

RESEARCH ARTICLE | FEBRUARY 05 2019

Electron beam generated polymer-backbone-hydroperoxides trigger the crosslinking of glass fibre polypropylene interphase **FREE**

Michael T. Müller ✉; Carsten Zschech; Uwe Gohs



AIP Conf. Proc. 2065, 030026 (2019)

<https://doi.org/10.1063/1.5088284>



CrossMark

Articles You May Be Interested In

Methyl Hydroperoxide in Photo-oxidation of Acetone

J. Chem. Phys. (May 2004)

Kinetics of Pyrolysis of Alkyl Hydroperoxides and Their O–O Bond Dissociation Energies

J. Chem. Phys. (June 2004)

Excited states and photodissociation of hydroxymethyl hydroperoxide

J. Chem. Phys. (May 2008)

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

Lock-in Amplifiers for your periodic signal measurements



Find out more



Electron Beam Generated Polymer- Backbone-Hydroperoxides Trigger the Crosslinking of Glass Fibre Polypropylene Interphase

Michael T. Müller^{a)}, Carsten Zschech^{b)}, Uwe Gohs^{c)}

Leibniz-Institut für Polymerforschung Dresden e.V. (IPF), Hohe Straße 6, 01069 Dresden, Germany

^{a)}Corresponding author: mueller-michael@ipfdd.de

^{b)}zschech@ipfdd.de

^{c)}gohs@ipfdd.de

Abstract. The objective of this work is the implementation of a free radical process which enables a grafting and crosslinking possibility in the polypropylene (PP) glass fibre (GF) interphase. For this purpose hydroperoxides were generated along the polymer backbone of the used PP film former, by an electron beam treatment. During a subsequently thermal treatment these peroxides decay to radicals which initiate a grafting and/or cross-linking reaction. To demonstrate the effect of cross-linking in the interphase on the composite strength, transverse tensile tests on unidirectional GF/PP composites and rheology test were applied.

Keywords: Fibre, interphase, glass fibre-reinforced thermoplastics electron beam treatment

PACS: 81.05.Ni; 81.05.Lg; 81.05.Qk; 61.25.hp

INTRODUCTION

The manufacturing of continuous glass fibre (GF) reinforced polypropylene (PP) composites enables cost effective products at low cycle time with a good balance between material price and mechanical performance. However, the high viscosity of polymer melt in comparison to thermosets resins hinders a sufficient wetting of the GF with the polymer, which influences the quality of consolidation negatively. Since the impregnation of reinforcing fibres depends also on the flow distance of the polymer, hybrid yarns were developed [1, 2]. Hybrid yarns consist of matrix and reinforcing fibres, which are homogeneously arranged in the hybrid yarn, whereby the required flow distance for an entire glass fibre impregnation decrease drastically. In addition, a water-based sizing (polymer emulsion) has to be applied in order to enhance the interfacial adhesion as well as ensure their further processing. Beside aminosilane and maleic anhydride-grafted (MAH-g) PP as coupling agents [3], it contains a lot of surfactants and low molecular components. In contrast to thermosets, the consolidation process of fibre reinforced PP composites involves the physical processes of melting and crystallization as well as chemical reactions between the fibre surface the aminosilane and the MAH-g-PP. Consequently, such additives are not chemically bonded to the thermoplastic matrix and reduce the required fibre-matrix adhesion in the interphase drastically. The objective of this work is to overcome this problem by implementing a free radical process to bind the low molecular additives [4]. Therefore, we generated hydroperoxides by an electron beam (EB) treatment of the PP film former, which are highly reactive during the thermal consolidation process [5] with respect to cross-linking and/or grafting within the interphase. To demonstrate the cross-linking effect on the composite strength, transverse tensile tests on unidirectional GF/PP composites and rheology test.

EXPERIMENTAL

For the glass fibre spinning, an commingled hybrid yarn [1, 2], 160 tex, 50/50 vol.% consisting, of continuous E-glass filaments (average diameter 17 μm) and PP filaments (HG455FB, $M_w=223900$ g/mol, Borealis, Austria) were simultaneously spun and sized using a aqueous 3-aminopropyltriethoxysilane (Dynasylan® AMEO, Evonik, Germany, 1 wt.%) and a modified or unmodified cationic stabilized MAH-g PP film former (10 wt.%, $M_w=31500$ g/mol, Michelman, OH, USA), aqueous emulsion. The PP film former was modified in a dry state. For this purpose, the PP film former was freeze-dried at -1 bar and -50 °C for about 19 h (Christ-Alpha 1-2 LD plus, Martin Christ Gefriertrocknungsanlagen GmbH, Germany). Subsequently, the resulting powder was irradiated with

a dose of 800 kGy at ambient air using an electron accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia). The modified film former was resolved in the water again using a high shear disperser. The gel content of modified PP was measured by extraction in xylene at 140 °C for 16 h using solvent extraction method [6]. The preparation of the unidirectional GF reinforced PP composites is conducted by yarn winding process on a steel mandrel frame. The hybrid yarn was consolidated by compression moulding (K207, Rucks GmbH, Germany) at 225 °C. After heating-up phase the temperature of 225 °C (10 K/min), at 10 bar compression, were kept constant for 21 minutes to be ensured a fully yarn melt up [3]. Subsequently, the pressure was increased up to the point where the glass fibres were fully wetted (45 bar, 2 min), followed by cooling down (70 K/min) to room temperature. The tensile test specimens were prepared using a diamond circular saw. Transverse tensile tests were performed according to ISO 527-4 specification using Zwick Universal Testing Machine (Allround Line, Zwick Roell, Germany) at room temperature at a constant cross-head speed of 1 mm/min. The tensile moduli reported here are average values of at least eight measurements. The thermal behaviour of the different modified PP was studied using differential scanning calorimetry (Q2000, TA Instruments, DE, USA). For the crystallinity calculation, an enthalpie (ΔH) of 207 J/g for 100 % crystalline polypropylene were used. Infra-red spectra were recorded using Vertex 80v (Bruker) spectrometer using a golden gate diamante ATR unit (SPECAC), 100 scans with a resolution of 4 cm^{-1} . EPR spectra were recorded at room temperature and in air using a MiniScope MS 200 (Magnettech Limited, Germany) operating in X band with a TE102 rectangular cavity.

RESULTS AND DISCUSSION

For the implementation of a cross-linking and/or grafting possibility of a PP film former, to bind the low molecular additives and enhances the interaction with the PP matrix, an EB treatment in air was applied. In the pre-examination, only pure PP was used to eliminate all side reaction which will take place in the case of a PP film former system. Thus, a possible mechanism can be derived for electron induced reactions of PP in air atmosphere at room temperature and the cross-linking mechanism (Figure 1), which can be transferred to of the PP film former system, afterwards. An EB treatment of PP in ambient air with 800 kGy leads to trapped radicals. The trapped the tertiary alkyl radicals can react with the very mobile bi-radical oxygen [B_1] to form a peroxy radical or can undergo β -scission [A] leading to carbon double bonds and secondary alkyl radicals. Afterward, the secondary alkyl radical can form a peroxy radical by reaction with the bi-radical oxygen [B_2]. Consequently, oxygen functionalities (like hydroperoxides [C]) are generated along the polymer backbone. The EPR spectra of irradiated PP (Figure 3, right)

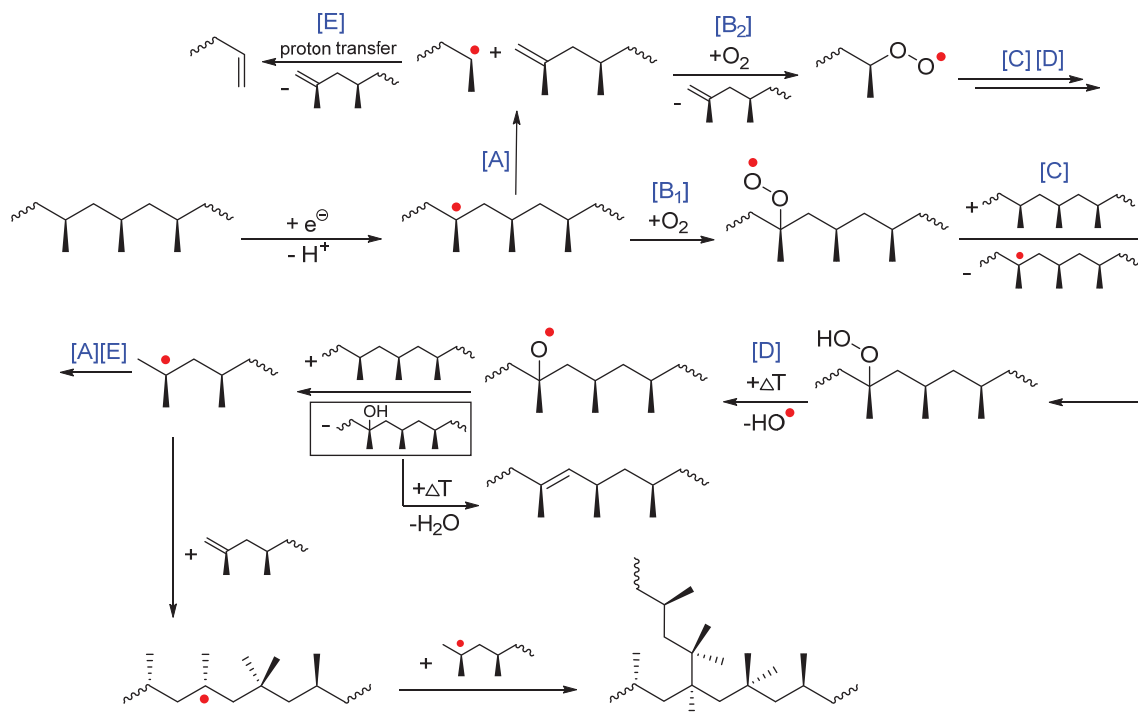


Figure 1 Possible mechanism of the functionalization during irradiation and a subsequent thermal induced cross-linking of PP

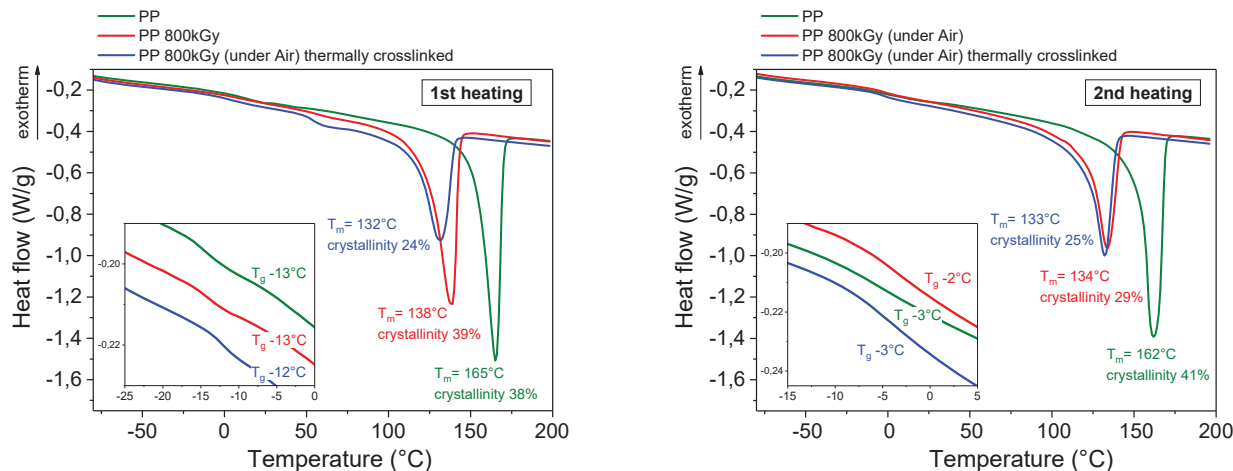


Figure 2 Thermal behavior of PP of non- and irradiated PP and of irradiated PP with a subsequent thermal treatment

support this mechanism model by showing a hyperfine structure of the trapped secondary-, tertiary alkyl radicals and of peroxyradicals. The incorporation of functional groups affects the crystallinity structure and therefore influences the melting and crystallization process (Figure 2). As a result, the crystallinity decreases from about 38–41 % to 24–27 % and the melting temperature reduce from 162–165 °C to 132–138 °C. The IR- spectra of the EB modified PP (Figure 3, left) confirms the formation of C=O functionalities (1670 - 1800 cm^{-1}), -OH (3200 - 3500 cm^{-1}), whereas the C=C (at 1640 cm^{-1} and 700 cm^{-1}) which was formed at prior processing, disappear after the EB treatment in ambient air. Immediately after thermal treatment [D], these C=O vibrations are vanishing whereby it can be concluded that these functionalities are highly thermal reactive. In the same moment the -C=CH₂ vibration increase, which can be attribute to β - chain scission [A/E] of the PP. The crystallinity did not recover to the initial value of 41 % after the thermal treatment, even though the C=O functional groups disappear. Probably, other crystal structure disorder reasons instead take place, for example the presents of a vinylidene group or a cross-link position between the PP chains. An evidence of existing cross-linking can be found in the rheology behaviour of the modified PP (Figure 4). The loss factor, of the irradiated PP with a subsequent thermal treatment, with a value between 2 and 4 ($\tan \delta$) indicated an ideal elastic behavior, whereby the factor of pure PP is in range of 10 and 200 ($\tan \delta$), which corresponds with a typical vicious elastic behavior. Also, the lower loss modulus and the partial higher storage modulus and the measure gel content of modified PP, after an extraction in xylene for 16 h with a value of 65 %, is a clear indication of cross-linking of EB modified PP after additional thermal treatment. By using a PP film former instead of pure PP, similar results can be obtained. A cross-linking behavior occurs after a thermal post treatment, which can be verified by the increased gel content of 54 % of the 800 kGy

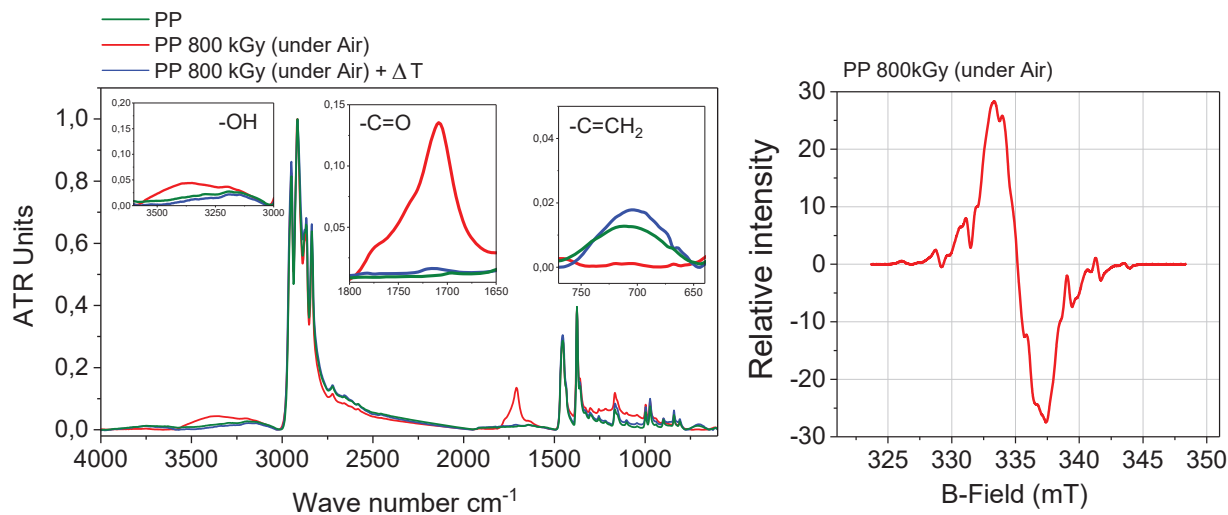


Figure 3 FT-IR spectra of non- and irradiated PP and of irradiated PP with a subsequent thermal treatment (left) and EPR spectra of irradiated PP (right)

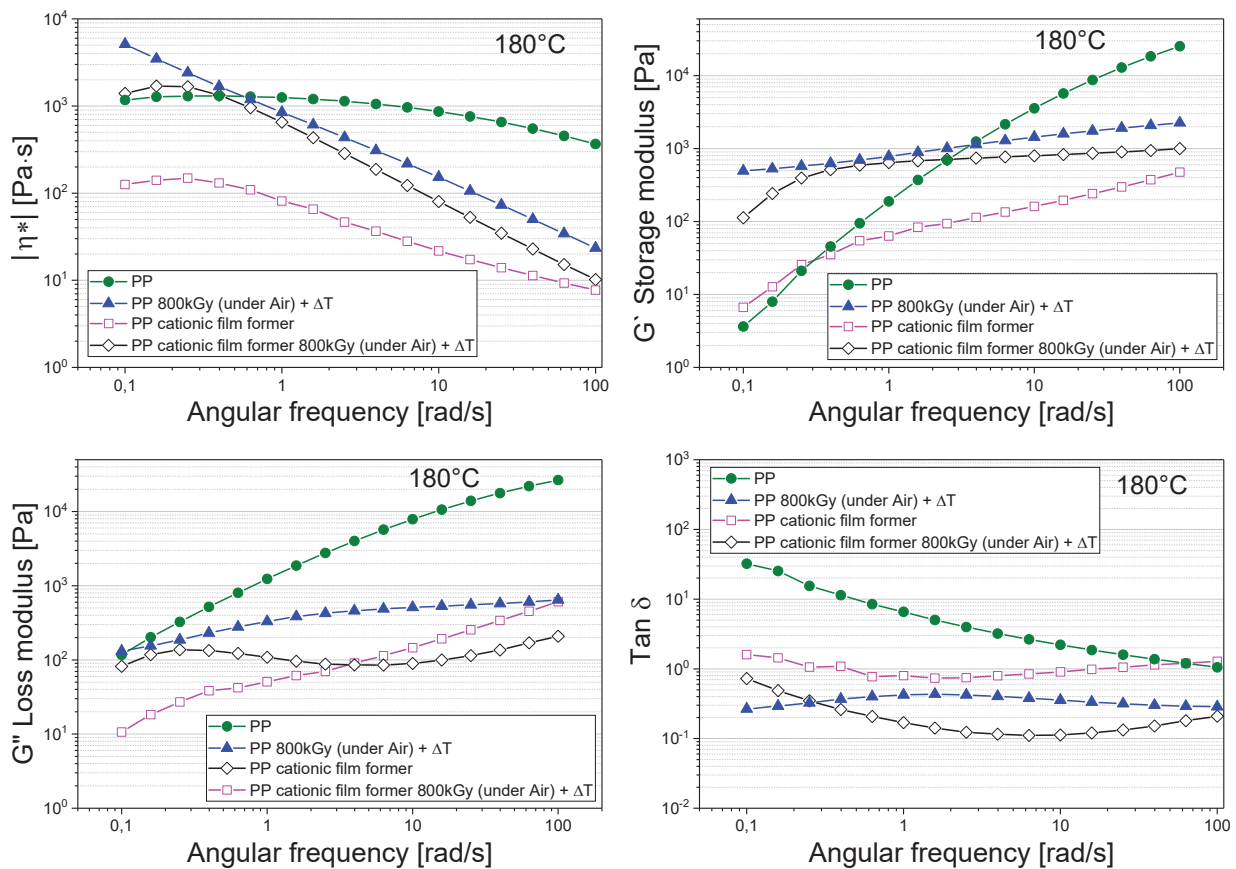


Figure 4 Rheology behavior at 180°C of non- irradiated PP and of irradiated PP with a subsequent thermal treatment

the PP film former in comparison to pure PP, can be attributed to the lower molecular mass which is additional irradiated PP film former and by the rheological results (Figure 4). The PP film former crystallinity decreases as well from about 21 % to 15 % and the melting temperature from 137 – 144 °C to 121 – 131 °C. The much lower initial crystallinity of combined a high maleic anhydride grafting density. To evaluate the influence of cross-linkable interphase in GF/PP composites the irradiated film former was applied at room temperature as an aqueous emulsion with silane during the preparation of commingled hybrid yarn, with a roller system. After a yarn dry process at room temperature, the preparation of the unidirectional GF composites is conducted by yarn winding process on a steel mandrel frame. In the subsequent consolidation process using compression moulding at 225°C under vacuum, the modified film former can initiated the cross-linking. The mechanical performance of the reactive interphase was tested for unidirectional GF/PP composites by transverse tensile tests mode (Figure 5). A measurement, transverse to the glass fibre direction is sensitive to the interphase strength whereby an increase also leads to enhanced mechanical performance in the transverse tensile test. The cross-linked interphase increases the transverse tensile strength from 22.5 MPa (at 1.0 % stain at break) to 25 MPa (at 1.3 % strain at break), which is a significant enhancement in the performance of about 10 %. At the same time, the young modulus decrease from 3360 MPa, for the unmodified Interphase, to 2800 MPa for the composites with the reactive interphase due to the occurring polymer degradation during the irradiation process.

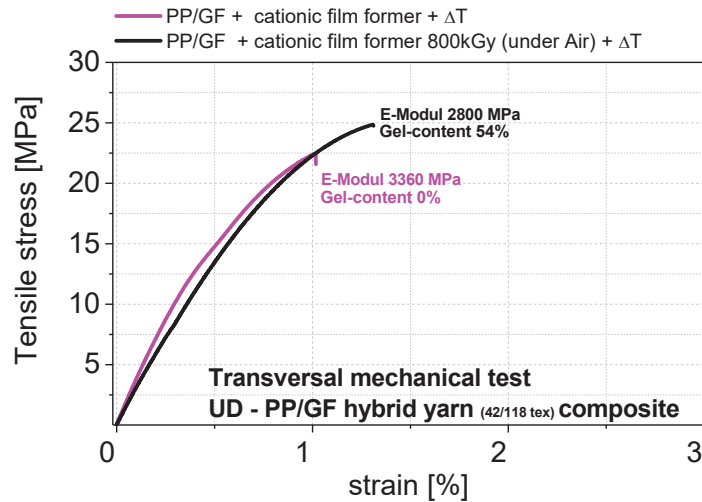


Figure 5 Influence of the curable interphase on the mechanical performance of unidirectional GF/PP composites having a fiber volume content of 50% (transverse tensile tests mode)

CONCLUSION

In contrast to fibre reinforced thermosets, a non-reactive consolidation process is used for fibre reinforced thermoplastics leading to reduced interfacial adhesion. In this study, we successfully developed and tested a temperature induced cross-linkable sizing by EB treatment of a commercial PP film former for continuous GF reinforced PP composites. Using FTIR, a possible mechanism of interphase cross-linking is proposed. The cross-linking of EB modified sizing is confirmed by gel content measurements. Finally, the transverse tensile strength of interphase crosslinked continuous GF reinforced PP composites was tested and enhanced by 10 %. Future studies are required to deeply understand the cross-linking mechanism within the complex sizing in order to transfer the approach of radical induced cross-linking of fibre matrix interphase to industrial application.

ACKNOWLEDGMENTS

This project was funded by the European Union, project Nanoleap (grant No. Horizon: H2020-NMP-PILOTS-2014; NMP-01-2014). We thank Falk Eberth for the glass fibre and hybrid yarn melt spinning. Further, we acknowledge the help of Jaqueline Hampel for gel content measurement, Sabine Krause DSC measurements and Mikhail Malanin for the FT-IR measurements. Additionally, we thank Roxana McMican from the Michelman company for providing the PP emulsion.

REFERENCES

1. E. Mäder, J. Rausch and N. Schmidt, *Composites Part A: Applied Science and Manufacturing* **39**, 612-623 (2008).
2. J. Rausch, R. C. Zhuang and E. Maeder, *Express Polym. Lett.* **4**, 576-588 (2010).
3. N. Wiegand and E. Mäder, *Fibers* **5**, 26 (2017).
4. U. Gohs, L. Girduškaite, L. Peitzsch, S. Rothe, C. Zschech, G. Heinrich and H. Rödel, *Advanced Engineering Materials* **18**, 409-416 (2016).
5. S. Shimada, Y. Hori and H. Kashiwabara, *Macromolecules* **18**, 170-176 (1985).
6. R. Boldt, U. Gohs, U. Wagenknecht and M. Stamm, *Polymer* **95**, 1-8 (2016).