



Accelerated ageing behaviour of poly ether block amide (PEBAX) and polybutylene terephthalate polyester (arnitel) thermoplastic elastomers

Ullah, J., Dixon, D., Saifullah, A. N. M., Doohar, T., & Magee, C. (2023). Accelerated ageing behaviour of poly ether block amide (PEBAX) and polybutylene terephthalate polyester (arnitel) thermoplastic elastomers. In A. Aji, F. Mighri, & H. E. Naguib (Eds.), *PROCEEDINGS OF THE 36TH CONFERENCE OF THE POLYMER PROCESSING SOCIETY – PPS36* (1 ed., Vol. 2607, pp. 090001-1 - 090001-4). Article 090001 (AIP Conference Proceedings; Vol. 2607). AIP Publishing. <https://doi.org/10.1063/5.0135938>

[Link to publication record in Ulster University Research Portal](#)

Published in:

PROCEEDINGS OF THE 36TH CONFERENCE OF THE POLYMER PROCESSING SOCIETY – PPS36

Publication Status:

Published (in print/issue): 23/05/2023

DOI:

<https://doi.org/10.1063/5.0135938>

Document Version

Publisher's PDF, also known as Version of record

General rights

Copyright for the publications made accessible via Ulster University's Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Ulster University's institutional repository that provides access to Ulster's research outputs. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact pure-support@ulster.ac.uk.

RESEARCH ARTICLE | MAY 23 2023

Accelerated ageing behaviour of poly ether block amide (PEBAX) and polybutylene terephthalate polyester (arnitel) thermoplastic elastomers

Jawad Ullah ; Dorian Dixon; Abu Saifullah; Thomas Dooher; Ciaran Magee



AIP Conf. Proc. 2607, 090001 (2023)

<https://doi.org/10.1063/5.0135938>



CrossMark

Articles You May Be Interested In

Pure And Modified Co-poly(amide-12-b-ethylene oxide) Membranes For Gas Separation Studied By Molecular Investigations

AIP Conference Proceedings (October 2010)

Preparation and characterization of polybutylene succinate (PBS) and polybutylene adipate-terephthalate (PBAT) biodegradable blends

AIP Conference Proceedings (July 2018)

Development of a bead foam based on the engineering polymer polybutylene terephthalate

AIP Conference Proceedings (January 2019)

500 kHz or 8.5 GHz?
And all the ranges in between.

Lock-in Amplifiers for your periodic signal measurements



Find out more



Accelerated Ageing Behaviour of Poly Ether Block Amide (PEBAX) and Polybutylene Terephthalate Polyester (Arnitel) Thermoplastic Elastomers

Jawad Ullah^{1, 2, a)}, Dorian Dixon^{1, 2}, Abu Saifullah³, Thomas Dooher⁴, Ciaran Magee⁵

¹*School of Engineering, University of Ulster, Jordanstown, BT37 0QB, Northern Ireland, United Kingdom*

²*NIBEC, School of Engineering, University of Ulster, Jordanstown, BT37 0QB, Northern Ireland, United Kingdom*

³*School of Mechanical and Design Engineering, University of Portsmouth, PO1 3DJ, United Kingdom*

⁴*Northern Ireland Advanced Composites and Engineering Centre, BT3 9DZ - Northern Ireland, United Kingdom*

⁵*Armstrong Medical, Coleraine Co. Londonderry, BT52 1BS - Northern Ireland, United Kingdom*

a) Corresponding author: jawadullah15@gmail.com

Abstract. The thermoplastic elastomers-PEBAX (PA1074) and two grades of Arnitel (VT3108, VT7812) which are commonly used in a range of medical devices, were aged at temperatures of 40 -100°C for a period of up-to 324 days, and at 60°C with elevated humidity. Understanding the effects of ageing on the behaviour of these thermoplastic elastomers used commonly in safety medical applications is crucial. The samples were characterised during ageing via mechanical testing, TGA (Thermogravimetric analysis) and DSC (Differential scanning calorimetry). It was observed that the samples discoloured during ageing with greater changes being observed at the higher ageing temperatures. The materials also displayed an increase in brittleness as a result of ageing, with the PEBAX showing more pronounced changes compared to the two grades of Arnitel tested.

INTRODUCTION

PEBAX (poly ether block amide) and Arnitel are thermoplastic elastomer copolymers which display similar elasticity to natural rubber. These polymers can be easily processed using conventional processing techniques such as extrusion and injection moulding¹. The block copolymer PEBAX consists of polyamide (PA) as the hard phase and a polyethylene oxide (PEO) which is poly ether, as the soft phase. The block copolymer Arnitel consists of polybutylene terephthalate (PBT) as the hard segment alternating with a soft segment on the polymer backbone. The presence of the soft segments in the copolymers make them inherently flexible. Both of these thermoplastic copolymers are used in various applications including permeable membranes, sportswear and power transmission belts¹. These materials are also used in the medical industry for breathable tubes and in angioplasty catheter balloons.

It is crucial to understand the ageing behaviour of materials that are to be used in critical medical parts. The medical device regulations (FDA and EU) also require data supporting the manufacturer's claimed shelf life. It is not commercially realistic to do real time testing as it takes several years and isn't cost effective. Therefore, accelerated ageing techniques are widely used industrially and are generally believed to be comparable to the natural ageing behavior^{1,2}. Accelerated ageing techniques have the benefits of early product launch with minimal chances of premature product failure.

The Arrhenius relationship is a common method used industrially, which is based on the rate of a chemical reaction increasing exponentially with temperature. If a reaction obeys the Arrhenius relationship, a linear relationship is observed between a log plot of the reaction rate versus the reciprocal of temperature¹. The Arrhenius relationship may fail at higher temperatures, as different degradation mechanisms may dominate. It is suggested in FDA guidance document on the ageing of medical packaging that accelerated ageing should occur at maximum of 60°C. It is also recommended that if the material is below the T_g at ambient temperature, that ageing should occur least 10°C below T_g . Accelerated ageing of polymers should be carried out at a temperature under which the polymer is in the same physical state as at ambient temperature. At room temperature, thermoplastic copolymers like PEBAX are typically between the glass transition temperatures of the hard (PA) and soft (PEO) segments¹. The accelerated ageing studies of these materials are typically carried out at temperatures of 45 to 55°C which is above the T_g of the hard segment, increasing the likelihood of non-Arrhenius ageing behaviour. An alternative approach known as 10°C rule, is

simplification of Arrhenius relationship, which is often used industrially. According to this rule, the rate of ageing reaction increases by a fixed factor for every 10⁰C rise in temperature. This assumes a particular value for the activation energy and may produce an over optimistic shelf-life estimate¹.

In this study PEBAX, two Arnitel grades and a 50/50 (W/W, %) blend of the two Arnitel grades were aged at 40°C, 50°C, 60°C, 80°C, 100°C and with elevated moisture at 60°C. The samples were characterised via DSC (Differential scanning calorimetry), TGA (Thermogravimetric analysis), and mechanical testing.

EXPERIMENTAL

The materials used were PEBAX and two grades of Arnitel. The PEBAX (MV1074) material was supplied by Arkema France Ltd. in the form of pellets. The grades of Arnitel used were VT3108 and VT7812 which are referred here as AR3108 and AR7812 respectively. The Arnitel material was supplied by DSM Engineering materials Dutch Ltd. in the form of pellets.

Rectangular samples (80×10×4mm) of PEBAX, the two grades of Arnitel (VT3108, VT7812) and a (50/50) blend of Arnitel were prepared using a Wittmann Battenfeld smart power 35 injection moulding machine. The injection moulding was carried out at a barrel temperature of 200°C and a pressure of 1000bar. The mould temperature was kept 30°C with a cooling time of 20s.

The samples were aged at a temperature of 40°C for 324days, 50°C for 162days, 60°C for 81days, 80°C for 21days, 100°C for 6days and with elevated moisture at 60°C for 81days in laboratory ovens. The ageing time used at various temperatures were selected according to the 10⁰C rule and is equivalent to ~4 years at 20°C. Samples were taken out each month for characterisation via tensile testing, DSC, TGA, and FTIR. Photographs of the aged and unaged samples were also taken.

Tensile testing was carried out in accordance with ISO 527-2 using Instron 5500R Universal testing machine fitted with a 2kN load cell at a crosshead speed of 50mm/min. Five specimens were tested for each interval and average is reported.

DSC was carried out using TA instrument Q100 over a temperature range of -80°C to 180 °C in a flowing nitrogen atmosphere at 10°C/min heating rate with sample size of approximately 5mg.

TGA was carried out using TA instrument SDT600 over a temperature range of 25 °C to 600 °C with a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the unaged samples and those aged at elevated temperatures. It is apparent from the figure that high temperature ageing resulted in discolouration of the samples. Giovanna et al also reported severe discolouration of unpigmented ABS samples after long-term ageing at elevated temperatures³. The samples at the higher temperatures showed more pronounced discolouration. The aged samples of PEBAX displayed a yellower/browner colour, while the Arnitel samples showed a pinker hue. The development of a yellow colour in aged PEBAX has previously been attributed to the build-up of low molecular weight fragments caused by chain scission¹.

Figure 2 (a), (b), (c) and (d) show the tensile strength of aged and unaged samples. A slight decrease in tensile strength was observed in the aged samples of Arnitel compared with unaged samples. The aged samples of PEBAX displayed more pronounced changes compared with the Arnitel samples. All the samples showed a slight increase in tensile modulus values consistent with embrittlement. However, the samples of Arnitel AR7812 and Arnitel blend showed a prominent drop in tensile modulus values when aged at elevated humidity. Arnitel AR7812 was observed to be absorbing water and this may be the reason for the drop-in modulus values. Compared to AR7812, Arnitel AR3108 was observed to display less significant changes in ageing behaviour with elevated humidity. A general trend of decreased elongation was also observed in all the aged samples.

Figure 3 (a) and (b) depicts the DSC and TGA curves for the PEBAX material before and after ageing. The glass transitions of the PEO and PA segments of Grade 7033 PEBAX, have been previously reported at -61 and +31°C respectively, and are labelled on figure 3 (a)¹. The development of a small new peak at ~100-110°C can be seen on the PEBAX samples aged at 60, 80 and 100°C. A similar feature was previously observed at ~112°C after ageing grade 7033 PEBAX, and was attributed to the melting of α crystalline domains in the PA regions¹. A slight increase in T_m is also observed after ageing which may be as result of small amount of crosslinking. The TGA results also showed little significance difference in the thermal degradation behaviour of the aged and unaged samples. However, there is

some evidence of a decrease in the degradation onset temperature after ageing, which may be due to the build-up of low molecular weight fragments.



Figure 1. Pictures of unaged and aged samples of PEBAX, AR 3108 (Aritel VT3108), AR 7812 (Aritel VT7812) and 50/50 (wt./wt. %) blend of Aritel grades at various temperatures.

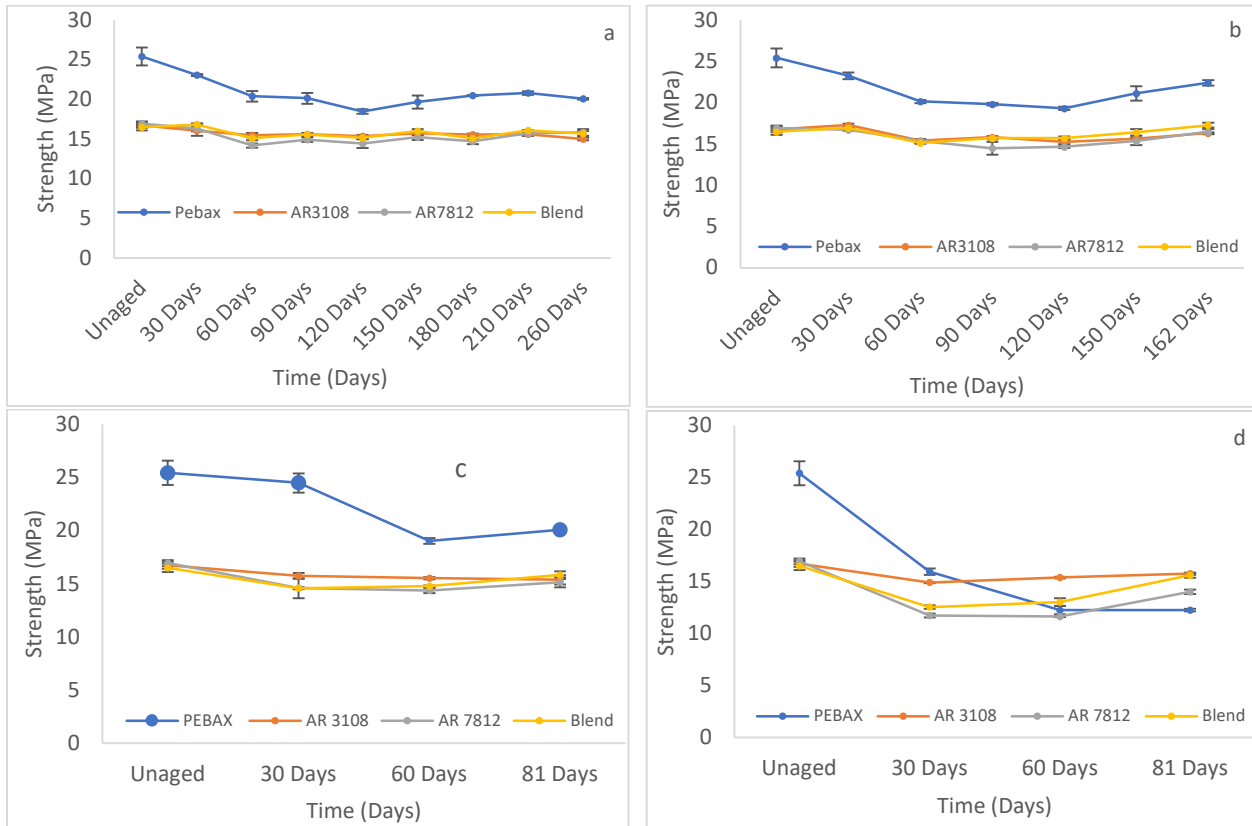


Figure 2. Tensile strength graphs of PEBAX, AR 3108 (Aritel VT3108), AR 7812 (Aritel VT7812) and 50/50 (wt./wt. %) blend of Aritel grades at (a) 40°C, (b) 50°C, (c) 60°C, and (d) 60°C with elevated humidity.

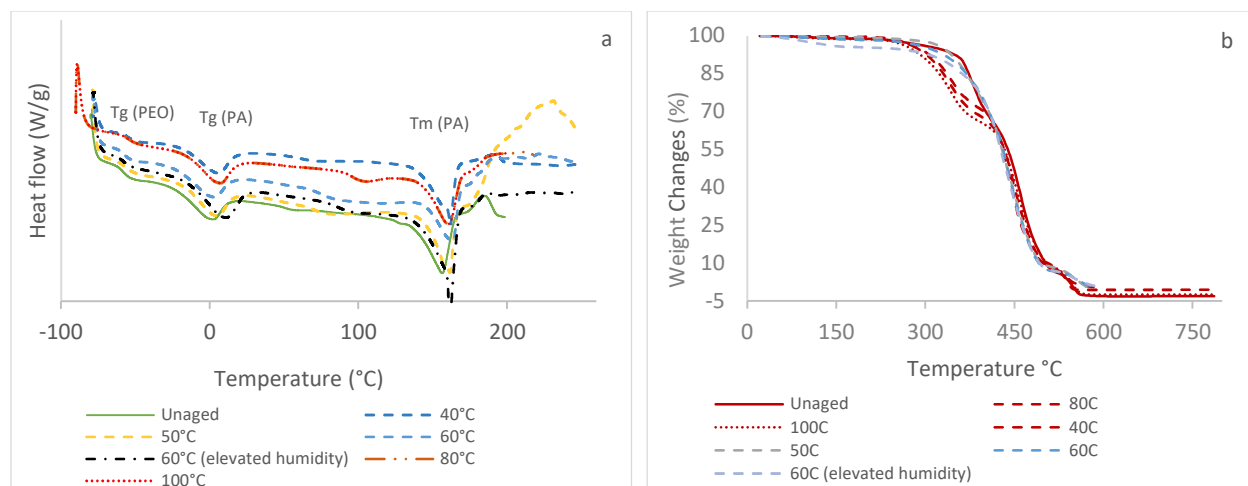


Figure 3. (a) shows the DSC melting curves of PEBAX at a range of temperature and (b) shows the TGA graphs of PEBAX.

CONCLUSIONS

Samples of PEBAX, two grades of Arnitel, and a Arnitel blend were aged at a range of temperatures, and it was observed that ageing resulted in discoloration. This effect was most evident at the higher ageing temperatures. The tensile testing for all the samples revealed that ageing resulted in an increase brittleness, with pronounced changes being observed in the PEBAX samples. The thermal analysis carried out via DSC and TGA showed only slight changes in the melting and degradation behaviour as a result of ageing. It can be concluded that ageing has a pronounced effect on the colouration and mechanical behaviour of the materials.

ACKNOWLEDGEMENT

We would like to express our appreciation to the research grant of The North West Centre for Advanced Manufacturing (NWCAM). NWCAM project is supported by the European Union's INTERREG VA Programme, managed by the Special EU Programmes Body (SEUPB). The views and opinions in this document do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB). "If you would like further information about NWCAM please contact the lead partner, Catalyst, for details".

REFERENCES

- ¹ D. Dixon and A. Boyd, *Polym. Eng. Sci.* **51**, 2203 (2011).
- ² A.A. Edidin, C.W. Jewett, A. Kalinowski, K. Kwarteng, and S.M. Kurtz, *Biomaterials* **21**, 1451 (2000).
- ³ G. Iannuzzi, B. Mattsson, and M. Rigdahl, *Polym. Eng. Sci.* **53**, 1687 (2013).