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CHAIN EXTENSION OF RECYCLED PA6

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ABSTRACT

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2   Recycling of polymers is a necessity in our intensively consuming polymer world but

3   the nature of polymers is such that they are prone to thermal degradation when re-extruded

4   and this poses technical challenges to recycling. This papers describes research that seeks to

5   rebuild the structure of degraded PA6. We present data from controlled experiments with

6   pristine pPA6 extruded to form a base recycle rPA6 to which we added two chain extenders,

7   separately: one with anhydride multifunctionality (ANHY), highly reactive with amide groups

8   and one with epoxy multifunctionality (EPOX), less reactive. We found from rheological data

9   carried out in the linear viscoelastic region (so as to study structural changes) a striking

10 difference in the ability of the chain extenders to rebuild structure: 306% increase in the

11 complex viscosity of rPA6/ANHY compared to 25% in that of rPA6/EPOX of the base rPA6.

12 Mechanical and thermal (DSC and TGA) tests confirmed the superior efficacy of the

13 multifunctional anhydride chain extender. Beside the practical benefit that ensues from this

14 research, it also provides a strategic platform to develop chain extenders for other degrading

15 polymers on the basis of understanding the degradation chemical reaction and targeting the

16 most reactive end group of the split chains.

17 Keywords: *Extrusion*, *Recycling, Degradation, Polyamide, Reactive Processing*

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1. INTRODUCTION

26   PA6 or nylon 6 as it is commonly known is one of the earliest discovered and most

27 used thermoplastic polymers [1]. It is tough, possesses high tensile strength and is highly

28 resistant to abrasian as well as to chemicals. These properties make it suitable for a variety of

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applications and some 7 millions tons of it are currently used throughout the world [2]. As with all thermoplastics, PA6 is processed in extruders and injection molding machines that is heated above its melt temperature (220 ^{0}C) and then shaped into an appropriate form. The bulk (about 60%) of the PA6 produced is used in the textile industry as a substitute of natural fibers to manufacture cheaply priced domestic and industrial carpets in particular. The remaing 40% is taken up by the consumer goods industry to manufacture housewares, toys and sport equipments, the packaging industry to manufacture films and the automotive industry to make products such as as radiators, fans, inlet manifolds, engine covers, brake hoses, door handles and fuel lines. All these products have a short life and have led to a burgeoning PA6 waste recycling industry as landfilling has become more and more unacceptable in a world of decreasing resources and increasing demand for disposable goods. There is however a major limitation to the recycling of PA6; it degrades under repeated thermal and mechanical reprocessing that are particular to extrusion and injection molding and this causes the polymer chain to break (chain scission) [3]. Such thermal degradation results in a lowering of the molecular weight and consequently of the melt strength. The reduction of molecular weight is detrimental to good mechanical properties and a low melt strength makes extrusion and injection molding difficult [4]. The solution to this problem is to find a way of rebuilding the molecular weight. One approach is to use the well-established solid state polymerization technique [5] where the recycled polymer pellets are heated, before being extruded, below their melting point under a dry oxygen atmosphere and purging with an inert gas to remove the reaction by-products. Such pre-extrusion conditioning is very effective but unfortunately quite expensive in a recycling context. We propose here the more economical approach of chain extension in which a chemical -a chain extender- is added in very small quantities (~1%) to the recycled polymer pellets to re-link the broken chains whilst the mix is being extruded. We have applied this technique successfully to pristine (i.e. not recycled) PA6 and observed that with the right chain extender formulation even pristine PA6 polymer chains can be lengthened. The concept of chain extension is not new and has been applied with varying success to a range of pristine and recycled polymers, including polyethylene terephthalate (PET), polycarbonate (PC), polybutylene terephthalate (PBT) and polylactic acid) (PLA) (see for example work by Li and Huneault [6], Eslami and Kamal [7] and Carrasco et al. [8] to name a few). The key to a successful chain extension is the efficacy of the functionalities -the end groups of the chain extenders- in reacting with the end groups of the polymer chains, broken or pristine. As shown in Fig.1, the thermal degradation of PA6

follows two paths depending on whether or not water is present. In the absence of water as it is the case in practice during industrial extrusion, scission of the thermally weakest bond, the alkyl-amide linkage, occurs resulting in amide end group ($O=C-NH_2$) and vinyl end group (-$CH=CH_2$) smaller chains [9]. All the evidence to date from previous research and our most recent work [10] is that the amide functionality is the one which is the most reactive (see work by Loontjens and Plum [11], Buccella et al. [3] and Tuna [10]). Thus an effective chain extender for PA6 thermally degraded in the absence of water is one that has a high amide reactivity. We test this hypothesis in this paper using Joncryl[®] ADR 3400, a styrene maleic anhydride copolymer with multiple anhydride groups manufactured by BASF. To reinforce further the strength of our argument that during normal moisture-free extrusion of PA6, no peptide scission occurs, we shall also use a multi-epoxy functional chain extender, Joncryl[®] ADR 4300, also manufactured by BASF. Multi-epoxy functional chain extender are reactive with carboxyl end groups and the expectation is that we should find very little reactivity in this case. The structures of both chain extenders are shown in Table 1. The method of measuring the extent of the chain extension reaction with both will be via rheological measurements as these are a direct foot print of molecular weight rebuilding. In addition, we shall also measure the mechanical properties of the extrudates obtained as the expectation is that these properties will be enhanced upon molecular weight rebuilding. Finally, and to ascertain, that the chain reactions have occurred upon addition of the chain extenders to the recycled PA6, we shall carry out DSC measurements to detect changes in the melting endotherms and TGA measurements to measure the off-setting of degradation upon the addition of the chain extenders.

2. EXPERIMENTAL METHOD

2.1. Materials

This study seeks to assess extending the chains of recycled PA6 (rPA6). In order to have an accurate base line, we used pristin PA6 (pPA6), extruded it once and deemed the product to be representative of a recycle PA6. The pristine PA6 was grade Akulon F-136 purchased from DSM. It is specified as having a melt temperature of 235 °C and a nominal melt viscosity of 2250 Pa.s at 260 °C. For the chain extenders, the two Joncryl[®] ADR 3400 and 4300 discussed in the introduction and presented in Table 1 were used. They differ markedly in their structures (anhydride compared to epoxy), glass transition temperatures

(133 °C compared with 60 °C), densities (600 kg/m^3 compared with 1080 kg/m^3) and molecular weights (10,000 g/mol. compared with 6800 g/mol.)

2.2. Extrusion

The chain extension of the recycled PA6 was performed in a small scale intermeshing co-rotating twin screw extruder of 3kg/hr nominal output. The diameter, D of the screws measured 19mm and the screw length, L was 28D. This Baker Perkins APV MP19 TC28 extruder was flexible in its operation in that it was formed of five zones (feed -1st mixing - compression - 2nd mixing - pumping), the temperatures and screw designs of which could be independently controlled. For these experiments and in order to ensure good dispersive mixing of the chain extender into the polymer melt we used 12 paddles positioned at 90° in the first mixing zone and 8 paddles positioned also at 90 ° in the second mixing zone. As accurate feeding was critical to the operation, two separate conveying feeders were used, one for the polymer pellets and one for the chain extender granules, both suitably calibrated prior to the trials. Prior to the experiments, the polymer and chain extenders were dried in a vacuum oven at 80 °C for 12 hours to ensure that the thermal degradation proceeded as described in Fig.1, noting that degradation in the presence of water would require a different strategy with regard to the choice of the chain extender.

In the actual trials, first the dried pristine PA6 was extruded into a 3 mm string pulled through a cold water long trough and then pelletised to form the recycled PA6. This recycled pellets were then dried in a vacuum oven at 80°C for 12 hours ready for chain extension in the twin extruder. The chain extender-PA6 dosage was kept constant at 1wt.% deemed to be sufficient from previous work [10], noting that the stochiometry of the polymer chain extension reaction is such that very little chain extender is required. Also from preliminary trials, zones temperature profile of 230-260-260-260-260 °C and screw speed of 100rpm were found to produce stable extrusion conditions. Extrusion below 260 °C was limited by an up shot in the torque on the drive motor. Trials above 260 °C were not carried out to avoid any possibility of severe thermal degradation. Flow rates of the melt passing through the extruder were measured by collecting a length of the extrudate over a 5 minutes period then weighting. Such measurements were repeated at least five times to determine an accurate value of the flow rate which was found to be 3 kg/hr when the screw was run at 100 rpm. At this speed, the residence time measured with a carbon black tracer was found to be 62 s.

2.3. Characterization

The characterization of the extrudates obtained was carried out using rheological, mechanical and thermal properties measurements as described below.

Rheology: A Malvern Bohlin CVO120 rheometer was used in these experiments with a parallel plate geometery (25 mm diameter plates) at a gap size of 1 mm. As the purpose of these experiments was to assess the effect of the chain extender on molecular weight rebuilding, i.e. the effect on structure, it was important to operate in the linear viscoelastic region so rather than destroying the structure with too much strain it was mildly deformed to pick out the slightest variation in the way it resisted deformation. An amplitude sweep determined that 0.1% strain was suitable. Then at this strain, frequency sweep tests were conducted across a frequency range of 0.1 to 100 Hz. For accuracy, the measurements were performed with three different samples of the same extrudate in each case (recycled, recycled+chain extender). The errors in the measurements were found to vary between 0.2 and 5.7%.

Mechanical Properties: A Messphysik Beta tensile instrument was used in these experiments with a 20 kN load at a cross-head speed of 5 mm/min with the strain measured using a video extensometer. Dumbbell shaped specimens were made by first molding samples of the extrudates at 240 °C in a hydraulic press (Moore Ltd, UK) under 300 MPa for 2 min then, after cooling to 30 °C, cutting them into the appropriate dumbbell shape using a Metaserv Instrument. To reduce experimental errors, at least five samples of the same extrudate in each case (recycled, recycled+chain extender) were used in the experiments. The data reported here and presented later provide the average results with standard deviations.

Thermal Properties: A TA Instruments Discovery Differential Scanning Calorimetry (DSC) was used to obtain the thermograms for heating-cooling-heating cycles of 25 °C→260 °C→25 °C→260 °C at a rate of 10 °C/min. under a nitrogen purge. From these thermograms, the glass transition (T_g), the melt temperature (T_m), the enthapy of melting (ΔH_m) were directly obtained. The degree of crystallinity (X_c) of the samples was calculated using:

$$\chi_c = \frac{\Delta H_m}{\omega \Delta H_m^o} \tag{1}$$

1   ΔH_m^o being the enthalpy of fusion for 100% crystalline PA6, taken here to be equal to 240 J/g

2   [12] and ω is weight fraction of PA6 used.

3   As for thermal decomposition, a TA Instruments Discovery Thermo-Gravimetric Analyzer

4   (TGA) was used to measure the rate of mass change of a 10 mg extrudate sample being

5   heated, under a nitrogen purge, from 25 to 600 °C at a heating rate of 10 °C/min. from which

6   measured mass change and the rate of mass change as a function of temperature, time and

7   atmosphere were obtained.

8   **RESULTS and DISCUSSION**

9   **3.1. Rheology**

10   Figs.2 and 3 present the data on how the structure deforms in the linear viscoelastic

11   region upon increases of frequency, the idea being to infer the effect of the chain extender on

12   molecular rebuilding by measuring variation in the values of the complex viscosity and

13   storage modulus. The focus here must be the data at the lowest frequency as clearly upon

14   higher frequencies the structure is destroyed and the effect cannot be discerned as well. The

15   data clearly show the reduction of the complex viscosity and storage modulus of PA6 as it is

16   being recycled. A complex viscosity of 1321 is measured for rPA6 compared to 2584 for

17   pPA6 at a frequency of 0.1 Hz. More striking however is the very positive chain extension

18   effect of Joncryl[®] ADR 3400, the chain extender with the multiple anhydride functionalities.

19   Although both chain extenders rebuild structure of the recycled PA6, comparatively, Joncryl[®]

20   ADR 4300, the chain extender with epoxy functionalities, shows poor performance as shown

21   in Figs.2 and 3. Taking as a base line, 0.1 Hz frequency, we observe the following values of

22   η^*: 2584 Pa.s for pPA6, 1321 Pa.s for the rPA6, 1653 Pa.s (25%increase) for rPA6/EPOX and

23   4037 Pa.s (306% increase) for rPA6/ANHY. Thus Joncryl[®] ADR 3400, the chain extender

24   with the multiple anhydride functionalities, not only rebuilds rPA6, it actually extends it

25   beyond the structure of the pristine pPA6. Joncryl[®] ADR 4300, the chain extender with the

26   epoxy functionalities does rebuild rPA6 but not even back to the level of the pristine pPA6. It

27   is noted here that Villalobos et al. [13] used also an epoxy functionalized chain extender,

28   Joncryl[®] ADR 4368 with PA6 (pristine not recycled) and reported a 107% enhancement in

29   melt shear viscosity which cannot be compared with our data expressed here as complex

30   viscosity.

The evidence is the same when we observe the data of Fig.3 which gives the storage modulus. This is not surprising as the complex viscosity and storage modulus are related. Specifically, we observe the following values of G' at 0.1Hz: 85 Pa for pPA6, 36.8 Pa for rPA6, as expected a reduction, here of 43%, 40.7 Pa for rPA6/EPOX, a small increase of 10% and 435.5 Pa for rPA6/ANHY, a leap of 368% on the base rPA6.

3.2. Mechanical Properties

Naturally, there is a close link between structure and mechanical properties. So any degradation or molecular rebuilding should be traced in the mechanical properties measured. It is important to note that we should not expect the very large extent of change measured in rheology. This is because in rheological measurements the deformation is in the melt phase. With the mechanical testing, the deformation is in the solid phase, requiring larger stresses. Figs.4a, b and c provide the appropriate tensile modulus, yield strength and yield strain data of the samples investigated here. The increase in the tensile modulus and yield strength of rPA6/ANHY and the essentially no change in rPA6/EPOX supports the rheological data and the conclusion on the efficacy of the chain extender with anhydride rather than epoxy functionalities.

With regard to yield strain, the data presented in Fig. 4c show a small but measurable difference in the samples, with rPA6/ANHY yielding the least strain (3%). A similar behaviour was previously reported [14-16]. Accordingly, multifunctional chain extenders result in long chain branching which increases entanglement density of the polymer structure and restricts orientation of polymer chains upon elongation. Such restriction during elongation leads to a decrease in strain values. Contrary to this, rPA6 showed the highest value of yield strain. The formation of shorter chains after thermal degradation results in larger mobility of polymer chains thus elongation increases.

3.3. Thermal Properties

As chain extension, if it occurs, would theoretically result in a larger volume being occupied by the polymer and also in the way the new polymer would crystallize, DSC data should reflect this in changes in the glass transition (T_g), the melt temperature (T_m), the enthapy of melting (ΔH_m) and the degree of crystallinity (X_c). The data of Fig.5 and Table 2 show these changes to be measurable but marginal only. The change in the endotherms (the

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shoulder), although small, is clear, explaining that chain extension did occur. This feature corresponds to the melting of γ (at around 209 ^{o}C) and α crystalline (at around 222 ^{o}C) phases [17]. These two major crystalline forms are typical polymorphism features of PA6. Here, the incorporation of chain extenders into PA6 promotes the formation of the γ crystalline phase [18,19]. The chain extenders slightly decreased the crystallinity of PA6 suggesting the packing of PA6 chains to form a crystal lattice is hindered by the chain extension and/or branching. Similar observations regarding the effect of chain extender on the crystallization behaviour of polymers were previously reported [3,16,20]. The recycled PA6 showed a lower T_g than the virgin PA6 and this can be explained by the larger free volume of chain ends enabling higher segmental mobility [21]. Contrary to that, rPA6/EPOX and rPA6/ANHY presented higher T_g than rPA6 due to the recoupling of the degraded chain ends.

The data obtained with TGA are presented in Fig.6. They show clearly that reprocessing of PA6, i.e. rPA6 exhibits more thermal degradation than pPA6. Also, we see that of the two chain extenders, the anhydride functionalized type performed better at compensating thermal degradation. This support the rheological and mechanical data presented earlier.

4. CONCLUSIONS

Recycled PA6 like many other polymers suffers thermo-mechanical degradation during re-extrusion and makes its recycling problematic. This degradation under normal moisture free conditions is due to the scission of PA6 $[NH-(CH_2)_5-CO]_n$ into smaller chains with amide $(O=C-NH_2)$ and vinyl $(-CH=CH_2)$ end groups. Here we presented an effective and economical strategy to offset degradation-the addition to the recycled polymer of a chemical extender with the *appropriate* functionality. Anhydride multifunctionality as evidenced from the rheological and mechanical properties data of this study was found to be extremely effective in rebuilding the structure of degraded PA6. Using controlled experiments in which we used pristine PA6, pPA6, extruded it once to produce a base line recycle PA6, rPA6 and compounded it with an anhydride multifunctional chain extender to produce rPA6/ANHY we found a 306% increase in the complex viscosity of rPA6/ANHY compared to rPA6. In comparison, rPA6/EPOX made with an epoxy multifunctional chain extender that targetted carboxylic end group barely increased in the complex viscosity (25%). This is proof that hydrolytic peptide scission is not the dominant degradation reaction of PA6 in industrial moisture-

free extrusion recycling. Mechanical properties, the tensile modulus in particular, further backed the findings that anhydride multifunctional chain extenders are the best suited to rebuild PA6 degraded structure. From a chemical reaction perspective, the DSC data gave further proof of the chain extension reaction occuring through a change in the crystallization endotherm. Finally, the TGA traces confirmed further the efficacy of the anhydride chain extender over the epoxy chain extender. The important overall conclusion is that the strategy for an effective chain extension of degraded polymers is first to establish the reaction that is occuring during degradation to identify the end groups of the broken chains and then develop chain extenders with functionalities that have good reactivity with these end groups.

5. ACKNOWLEDGEMENTS

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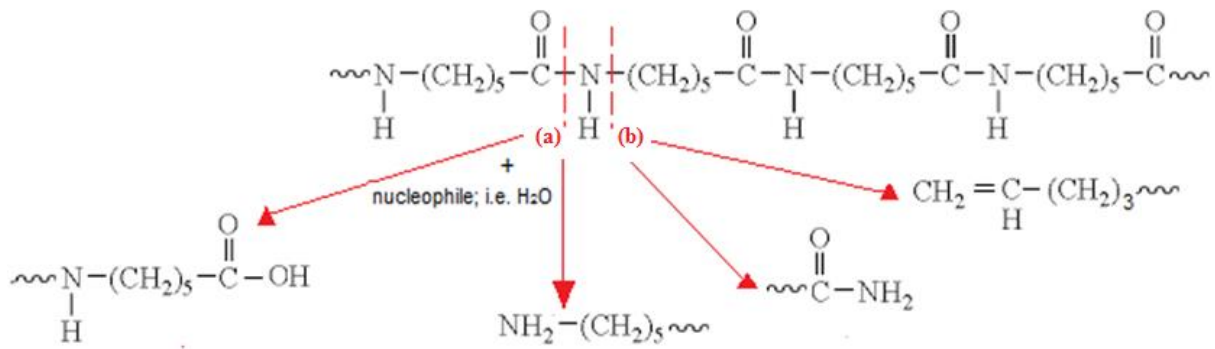
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FIGURE CAPTIONS

Fig.1: Thermal degradation mechanisms of PA6: (a) in the presence of a nucleophile, particularly water, (b) in the absence a nucleophile
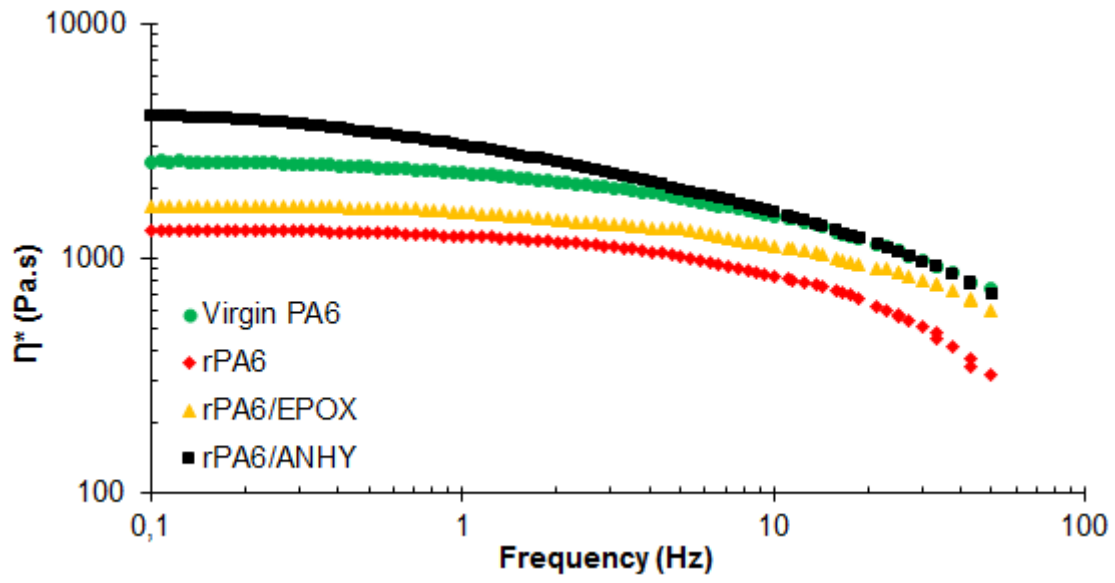
Fig.2: Complex viscosity η^* vs. frequency

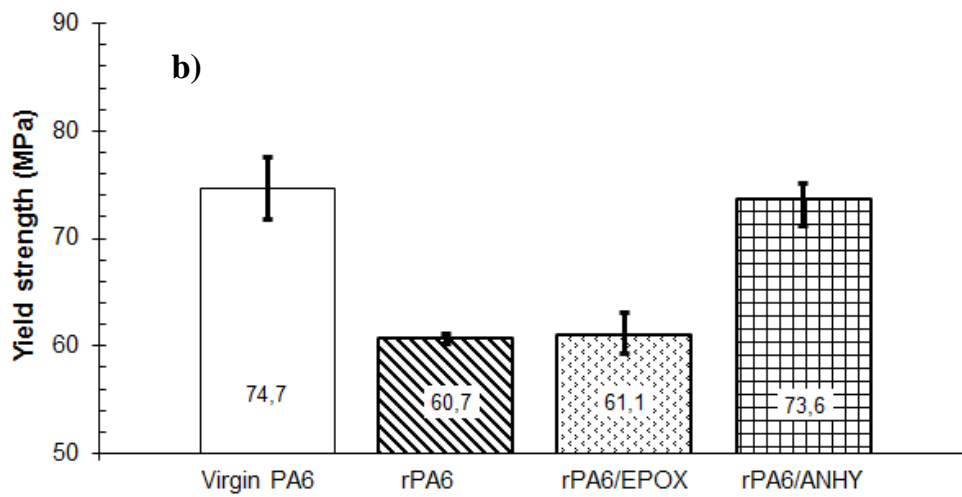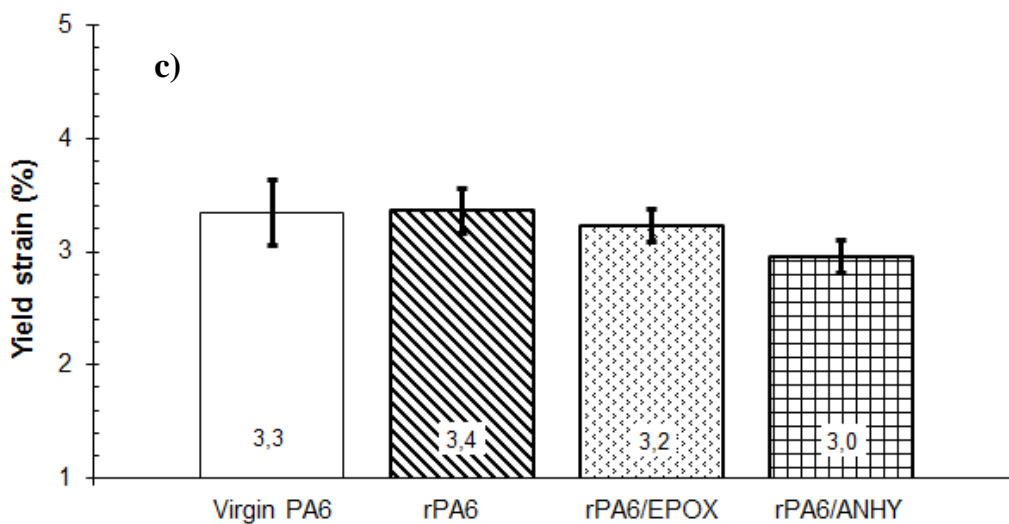1   **Fig.3**: Storage modulus G' vs. frequency

2   **Fig.4:** a) Tensile modulus, b) yield strength and c) yield strain data

3   **Fig.5:** DSC heating thermograms

4   **Fig.6:** TGA curves

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Fig.1: Thermal degradation mechanisms of PA6: (a) in the presence of a nucleophile, particularly water, (b) in the absence a nucleophile

Fig.2: Complex viscosity η^{*} vs. frequency

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Fig.3: Storage modulus G' vs. frequency

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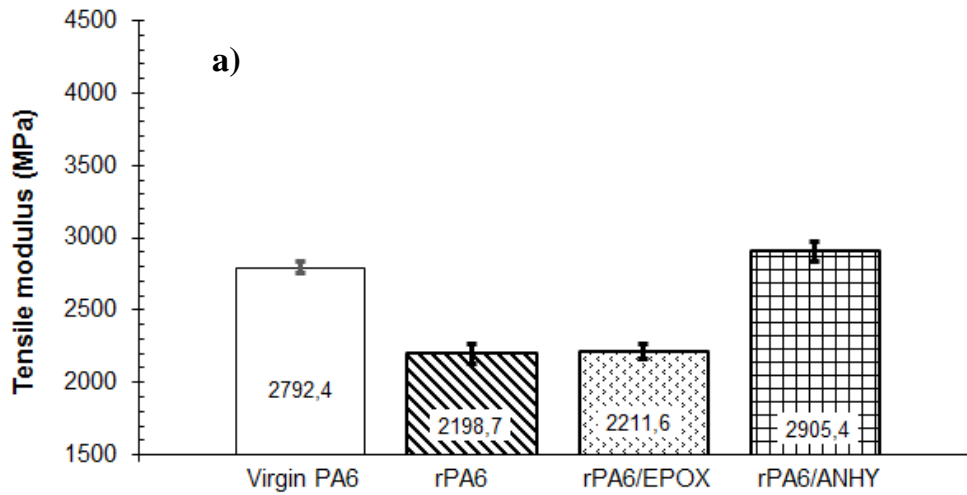
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4   **Fig.4:** a) Tensile modulus, b) yield strength and c) yield strain data
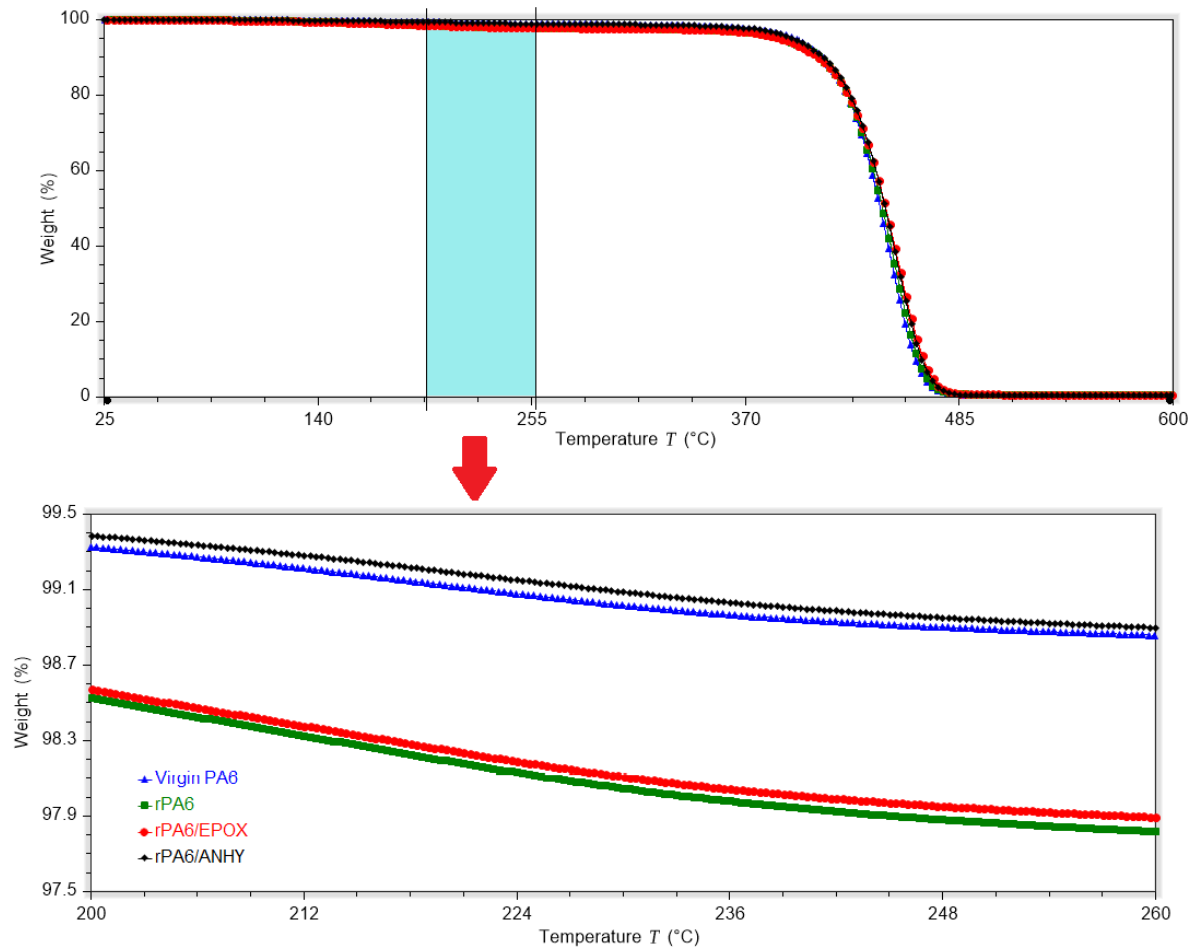
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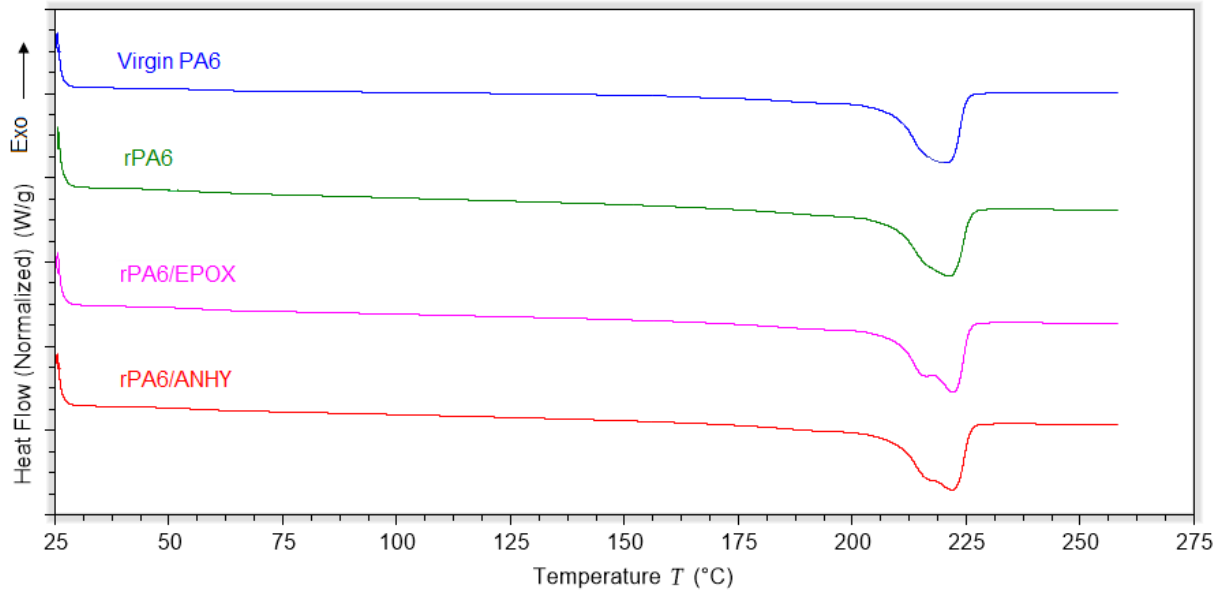
Fig.5: DSC heating thermograms
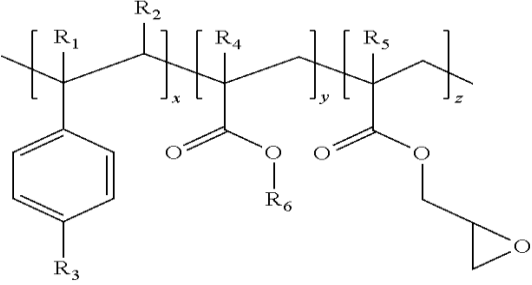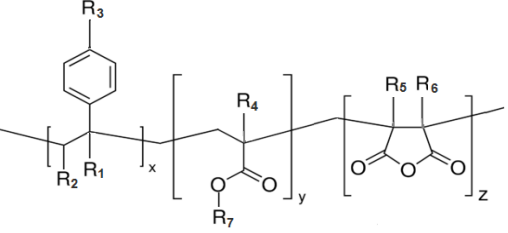
Fig.6: TGA curves

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1   **Table 1:** Chemical structure of Joncryl epoxy and anhydride chain extenders

Chain extender	Chemical structure
Joncryl® ADR 4300	R1-R6 are H, CH₃, a higher alkyl group or combinations of them; R7 is an alkyl group and x, y and z are all between 1 and 20.
Joncryl® ADR 3400	R1-R5 are H, CH₃, a higher alkyl group or combinations of them; R6 is an alkyl group and x, y and z are all between 1 and 20.

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1   **Table 2:** Thermal properties of virgin PA6, rPA6 and rPA6-chain extenders

Sample	T_g (^{o}C)	T_m (^{o}C)	T_c (^{o}C)	X_c (%)	T_{onset} (^{o}C)
Virgin PA6	53.7	221.1	188.4	20.2	395.9
rPA6	51.8	221.5	187.9	19.7	389.2
rPA6/EPOX	52.8	208.4/222.6	187.5	18.2	388.7
rPA6/ANHY	54.9	209.2/222.2	188.1	18.2	396.0

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