speed	9,99 RPM (3V)
Shaft length	256 mm
Copper tube inner diameter	12.2 mm
Copper tube outer diameter	14 mm
Transmission ratio	3

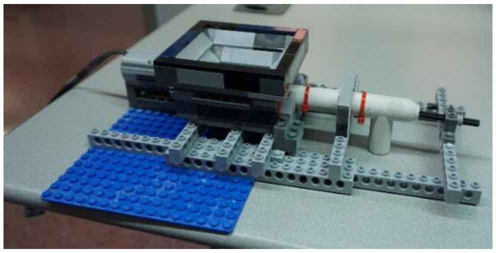

Figure 2. Lego- Doser.

A.3 Twin Screw Extruder Collin

Table 3. Twin screw co-rotated extruder COLLIN Kneader characteristics [36]

Extruder	Characteristics
Model	Kneter 25X36D
Screw diameter	25
L/D relation	36
Maximum speed of the spindles	260 RPM
Torque per shaft (Nm)	2 x 90

Figure 3. Co-rotating Twin Screw Extruder COLLIN Kneter 25 x 36D.

A.4 Chill-Roll Collin GMBH

Table 4. Chill-Roll Collin characteristics [37]

Roll	Characteristics
Model	CR 72-T
Dimensions (length, width and height)	825 x 550 x 635 mm
Weight	55 Kg
Roll diameter	72 mm
Roll Width	190 mm
spin speed	0.5 – 14 m/min
Interval spacing between the rollers	0.1 – 2 mm
Torque	0,9 N*m

Figure 4. Roll Mills Collin GMBH.

A.5 Chill-Roll Temperature controller

Table 5. Band conveyor (Brabender belt) characteristics [38]

Temperature controller	Characteristics
Model	TW9
Maximum temperature	90°C
Working fluid	Water
Heating power	9 kW
Cooling type	indirect
Pump power	0,75 kW

Temperature controller	Characteristics
Maximum pump flow	60 L/min
Maximum pump pressure	40 m
Dimensions (length, width and height)	250 x 686 x 678 mm
Weight	55 Kg

Figure 5. Chill-Roll Temperature Controller**.**

A.6 Band conveyor

Table 6. Band conveyor (Brabender belt) characteristics [39]

Band conveyor	Characteristics
Model	Brabender Conveyor belt
Speed	0,6-0,6 m/min
Dimensions (length, width and height)	120 x 1150 x 1250 mm
Voltage and frequency	200 – 240V / 50/60 Hz

Figure 6. Band conveyor.

A.7 PIOVAN desiccant dryer (PLA and REX-PLA)

Table 7. PIOVAN desiccator characteristics.[40]

PIOVAN desiccator	Characteristics
Model	DSN506ME
Air flow	80 m3/h
Process fan power	0.2 kW
Heating power	3 kW
Power regeneration	3 kW
Power installed	3.2 kW
Maximum temperature	200 °C
Average consumption at 80°C	0.95 kWh
Dimensions (length, width and height)	250 x 550 x 870 mm
Weight	140 Kg

Figure 7. PIOVAN desiccant dryer for PLA and REX-PLA extrusion.

A.8 Hopper desiccant dryer

Table 8. PIOVAN Hopper desiccator characteristics. [41]

Hopper	Characteristics
Model	T30
Size	30 dm^3
Diameter	434 mm
Height	735 mm
Weight	17 Kg

Figure 8. PIOVAN Hopper desiccant dryer for PLA and REX-PLA extrusion.

A.9 Vacuum pump Telstar (volatile gases in extruder)

Table 9. Vacuum pump Telstar[42]

Vacuum pump	Characteristics
Model	S-4
Nominal flow (50 Hz)	4 m^3/h
Stages	1
Vacuum limit	30 mbar
Oil capacity	0,2 L
Weight	9,5 Kg
Rotation speed (50 Hz)	1450 RPM
Engine power	0,15 kW
Recovery	950 mbar

Figure 9. Vacuum pump used during extrusion.

A.10 Twin screw dispenser (Nanosilica masterbatch dispenser)

Table 10. Twin screw volumetric feeder.

Twin screw dispenser	Characteristics
Engine model	FLENDER ATB-LOHER 0530/84
Power	0,25 kW
Voltage	380-420 V
Type of screw	Twin screw co-rotating feeders
Flow rate	5,6 -6800 dm^3/h

Figure 10. Twin screw doser for masterbatch.

A.11 Analytical balance COBOS, precision DK (For TGA testing)

Table 11. Balance COBOS[43]

Balance	Characteristics
Model	AUW120D
Maximum Weight	120 g- 42g
Minimum Weight	1 mg
Precision	0,1 mg/0,01 mg
Weighing pan diameter	80 mm

Figure 11. Balance COBOS for TGA test.

A.12 Analytical Balance Mettler Toledo

Table 12. Balance Mettler Toledo[44]

Balance	Characteristics
Model	PB303-S DeltaRange
Maximum Weight	310 g- 60g
Minimum Weight	0,02 g
Precision	10 mg/1 mg
Weighing pan diameter	180 mm

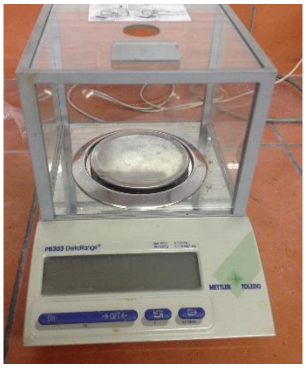

Figure 12. Balance Mettler Toledo.

A.13 Balance COBOS for large mass quantities

Table 13. Balance COBOS 501 for large quantities.

Balance	Characteristics
Model	501
Maximum Weight	5110 g
Minimum Weight	5 g
Precision	0,1 g
Weighing pan diameter	20 cm

Figure 13. Balance COBOS used for large mass quantities.

B. Real data registration during extrusion

On this section will be exposed the recording of the temperature, pressure and intensity during the extrusion of each material analyzed. For simplicity only **one day** of processing will be show since the behavior is similar in the processing of the same polymer each day.

B.1 PLA and Joncryl extrusion parameters.

The specifications of this process are in the Experimental Chapter specifically in the section **II.2.1.1 Preparation of REX-PLA** of the conditioning of raw material.

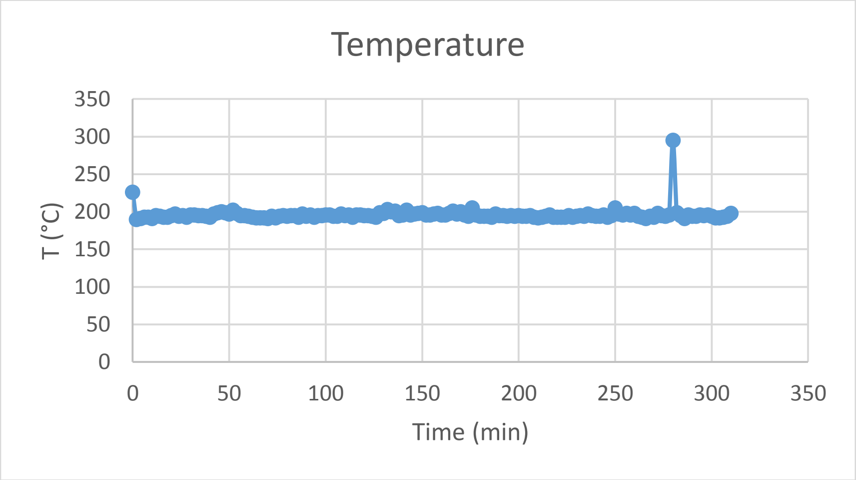

Figure 14. Temperature registration during REX-PLA production.

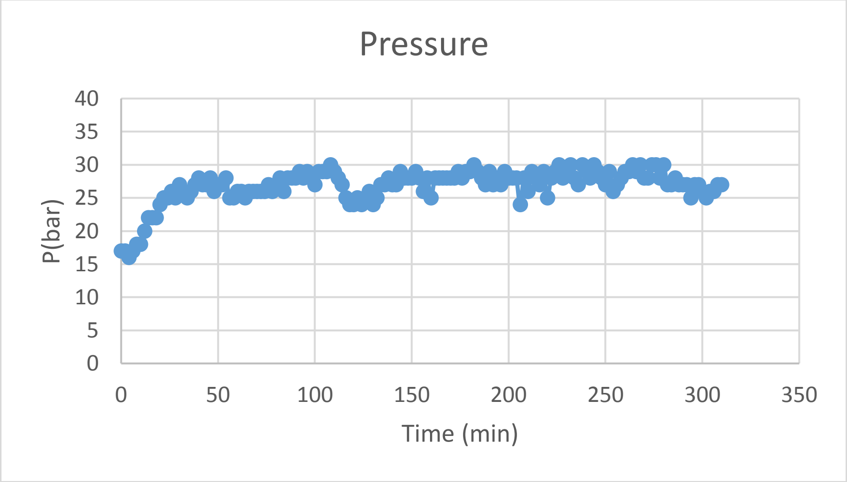

Figure 15. Pressure registration during REX-PLA production.

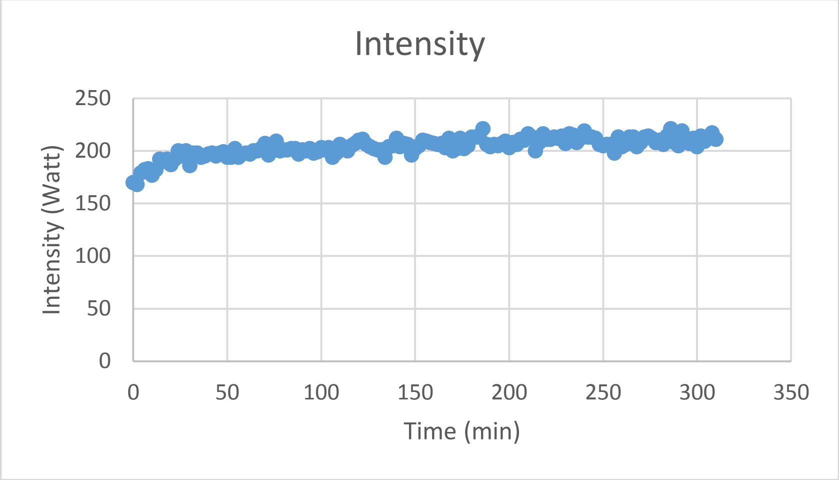

Figure 16. Intensity registration during REX-PLA production.

B.2 REX-PLA with unmodified nanosilica extrusion parameters.

Following the record of the variables during the first masterbatch of unmodified nanosilicea extrusion. The specifications of this process are in the Experimental Chapter specifically in the section **II.2.2.1.1 First extrusion** of the Preparation of REX-PLA nanocomposites.

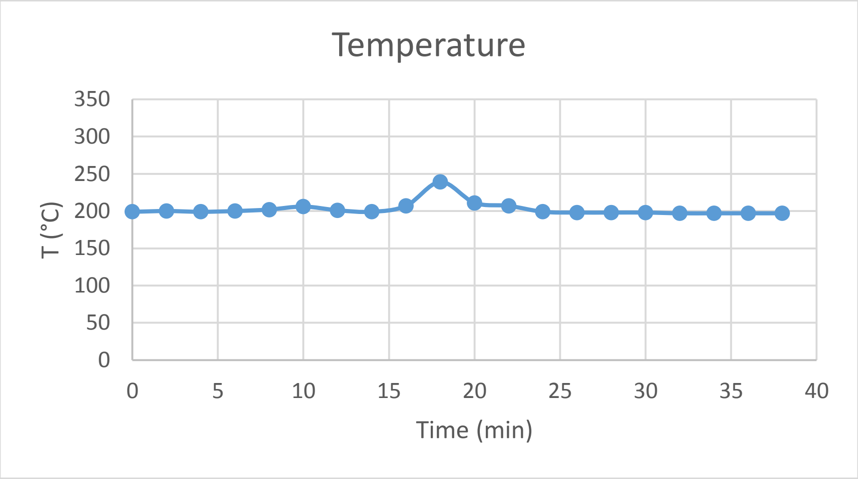

Figure 17. Temperature registration during REX-PLA/SiO_2 production.

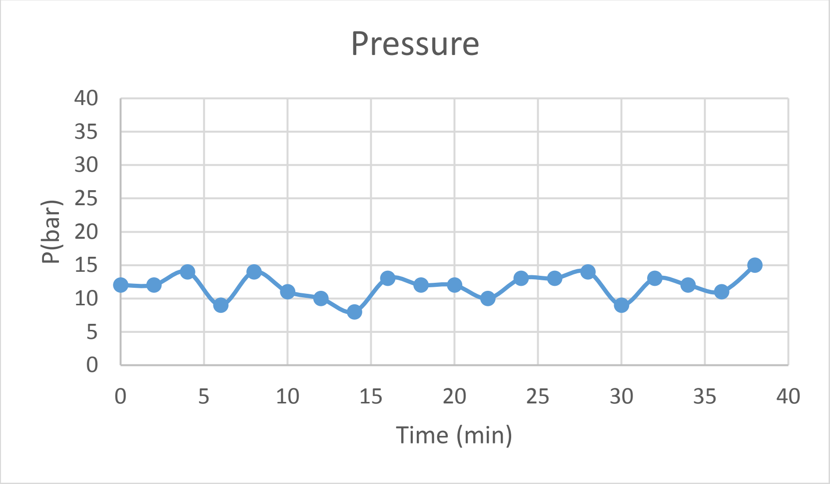

Figure 18. Pressure registration during REX-PLA/SiO_2 production.

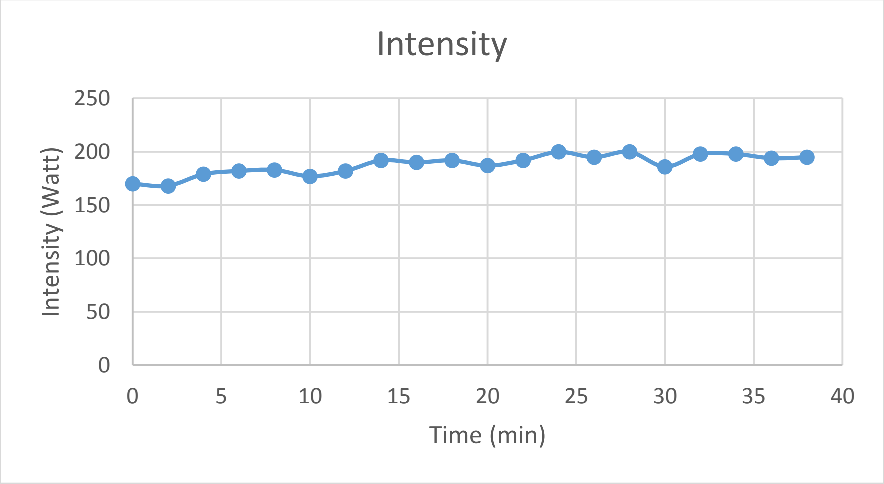

Figure 19. Intensity registration during REX-PLA/SiO_2 production.

B.3 REX-PLA with nanosilica modified with amino group extrusion parameters.

Following the record of the variables during the first masterbatch of nanosilica modified with amino group extrusion. The specifications of this process are in the Experimental Chapter specifically in the section **II.2.2.1.3 Second extrusion** of the Preparation of REX-PLA nanocomposites.

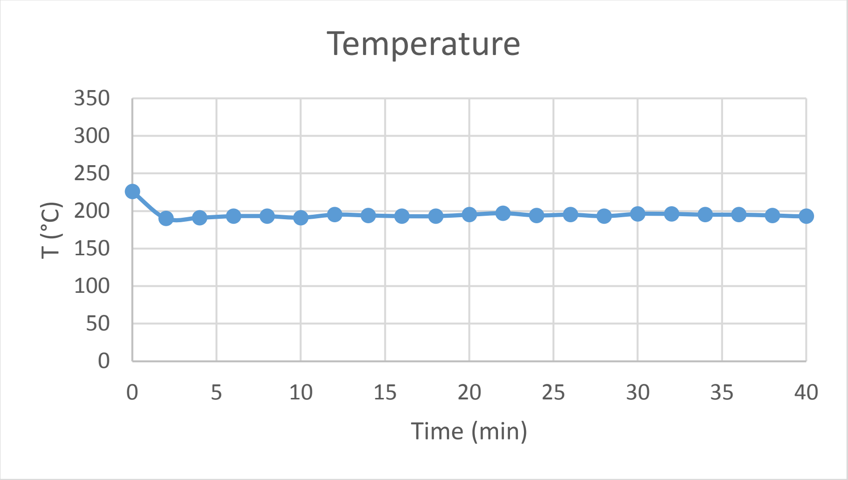

Figure 20. Temperature registration during REX-PLA/Am.SiO_2 production.

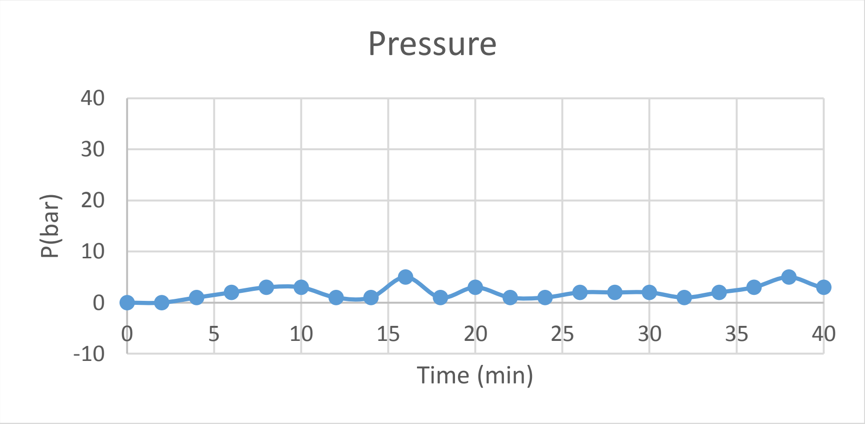

Figure 21. Pressure registration during REX-PLA/Am.SiO_2 production.

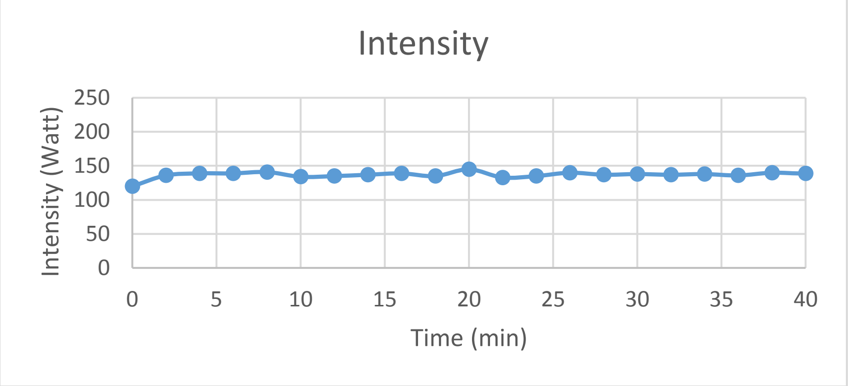

Figure 22. Intensity registration during REX-PLA/Am.SiO_2 production.

B.4 REX-PLA with nanosilica modified with epoxy group extrusion parameters.

Following the record of the variables during the first masterbatch of nanosilica modified with epoxy group extrusion. The specifications of this process are in the Experimental Chapter specifically in the section **II.2.2.1.3 First extrusion** of the Preparation of REX-PLA nanocomposites.

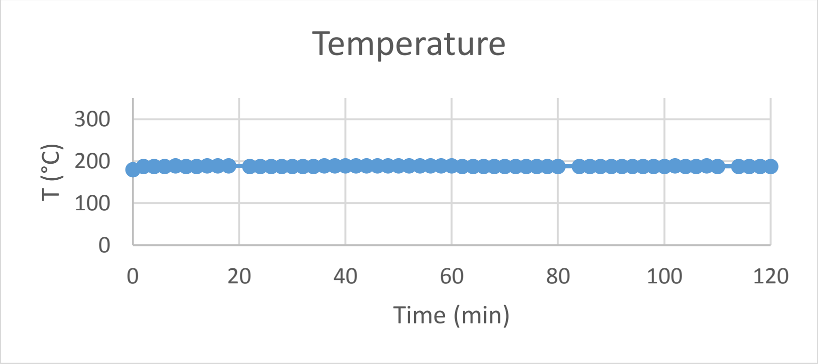

Figure 23. Temperature registration during REX-PLA/Ep.SiO_2 production.

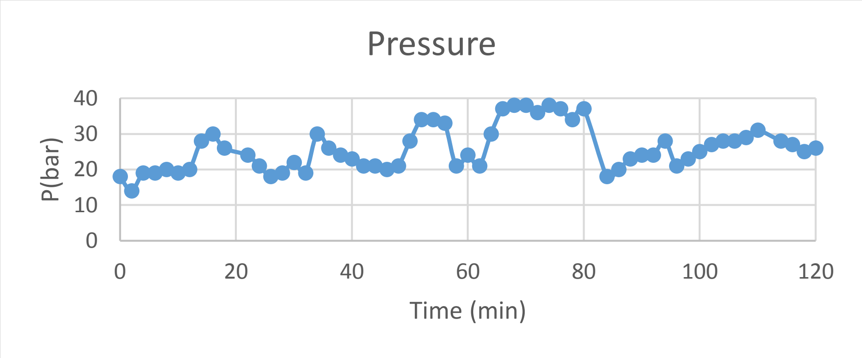

Figure 24. Pressure registration during REX-PLA/Ep.SiO_2 production.

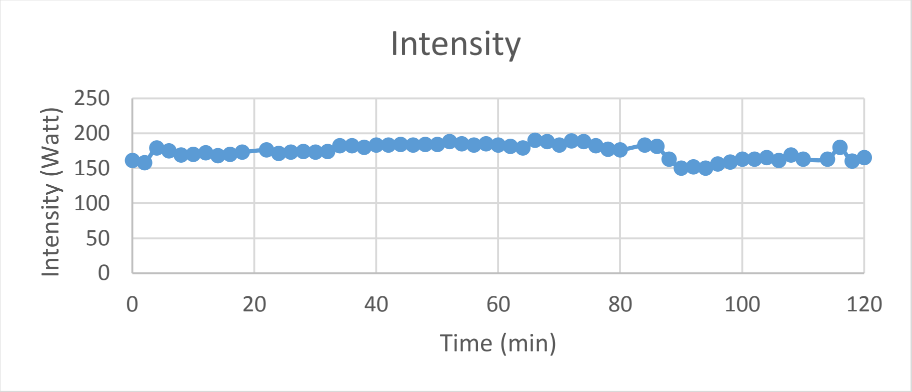

Figure 25. Intensity registration during REX-PLA/Ep.SiO_2 production.

B.5 Film production extrusion parameters.

In this section the real parameters during the extrusion of all the pellets to obtain films, the process specification can be seen in the **II.2.2.2 Homogenization and preparation of films: Third extrusion** of the Experimental chapter. Since all the film with nanoparticle production were done with the same condition of extrusion will be exposed on the same graph.

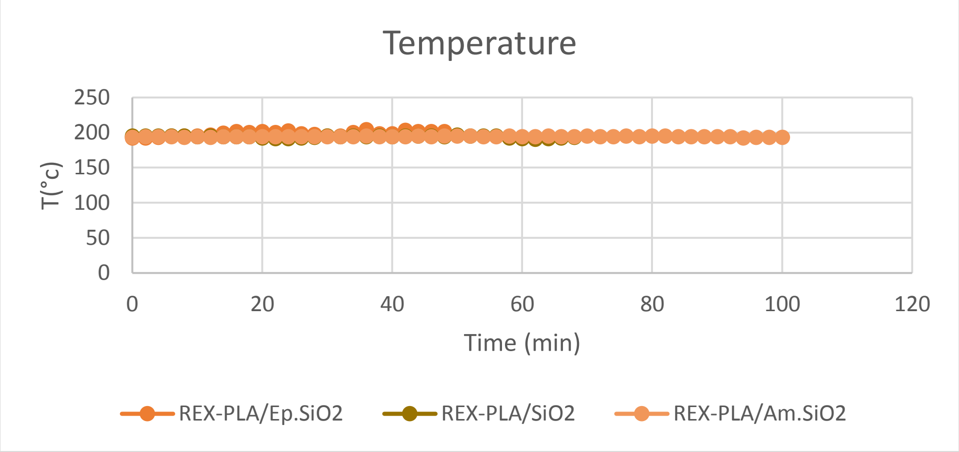

Figure 26. Temperature registration during Film with nanoparticles production.

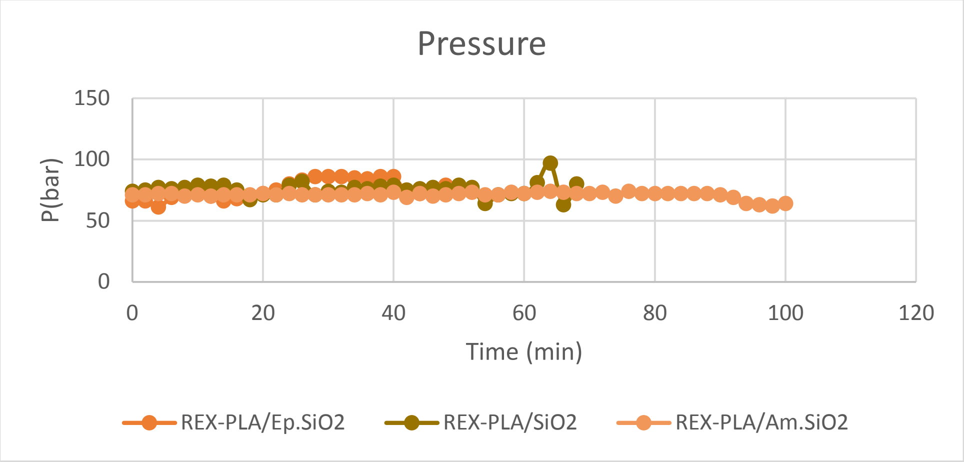

Figure 27. Pressure registration during Film with nanoparticles production.

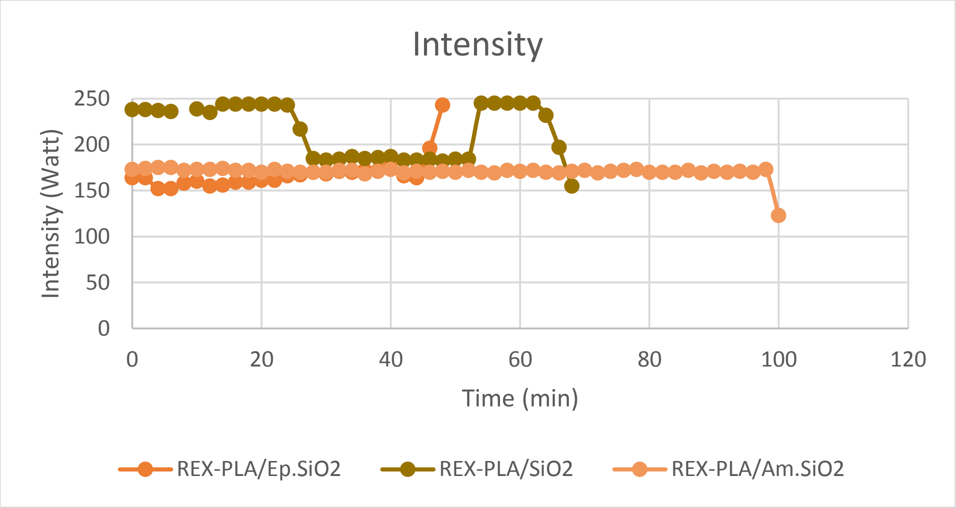

Figure 28. Intensity registration during Film with nanoparticles production.

B.6 REX-PLA 3 times processed film production extrusion parameters.

Next the parameters during the extrusion of REX-PLA film 3 time extruded. The conditions fixed for this process can be seen in the **II.2.2.2 Homogenization and preparation of films: Third extrusion** of the Experimental chapter.

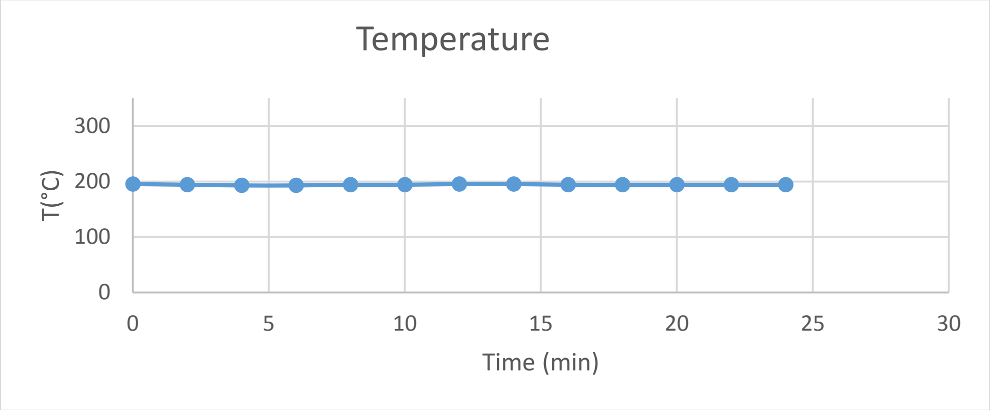

Figure 29. Temperature registration during net REX-PLA Film production.

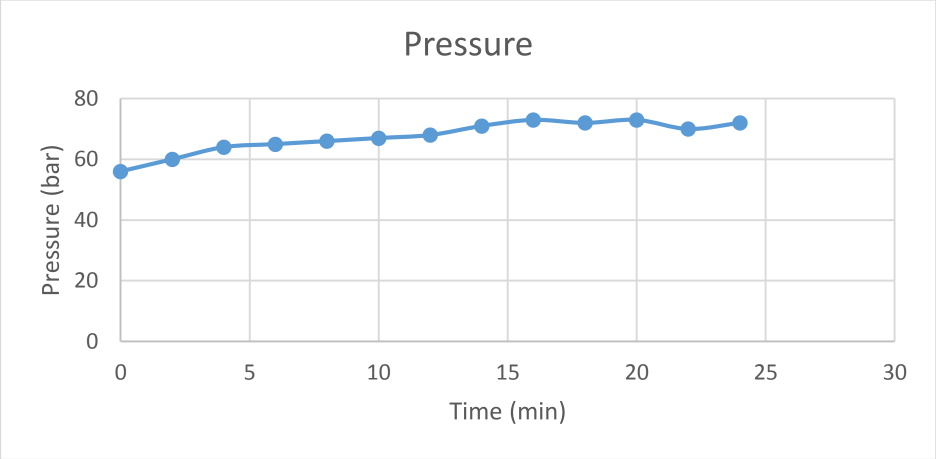

Figure 30. Pressure registration during net REX-PLA Film production

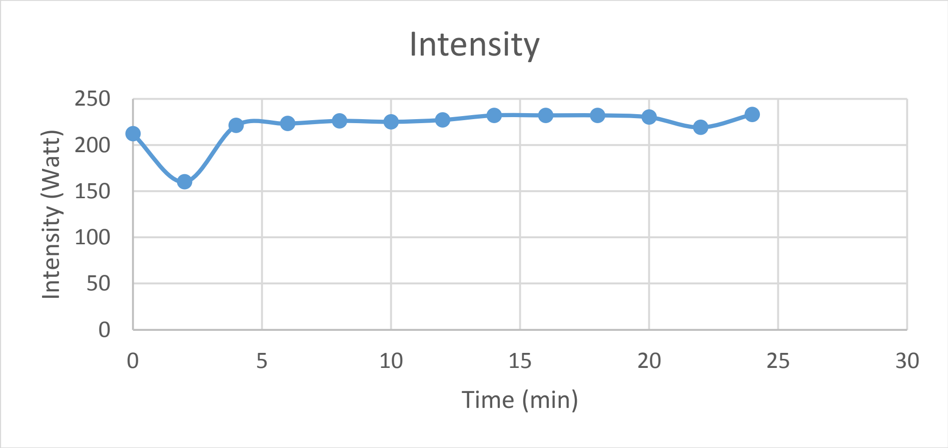

Figure 31. Intensity registration during net REX-PLA Film production.

C. Experimental procedure scheme

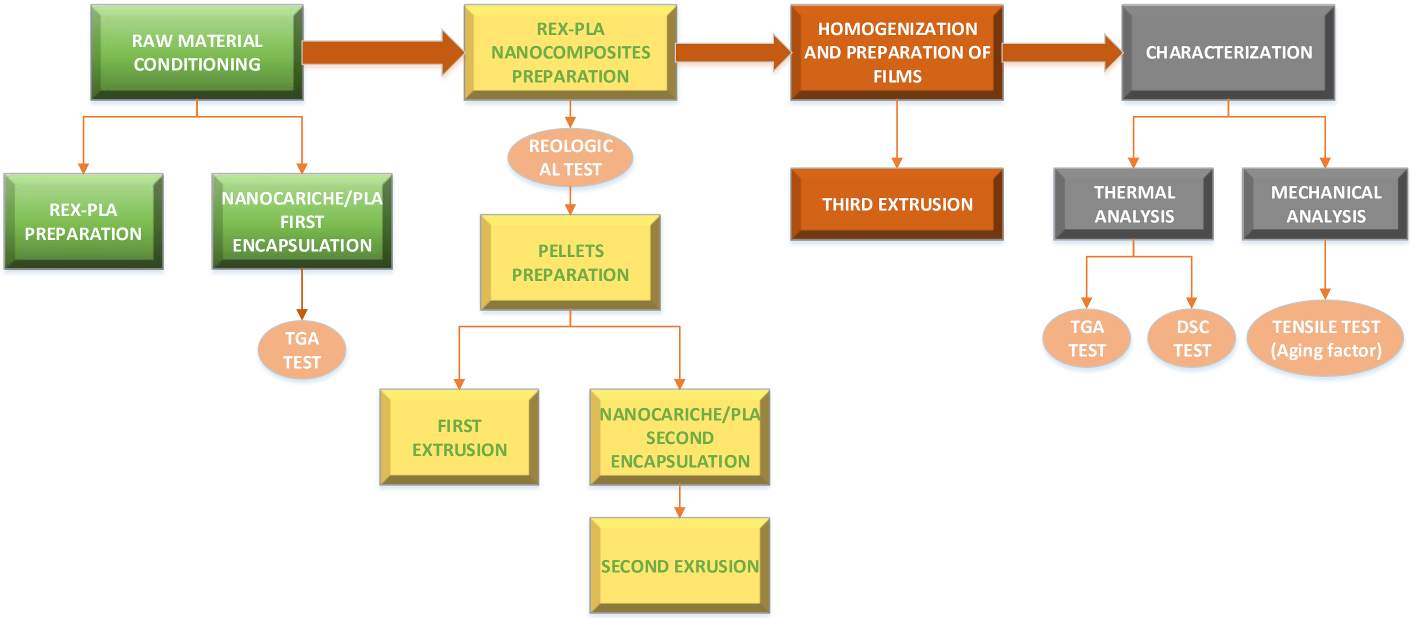

Figure 32.Scheme of the experimental procedure