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CHAIN EXTENSION OF RECYCLED PA6

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ABSTRACT

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Recycling of polymers is a necessity in our intensively consuming polymer world but the nature of polymers is such that they are prone to thermal degradation when re-extruded and this poses technical challenges to recycling. This papers describes research that seeks to rebuild the structure of degraded PA6. We present data from controlled experiments with pristine pPA6 extruded to form a base recycle rPA6 to which we added two chain extenders, separately: one with anhydride multifunctionality (ANHY), highly reactive with amide groups and one with epoxy multifunctionality (EPOX), less reactive. We found from rheological data carried out in the linear viscoelastic region (so as to study structural changes) a striking difference in the ability of the chain extenders to rebuild structure: 306% increase in the complex viscosity of rPA6/ANHY compared to 25% in that of rPA6/EPOX of the base rPA6. Mechanical and thermal (DSC and TGA) tests confirmed the superior efficacy of the multifunctional anhydride chain extender. Beside the practical benefit that ensues from this research, it also provides a strategic platform to develop chain extenders for other degrading polymers on the basis of understanding the degradation chemical reaction and targeting the most reactive end group of the split chains.

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

1. INTRODUCTION

PA6 or nylon 6 as it is commonly known is one of the earliest discovered and most used thermoplastic polymers [1]. It is tough, possesses high tensile strength and is highly resistant to abrasian as well as to chemicals. These properties make it suitable for a variety of

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

1 follows two paths depending on whether or not water is present. In the absence of water as it
2 is the case in practice during industrial extrusion, scission of the thermally weakest bond, the
3 alkyl-amide linkage, occurs resulting in amide end group ($\text{O}=\text{C}-\text{NH}_2$) and vinyl end group ($-\text{CH}=\text{CH}_2$)
4 smaller chains [9]. All the evidence to date from previous research and our most
5 recent work [10] is that the amide functionality is the one which is the most reactive (see work
6 by Loontjens and Plum [11], Buccella et al. [3] and Tuna [10]). Thus an effective chain
7 extender for PA6 thermally degraded in the absence of water is one that has a high amide
8 reactivity. We test this hypothesis in this paper using Joncryl[®] ADR 3400, a styrene maleic
9 anhydride copolymer with multiple anhydride groups manufactured by BASF. To reinforce
10 further the strength of our argument that during normal moisture-free extrusion of PA6, no
11 peptide scission occurs, we shall also use a multi-epoxy functional chain extender, Joncryl[®]
12 ADR 4300, also manufactured by BASF. Multi-epoxy functional chain extenders are reactive
13 with carboxyl end groups and the expectation is that we should find very little reactivity in
14 this case. The structures of both chain extenders are shown in Table 1. The method of
15 measuring the extent of the chain extension reaction with both will be via rheological
16 measurements as these are a direct footprint of molecular weight rebuilding. In addition, we
17 shall also measure the mechanical properties of the extrudates obtained as the expectation is
18 that these properties will be enhanced upon molecular weight rebuilding. Finally, and to
19 ascertain, that the chain reactions have occurred upon addition of the chain extenders to the
20 recycled PA6, we shall carry out DSC measurements to detect changes in the melting
21 endotherms and TGA measurements to measure the off-setting of degradation upon the
22 addition of the chain extenders.

23 **2. EXPERIMENTAL METHOD**

24 **2.1. Materials**

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

1 (133 °C compared with 60 °C), densities (600 kg/m³ compared with 1080 kg/m³) and
2 molecular weights (10,000 g/mol. compared with 6800 g/mol.)

3 **2.2. Extrusion**

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

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

1 2.3. Characterization

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

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

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

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

28
$$\chi_c = \frac{\Delta H_m}{\omega \Delta H_m^o} \quad (1)$$

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 Joncryn[®] ADR 3400, the chain extender with the multiple anhydride functionalities.
19 Although both chain extenders rebuild structure of the recycled PA6, comparatively, Joncryn[®]
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 Joncryn[®] 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. Joncryn[®] 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 Joncryn[®] 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.

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

6 **3.2. Mechanical Properties**

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

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

25 **3.3. Thermal Properties**

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

1 shoulder), although small, is clear, explaining that chain extension did occur. This feature
2 corresponds to the melting of γ (at around 209 °C) and α crystalline (at around 222 °C) phases
3 [17]. These two major crystalline forms are typical polymorphism features of PA6. Here, the
4 incorporation of chain extenders into PA6 promotes the formation of the γ crystalline phase
5 [18,19]. The chain extenders slightly decreased the crystallinity of PA6 suggesting the
6 packing of PA6 chains to form a crystal lattice is hindered by the chain extension and/or
7 branching. Similar observations regarding the effect of chain extender on the crystallization
8 behaviour of polymers were previously reported [3,16,20]. The recycled PA6 showed a lower
9 T_g than the virgin PA6 and this can be explained by the larger free volume of chain ends
10 enabling higher segmental mobility [21]. Contrary to that, rPA6/EPOX and rPA6/ANHY
11 presented higher T_g than rPA6 due to the recoupling of the degraded chain ends.

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

17 4. CONCLUSIONS

18 Recycled PA6 like many other polymers suffers thermo-mechanical degradation
19 during re-extrusion and makes its recycling problematic. This degradation under normal
20 moisture free conditions is due to the scission of PA6 $[\text{NH}-(\text{CH}_2)_5-\text{CO}]_n$ into smaller chains
21 with amide ($\text{O}=\text{C}-\text{NH}_2$) and vinyl ($-\text{CH}=\text{CH}_2$) end groups. Here we presented an effective and
22 economical strategy to offset degradation-the addition to the recycled polymer of a chemical
23 extender with the *appropriate* functionality. Anhydride multifunctionality as evidenced from
24 the rheological and mechanical properties data of this study was found to be extremely
25 effective in rebuilding the structure of degraded PA6. Using controlled experiments in which
26 we used pristine PA6, pPA6, extruded it once to produce a base line recycle PA6, rPA6 and
27 compounded it with an anhydride multifunctional chain extender to produce rPA6/ANHY we
28 found a 306% increase in the complex viscosity of rPA6/ANHY compared to rPA6. In
29 comparison, rPA6/EPOX made with an epoxy multifunctional chain extender that targetted
30 carboxylic end group barely increased in the complex viscosity (25%). This is proof that
31 hydrolytic peptide scission is not the dominant degradation reaction of PA6 in industrial moisture-

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

10 **5. ACKNOWLEDGEMENTS**

11 The authors acknowledge BASF, Germany for supplying Joncryl[®] ADR 4300 and
12 Joncryl[®] ADR 3400.

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23 **6. REFERENCES**

24 1. M. Kohan, *Nylon Plastics Handbook*, Hanser Publishers, Cincinnati, (1995).

25 2. M. Scheibitz, R. Kaneko and P. Spies, *Kunstst. Int.*, **10**, 40-44 (2016).

- 1 3. M. Buccella, A. Dorigato, E. Pasqualini, M. Caldara, and L. Fambri, *Polym. Eng. Sci.*,
2 **54**, 158–165 (2014).
- 3 4. I. Goitisoló, J.I. Eguizabal, and J. Nazabal, *Polym. Degrad. Stab.*, **93**, 1747-1752
4 (2008).
- 5 5. J. Scheirs and T.E. Long, *Modern Polyesters: Chemistry and Technology of Polyesters
6 and Copolyesters*, John Wiley & Sons, Sussex, (2003).
- 7 6. H. Li, and M.A. Huneault, *J. Appl. Polym. Sci.*, **122**, 134–141 (2011).
- 8 7. H. Eslami, and R.M. Kamal, *J. Appl. Polym. Sci.*, **129**, 2418-2428 (2013).
- 9 8. F. Carrasco, J. Cailloux, P.E. Sánchez-Jiménez, and M.L. MasPOCH, *Polym. Degrad.
10 Stab.*, **104**, 40-49 (2014).
- 11 9. S.V. Levchik, E.D. Weil, and M. Lewin, *Polym. Int.*, **48**, 532-557 (1999).
- 12 10. B. Tuna, Chain extension of polyamide-6 and polyamide-6/organoclay
13 nanocomposites, Ph.D. Thesis, University of Bradford (2016).
- 14 11. J.A. Loontjens, and B.J.M. Plum, U.S. Patent, 6,228,980 B1 (2001).
- 15 12. E. Logakis, C. Pandis, V. Peoglos, P. Pissis, C. Stergiou, J. Pionteck, P. Potschke, M.
16 Micusik, and M. Omastova, *J. Polym. Sci. Pol. Phys.*, **47**, 764-774 (2009).
- 17 13. M. Villalobos, A. Awojulu, T. Greeley, G. Turco, and G. Deeter, *Energy*, **31**, 3227–
18 3234 (2006).
- 19 14. N. Najafi, M.C. Heuzey, and P.J. Carreau, *Compos. Sci. Technol.*, **72**, 608-615 (2012).
- 20 15. R. Al-Itry, K.S. Lamnawar, and A. Maazouz, *Polym. Degrad. Stab.*, **97**, 1898-1914
21 (2012).
- 22 16. A. Ghanbari, M.C. Heuzey, P.J. Carreau, and M.T. Ton-That, *Polymer*, **54**, 1361-1369
23 (2013).
- 24 17. D. Garcia-Lopez, J.F. Fernandez, J.C. Merino, J. Santaren, and J.M. Pastor, *Compos.
25 Sci. Technol.*, **70**, 1429-1436 (2010).
- 26 18. T.D. Fornes, and D.R. Paul, *Polymer*, **44**, 3945-3961 (2003).

- 1 19. S. Xie, S. Zhang, H. Liu, G. Chen, M. Feng, H. Qin, F. Wang, and F. Yang, *Polymer*,
2 **46**, 5417-5427 (2005).
- 3 20. C. Lu, R. Ye, Y. Yang, X. Ren, and X. Cai, *J. Macromol. Sci. Phys.*, **50**, 350-362
4 (2015).
- 5 21. G. Fox, and P.J. Flory, *J. Appl. Phys.*, **21**, 581-591 (1950).

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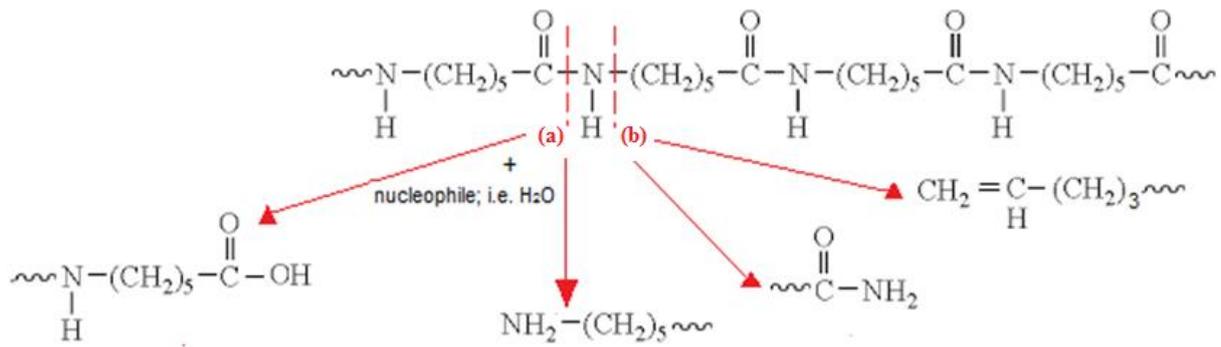
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149 **FIGURE CAPTIONS**

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

152 **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

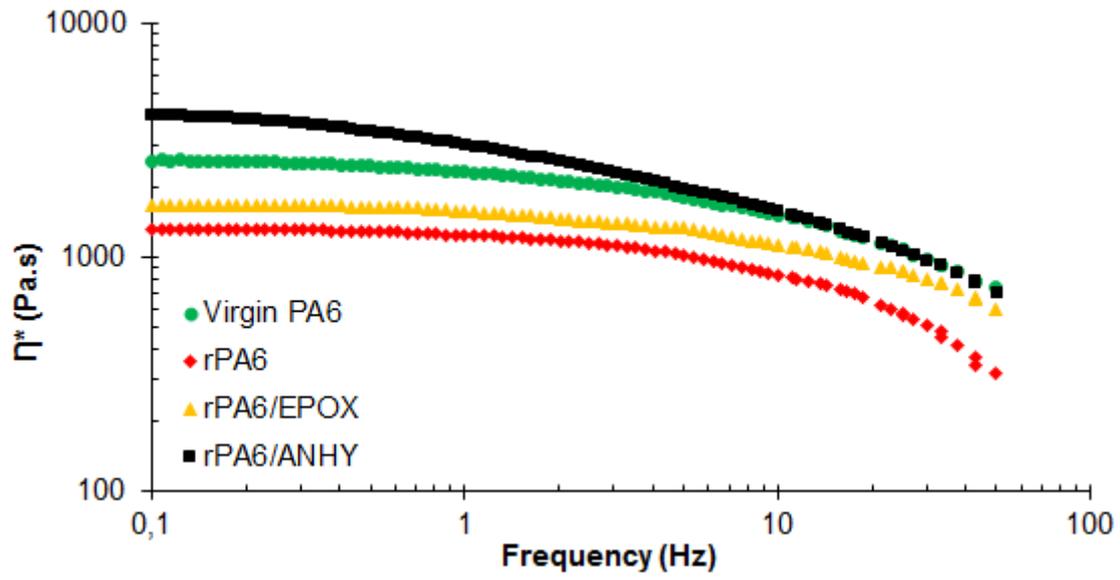


Fig.2: Complex viscosity η^* vs. frequency

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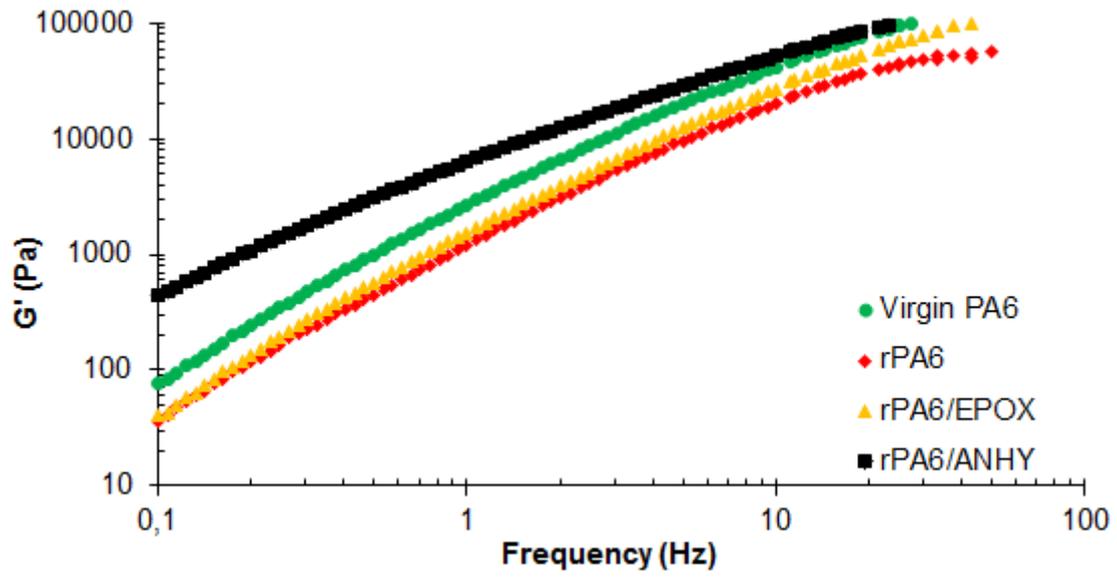
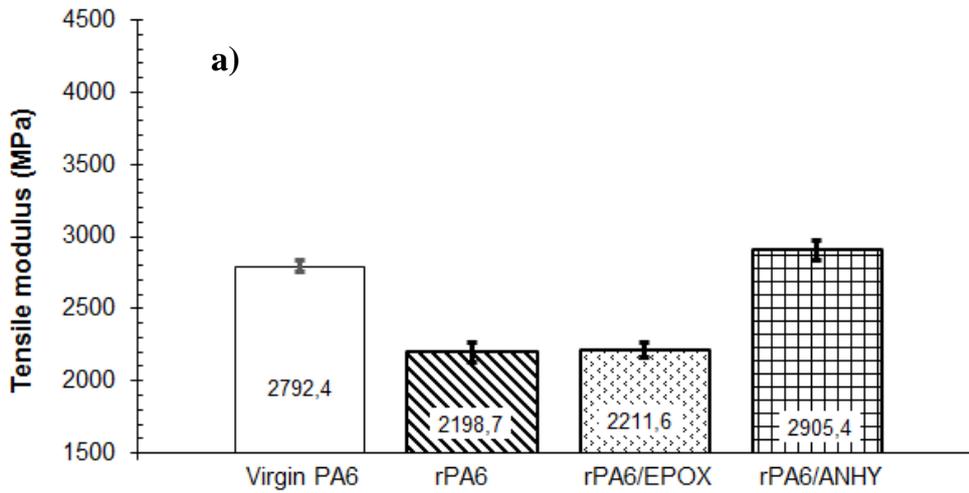
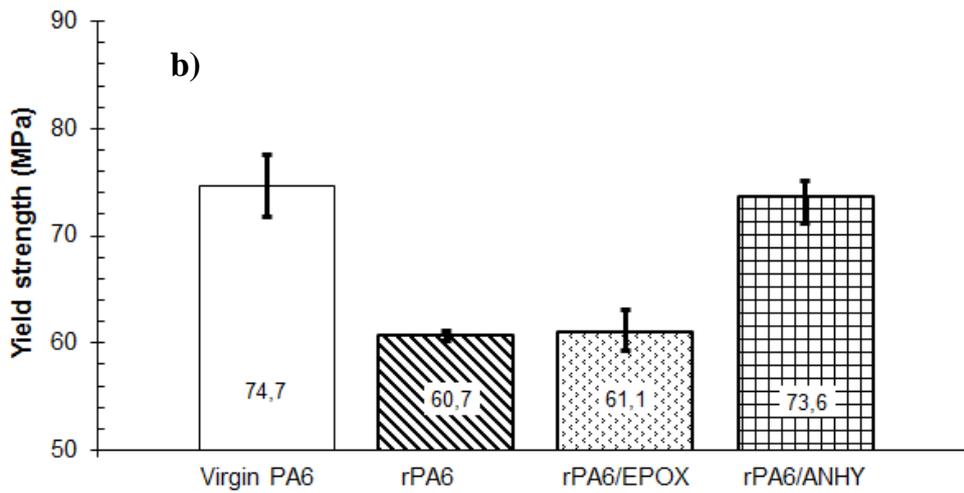


Fig.3: Storage modulus G' vs. frequency

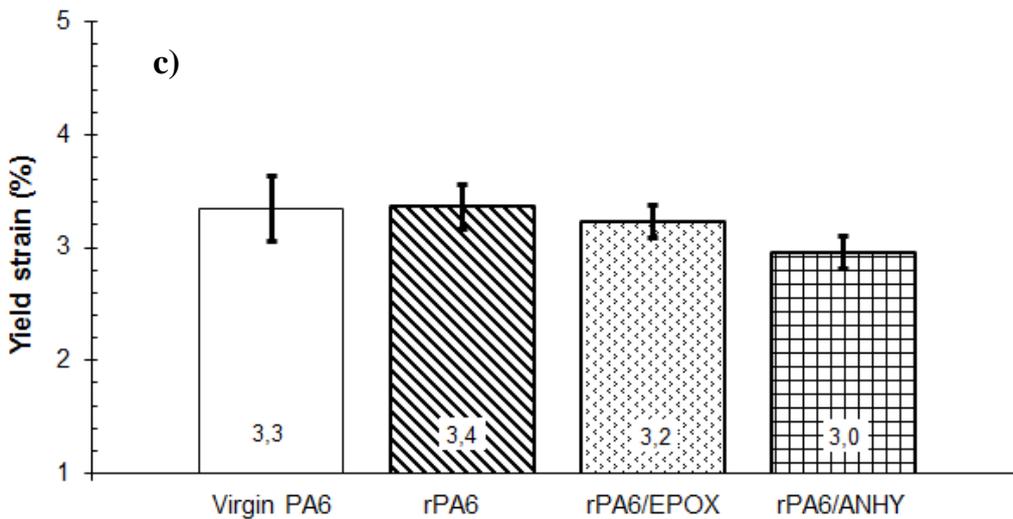
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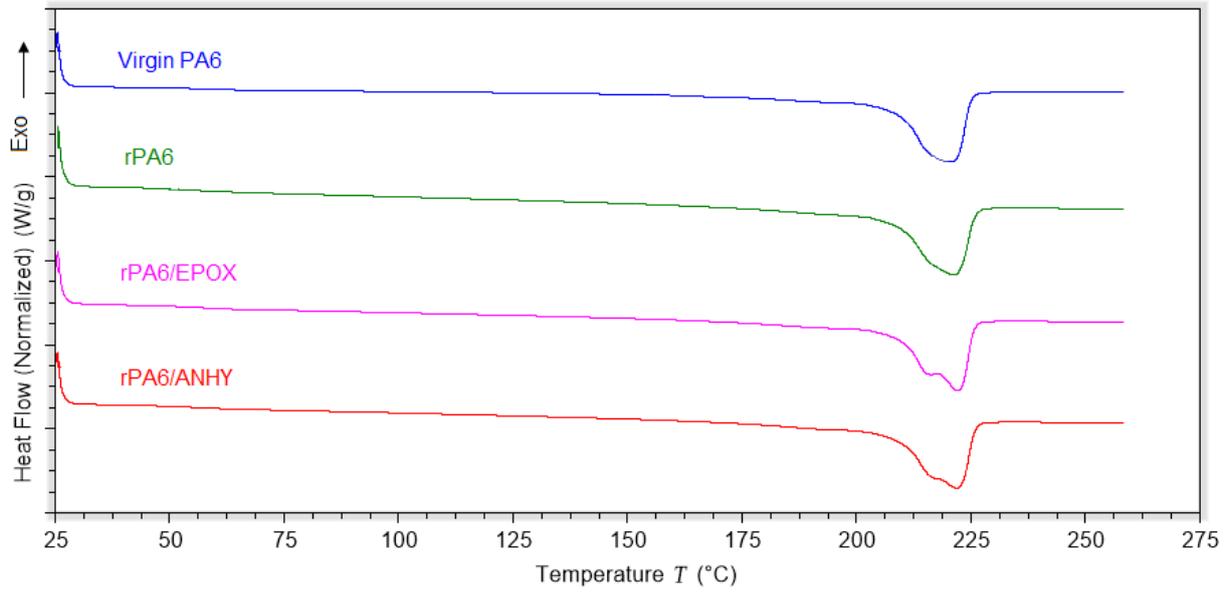


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Fig.4: a) Tensile modulus, b) yield strength and c) yield strain data

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Fig.5: DSC heating thermograms

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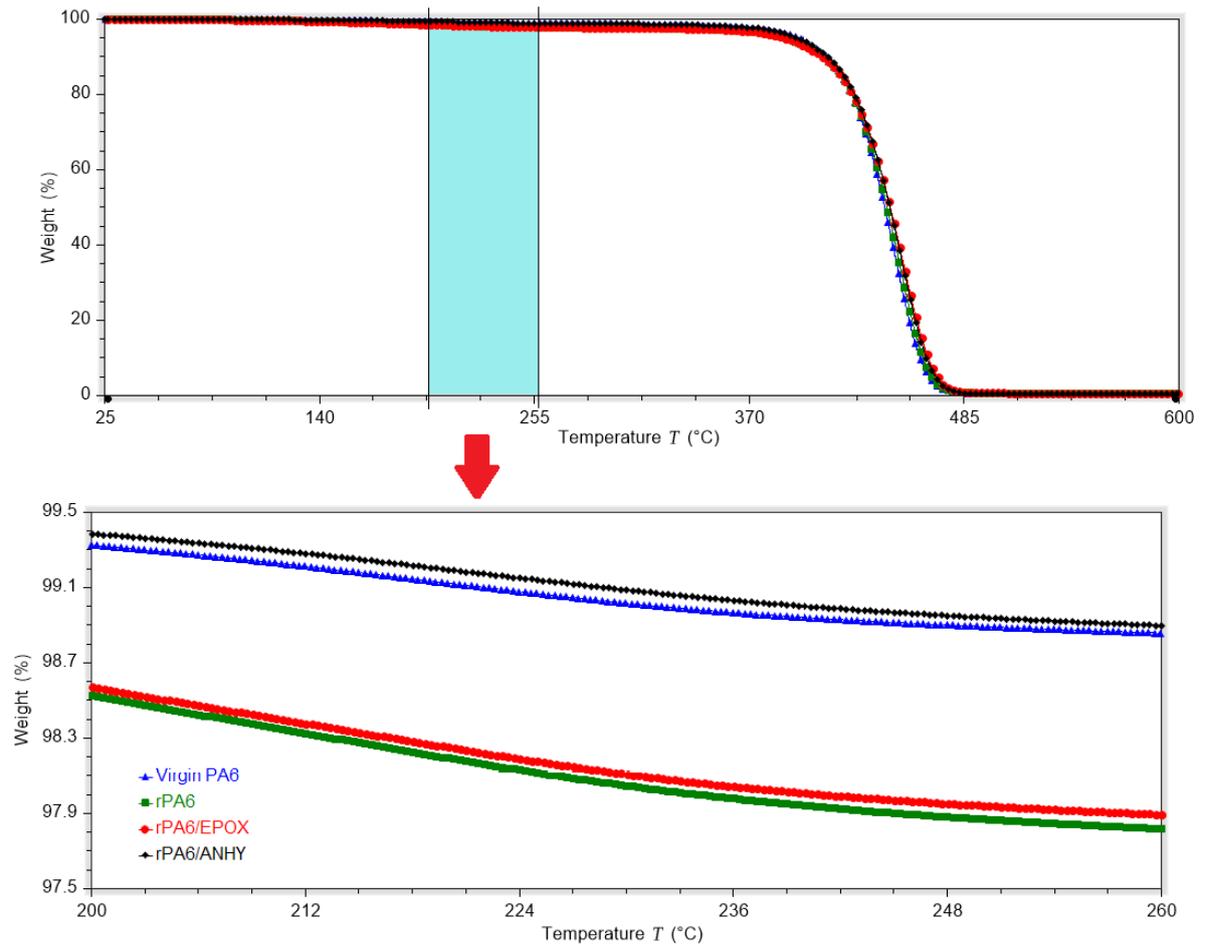
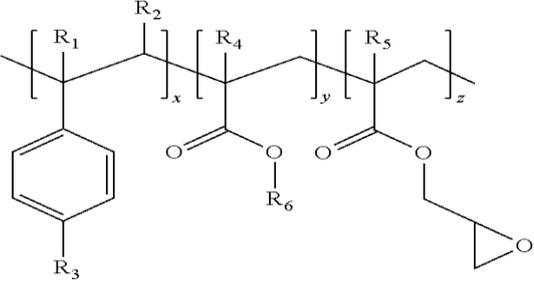
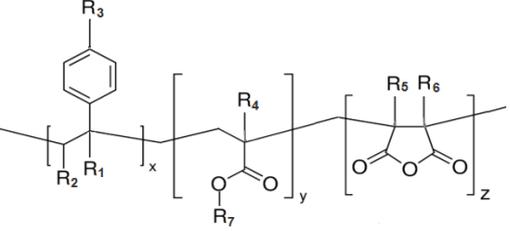


Fig.6: TGA curves

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

Chain extender	Chemical structure
Joncryl [®] ADR 4300	 <p>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.</p>
Joncryl [®] ADR 3400	 <p>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.</p>

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

Sample	T_g (°C)	T_m (°C)	T_c (°C)	X_c (%)	T_{onset} (°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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