

A Dynamic Mechanical Thermal T-Peel Test Approach to Characterize Interfacial Behavior of Polymeric Textile Composites

J. R. Büttler, T. Pham

I. INTRODUCTION

Abstract—Basic understanding of interfacial mechanisms is of importance for the development of polymer composites. For this purpose, we need techniques to analyze the quality of interphases, their chemical and physical interactions and their strength and fracture resistance. In order to investigate the interfacial phenomena in detail, advanced characterization techniques are favorable. Dynamic mechanical thermal analysis (DMTA) using a rheological system is a sensitive tool. T-peel tests were performed with this system, to investigate the temperature-dependent peel behavior of woven textile composites. A model system was made of polyamide (PA) woven fabric laminated with films of polypropylene (PP) or PP modified by grafting with maleic anhydride (PP-g-MAH). Firstly, control measurements were performed with solely PP matrixes. Polymer melt investigations, as well as the extensional stress, extensional viscosity and extensional relaxation modulus at -10°C , 100°C and 170°C , demonstrate similar viscoelastic behavior for films made of PP-g-MAH and its non-modified PP-control. Frequency sweeps have shown that PP-g-MAH has a zero phase viscosity of around $1600\text{ Pa}\cdot\text{s}$ and PP-control has a similar zero phase viscosity of $1345\text{ Pa}\cdot\text{s}$. Also, the gelation points are similar at $2.42\cdot 10^4\text{ Pa}$ (118 rad/s) and $2.81\cdot 10^4\text{ Pa}$ (161 rad/s) for PP-control and PP-g-MAH, respectively. Secondly, the textile composite was analyzed. The extensional stress of PA66 fabric laminated with either PP-control or PP-g-MAH at -10°C , 25°C and 170°C for strain rates of $0.001 - 1\text{ s}^{-1}$ was investigated. The laminates containing the modified PP need more stress for T-peeling. However, the strengthening effect due to the modification decreases by increasing temperature and at 170°C , just above the melting temperature of the matrix, the difference disappears. Independent of the matrix used in the textile composite, there is a decrease of extensional stress by increasing temperature. It appears that the more viscous is the matrix, the weaker the laminar adhesion. Possibly, the measurement is influenced by the fact that the laminate becomes stiffer at lower temperatures. Adhesive lap-shear testing at room temperature supports the findings obtained with the T-peel test. Additional analysis of the textile composite at the microscopic level ensures that the fibers are well embedded in the matrix. Atomic force microscopy (AFM) imaging of a cross section of the composite shows no gaps between the fibers and matrix. Measurements of the water contact angle show that the MAH grafted PP is more polar than the virgin-PP, and that suggests a more favorable chemical interaction of PP-g-MAH with PA, compared to the non-modified PP. In fact, this study indicates that T-peel testing by DMTA is a technique to achieve more insights into polymeric textile composites.

Keywords—Dynamic mechanical thermal analysis, interphase, polyamide, polypropylene, textile composite, T-peel test.

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BASIC understanding of textile composites is of interest for the development of technical textiles and for the exploration of new products for light-weight applications. Well-known strong polymer fibers are aromatic PA and ultra-high molecular weight polyethylene. Also, PA is a thermoplast with excellent mechanical properties, which makes PA fibers suitable as reinforcing material in other polymers. The choice of the matrix depends on many factors, such as its adhesion to the fibers, and its thermal and viscoelastic behavior. The adhesion between the textile reinforcement and the matrix is mainly measured by lap-shear, T-Peel- or micro-bond testing [1]. The advantages of these methods are that they are straight forward, yield direct information about how much force is needed to break the bond and they are easy to handle. Unfortunately, those analytical methods give only information about the bond strength. The missing factor is chemical and physical information about the interphase. For example, the changes of the adhesion at different temperatures, and the viscoelastic behavior during extension and chemical interactions. This knowledge is required to obtain more insight into the interphase and is simultaneously useful for the development of polymeric composites.

Previous research has shown that bond strength between PA and polyethylene (PE) or PP increases after interfacial modification. It is demonstrated that the adhesion between PA6 and PE increases if the interphase is modified with a compatibilizer, a triblock copolymer made of styrene, ethylene, butylene and MAH [2] or if PE is grafted with MAH [3]. The adhesive strength between PA fabric and PP is increased as well, in case the PP matrix is treated with plasma [4]. Furthermore, AFM and nano-IR technology serve as an optimal tool to investigate composites at microscopic level. The interfacial structure of a PA-PE multilayer film has been analyzed by AFM and nano-IR [5].

In this study, PA66 textile was embedded in PP with or without MAH grafting in order to develop a DMTA method for interfacial strength analysis. PP is suitable for this purpose, as it has a lower melting point than PA and its modification by grafting with MAH likely increases the adhesion strength towards PA. The DMTA was performed using a rheometer in a T-peel test configuration. The advantage of this system is the high sensitivity and the analysis can be performed at a range temperatures under continuous and oscillation dynamic conditions. Standard lap-shear testing was used as a control method. Additionally, AFM, nano infrared (nano-IR) and

Lorenz-contact resonance (LCR) analysis was performed to characterize the textile composite at microscopic scale and attenuated total reflectance Fourier-Transform-Infrared Spectroscopy (ATR-FTIR) and water contact angle measurements were performed in order to obtain chemical information on the matrices. The data of this study provide more knowledge about the interaction between PA66 fabric and PP and about the possibility to use DMTA for T-peel testing.

II. EXPERIMENTAL

A. Materials

Films of PA6 (Durethan B30S, thickness 150 μm , melting temperature ca. 222 $^{\circ}\text{C}$) and PP (HD204CF, non-modified, thickness 100 μm , melting temperature ca. 162 $^{\circ}\text{C}$) were obtained from Lanxess AG (Germany) and Borealis AG (Austria) respectively, and used after cleaning with ethanol. Granules of PP (HC101BF, PP-control) and PP-g-MAH (BB127E) were obtained from Borealis (Austria) and pressed into films between two PTFE sheets at 190 $^{\circ}\text{C}$ and 30 bar for 4 min on a Polystat 200T press (ServiTec GmbH, Germany). PP-control is a homopolymer with a melt flow rate of 3.2 g/10min and a melting temperature of about 162 $^{\circ}\text{C}$. PP-g-MAH is grafted with 0.16 wt% MAH, having a melt flow rate of 7.5 g/10 min and a melting temperature of about 165 $^{\circ}\text{C}$. The melting points were determined in our laboratory with differential scanning calorimetry (DSC). A PA66 woven fabric of thickness 130 μm was obtained from Getzner Textil AG (Austria), and used after rinsing with acetone for 5 min and drying.

B. Material Characterization

ATR-FTIR was performed on a Vector 22 spectrometer from Bruker. All samples were scanned from wavenumbers 500-4000 cm^{-1} for 128 scans at resolution of 2 cm^{-1} . The contact angles were determined with demineralized water at 20 \pm 2 $^{\circ}\text{C}$ on a Krüss Easy drop instrument using onboard software.

C. Composite Formation

The samples for lap-shear and T-peel testing were laminated under 40 bar for 5 minutes at 210 $^{\circ}\text{C}$ and under 50 bar for 3 minutes at 225 $^{\circ}\text{C}$, respectively, on a Polystat 200T press (ServiTec GmbH, Germany). A piece of PP HD204CF or PP-g-MAH film (20x20 mm) was laminated between two strips of PA66 fabric (20x150 mm) for the lap-shear test. The sample dimensions for the T-peel testing was 5x50 mm, with an area of 5x25 mm laminated with PP-control or PP-g-MAH.

D. AFM, Nano-IR and LCR

A cross section of the textile composite embedded in epoxy resin was used for nano-IR and LCR analysis based on AFM operating in contact mode (nano IR 2, Anasys Instruments, USA). Nano-IR scanning was performed from 1300-1800 cm^{-1} at 2.55% power and LCR imaging at a drive frequency of 342 kHz.

E. Interfacial Adhesion Analysis

The single lap-shear tests, as illustrated in Fig. 1 (a), were performed on a Zwick/Roell Z010 machine (Zwick GmbH Co.KG, Germany) with a gauge length of 30 mm and an extension rate of 50 mm/min. Tests were performed in 5-fold. The DMTA module of the Modular Compact Rheometer MCR 302 (Anton Paar GmbH, Austria), with attached convection temperature control device was used for T-peel tests (Fig. 1 (b)). The parameters for the DMTA were set as follows: constant torque at 1 N·m, constant extensional strain rate at 0.001 s^{-1} , 0.01 s^{-1} , 0.1 s^{-1} or 1 s^{-1} and constant temperature at -10 $^{\circ}\text{C}$, 0 $^{\circ}\text{C}$, 25 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$ or 170 $^{\circ}\text{C}$. The temperatures of -10 $^{\circ}\text{C}$ and 0 $^{\circ}\text{C}$ were achieved with liquid nitrogen. The free sample length was 20 mm. All measurements were performed twice. Additionally, frequency sweeps of polymer melts were performed at 240 $^{\circ}\text{C}$, 5% strain and a gap of 0.20 mm with the same rheometer switched to the parallel-plate setting.

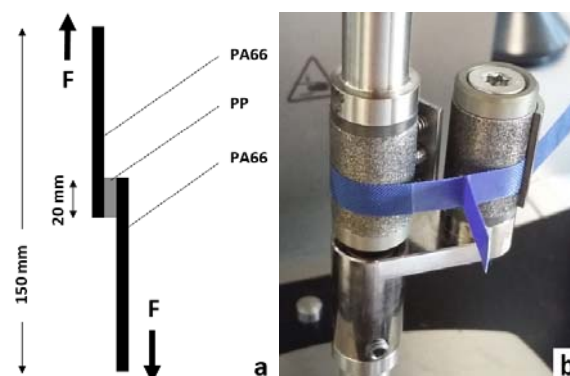


Fig. 1 Different tensile test systems. Single lap-shear test scheme for adhesive shear analysis at room temperature (a) and the universal extensional fixture (UXF) setting of the rheometer for adhesive T-peel strength testing at variable temperatures (b)

III. RESULTS & DISCUSSION

A. Nano-IR and LCR Characterization of the Textile Composite

The composite made of PA66 woven fabric embedded in PP matrix, was analyzed at microscopic level, including chemical characterization by nano-IR and mechanical characterization by LCR. First, a cross section of the textile composite was investigated by AFM, in order to ensure that the PA fibers are totally wetted by the PP-g-MAH matrix.

AFM imaging (Fig. 2 (a)) shows both circular and elongated structures, corresponding to sections of PA fibers in crosswise and longitudinal directions respectively. The matrix is observed in between the fibers. The fibers are completely embedded in the PP-g-MAH matrix, as no gaps are visible between the matrix and fibers (Fig. 2 (a)). Secondly, the single areas of the cross section were analyzed by nano-IR, in order to obtain chemical confirmation for the different structures. As shown in the IR spectra in Fig. 2 (b), the spectrum of the matrix, indeed has PP specific peaks in the range of 1350-1500 cm^{-1} , especially at 1376 cm^{-1} . Whereas, the peak at 1640

cm^{-1} of the spectrum obtained of the fiber cross section, is typical for amide I in PA. The shoulder at 1664 cm^{-1} is most likely due to the presence of PP-g-MAH, which might be slightly transferred to the PA area during cutting the composite.

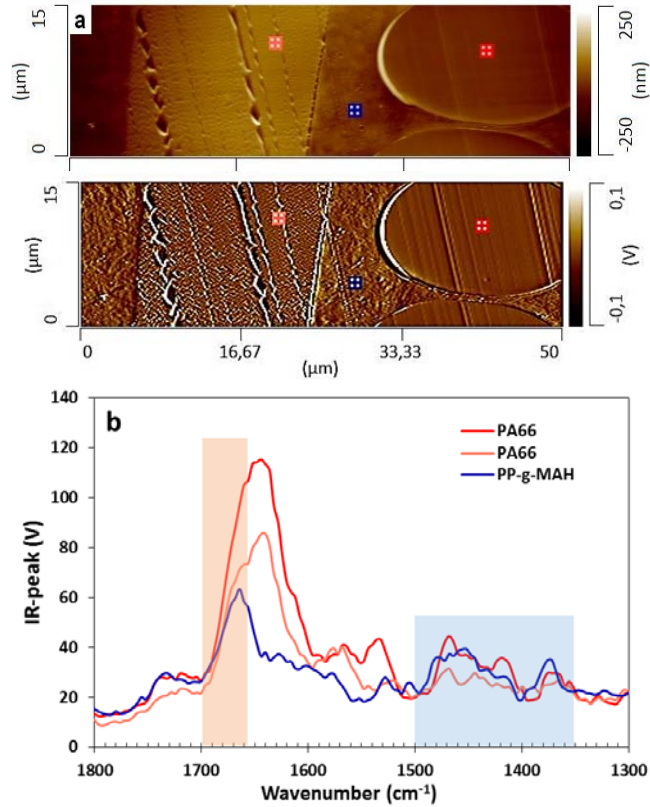


Fig. 2 AFM and nano-IR analysis of the PA66/PP-g-MAH woven fabric composite. AFM height and deflection image (a) and nano-IR scanning (b) of the composite cross section. The color of the markers in the AFM image correspond to the colors of the IR spectra. The peaks in the range of $1350\text{-}1500 \text{ cm}^{-1}$, especially at 1376 cm^{-1} , are typical for PP and the peak at 1640 cm^{-1} is typical for amide I in PA. The shoulder at 1664 cm^{-1} is likely due to the PP modification

Additionally, LCR measurements were performed to analyze the mechanical stiffness of the composite. Again, the AFM image shows that the PA fibers are completely wetted by the PP matrix (Fig. 3 (a)). The LCR scanning of the fiber and matrix reveals that those materials have a different mechanical property. The amplitude maximum of PP is at 330 kHz and the maximum of PA66 at 342 kHz (Fig. 3 (b)). This indicated that PA66 has a higher stiffness than PP. This increased stiffness of PA becomes even more visible by LCR imaging at 342 kHz. Fig. 3 (c) represents the results from LCR imaging. The round structures of the PA fiber cross sections are clearly detected as a less soft material than the surrounding PP matrix.

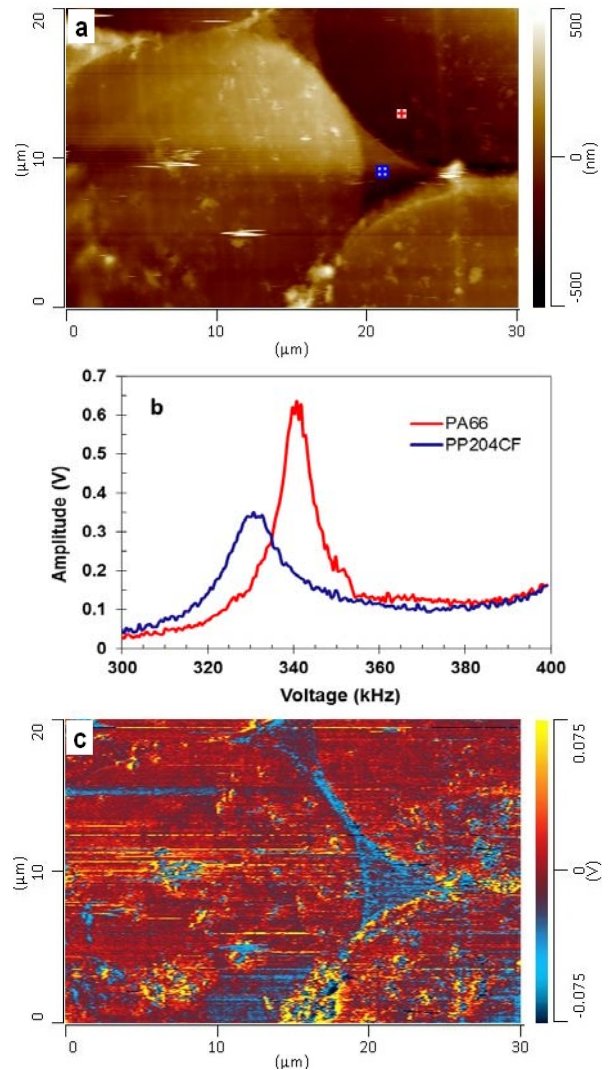


Fig. 3 AFM-LCR of the PA66/PP HD204CF textile composite. Height image containing the markers for LCR scanning (a) and LCR spectra of PA and PP (b). The color of the spots in the AFM image correspond to the colors of the spectra. The amplitude maximum of PP is at 330 kHz and the maximum of PA66 at 342 kHz indicating that PA66 has a higher stiffness than PP. LCR imaging at 342 kHz (c)

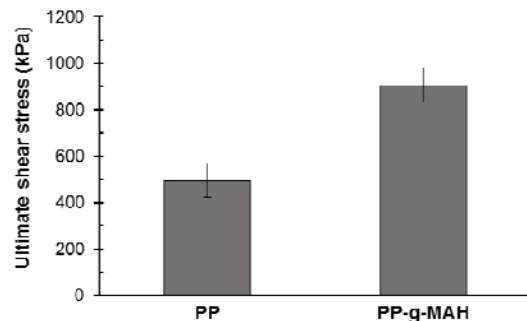


Fig. 4 Lap-shear test of PA66 fabric laminated with PP without (PP) or with interphase modification by PP-g-MAH

B. Adhesive Lap-Shear Testing and Chemical Causes for the Increased Adhesion after Interfacial Modification

Adhesive shear testing has shown that interphase modification in composites can be favorable to increase the bond strength between PA fabric and PP. As shown in Fig. 4, the shear stress is almost two-fold higher in case the PA fabric is laminated with PP-g-MAH, compared to the laminate containing non-modified PP. Thus, the adhesion between PA fibers and PP-g-MAH is better, compared to the adhesion with PP having no functional chemical groups. The MAH group, covalently bound to the PP backbone, is the reason behind this increased adhesion.

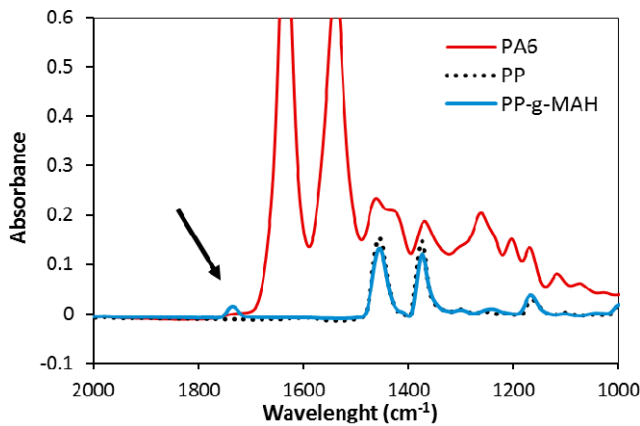


Fig. 5 FTIR-ATR spectra of the indicated polymers. It has shown that a carboxylic peak is present in the PP-g-MAH film at 1735 cm^{-1}

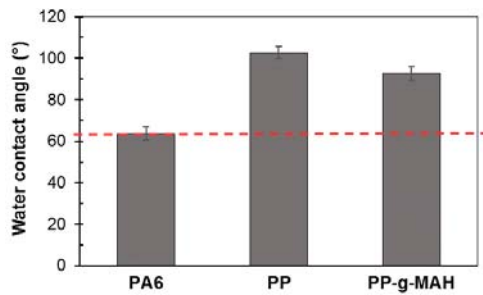


Fig. 6 Water contact angle on the surface of films made of the indicated polymers

The FTIR-ATR spectrum (Fig. 5) represents the chemical change of PP-g-MAH compared to non-modified PP. The peak at 1735 cm^{-1} shows the presence of carboxylic groups in PP-g-MAH, whereas the non-modified PP has no additional peaks. Likewise, the water contact angle demonstrates that non-modified PP is more inert compared to PP-g-MAH (Fig. 6). The contact angle of non-modified PP lies around 102.8° , 39° larger compared to the one of PA, which lies around 63.7° , indicating a non-favorable interaction, as PA is much more polar than PP. The difference of polarity between PA and PP-g-MAH however is less. PP-g-MAH has a contact angle around 92.7° , 10° less compared to the one of PP. This decrease is caused by the MAH group, which contains hydrogen bond acceptors and has therefore an increased polarity. The additional interaction between PA and PP-g-

MAH is explained by the reaction between NH_2 end groups of PA and MAH groups of modified PP (Fig. 7)

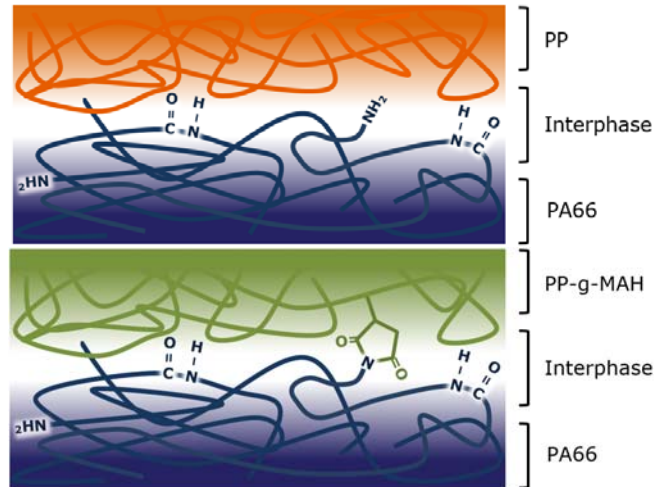


Fig. 7 Schematic view on possible interphase strengthening interactions between PA and PP after PP modification by grafting with MAH

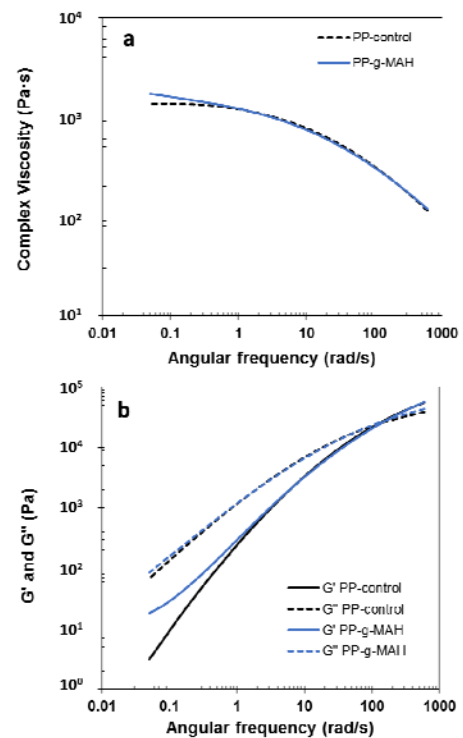


Fig. 8 Rheological characterization of the non-modified (PP HC101BF) and modified (PP-g-MAH). The complex viscosity (a), storage modulus (G') and loss modulus (G'') (b) was determined by the parallel plate rheological system at 240°C

C. Basic Rheological Characterization of PP-Control and PP-g-MAH Used as Matrix in the Textile Composite

For further investigations, it is useful to obtain more insight on the adhesive behavior between the polymers of the textile composite at different temperatures.

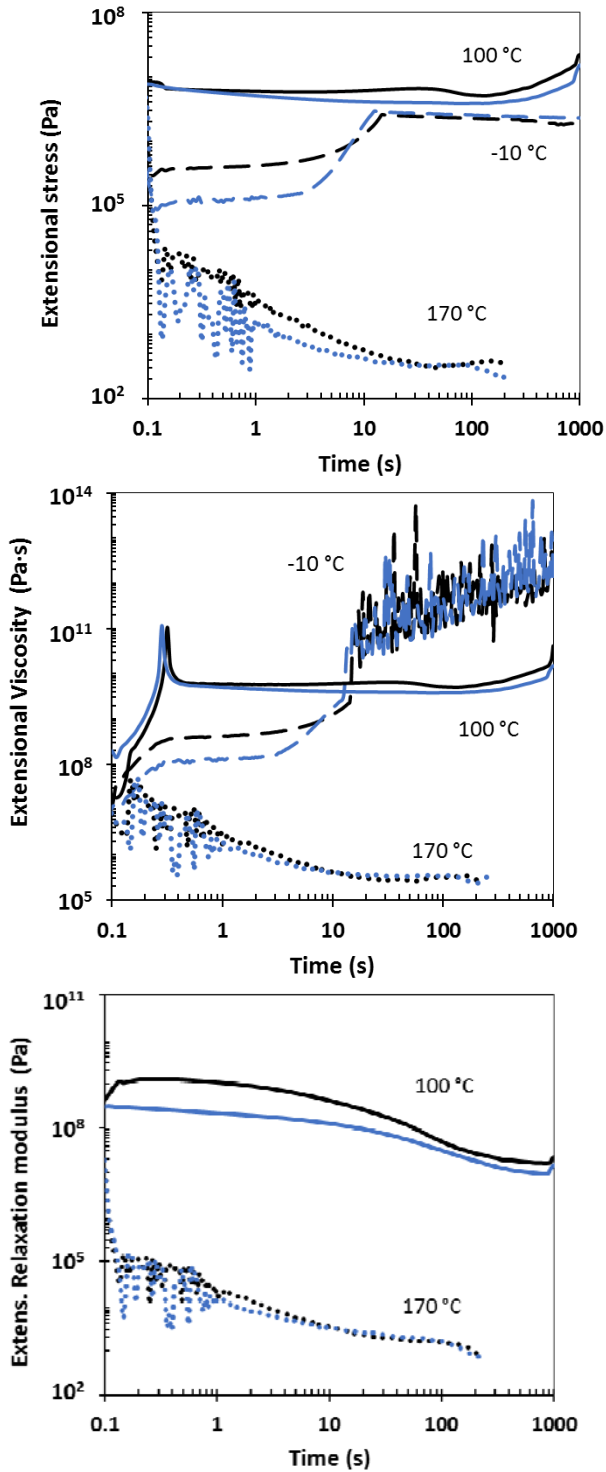


Fig. 9 Extensional stress, extensional viscosity and extensional relaxation modulus of PP-g-MAH (blue) and non-modified PP HC101BF (black). Data are obtained with DMTA using PP films in a rheometer at -10 °C, 100 °C and 170 °C and an extensional strain rate of 0.001 s⁻¹

As control, non-modified PP HC101BF is found with similar behavior compared to PP-g-MAH. The melting temperatures for PP-control, PP-g-MAH and PA6, derived from DSC measurements (data not shown), are around 162 °C,

165 °C and 222 °C, respectively. Frequency sweeps, obtained with the parallel plate rheological system, has shown that PP-g-MAH has a relative high zero phase viscosity of around 1600 Pa·s (Fig. 8 (a)). PP-control has a similar zero phase viscosity of 1345 Pa·s. Also the storage- and loss moduli of those polymers are almost identical (Fig. 8 (b)). The gelation point (cross section between storage- and loss modulus) is at 2.42*10⁴ Pa (118 rad/s) and 2.81*10⁴ Pa (161 rad/s) for PP-control and PP-g-MAH, respectively. In addition, extensional DMTA with PP-control and PP-g-MAH films were performed using a rheometer. Fig. 9 shows that the extensional stress, extensional viscosity and extensional relaxation modulus (Fig. 9) of PP-control and PP-g-MAH are similar at -10 °C, 100 °C and 170 °C. The measurement at 25 °C (data not illustrated) is similar to the extensional stress at 100 °C and to the extensional viscosity at -10 °C. The extensional relaxation modulus at -10 °C and 25 °C is 0 Pa. At lower temperatures, the stress on PP-g-MAH is slightly larger, and at higher temperatures slightly lower, compared to PP-control. Overall, polymer melt investigations as well as the extensional experiments demonstrate similar viscoelastic behavior for PP-control and PP-g-MAH.

D. Adhesive Viscoelastic Behavior of the Textile Composite at Different Temperature

The viscoelastic behavior of the textile composite was studied by extensional DMTA performed with a rheometer. The textile laminate was first analyzed using the lap-shear model, as described above. However, the lap-shear test needs more than 5 N at lower temperatures, which exceeds the tensile force of the rheometer. Around the melting temperature, the bond strength of the PA fabric either with non-modified PP or with PP-g-MAH is similar (data not shown). This suggests that the modification of the PP only plays a limited role in the adhesion to the textile if the matrix is in molten state.

In order to obtain nevertheless more information about the changed adhesion after matrix modification at lower temperatures, the setting of the lap-shear test was transferred to T-peel testing, since the stress needed for T-peel tests is lower, compared to lap-shear testing. Fig. 10 illustrates the extensional stress of PA66 fabric laminated with either PP HC101BF or PP-g-MAH at -10 °C, 25 °C and 170 °C for different strain rates of 0.001 – 1 s⁻¹. At -10 °C there is a clear increase of extensional stress if the PP matrix contains MAH. This counts for all strain rates. These results show that the PP modification improves the adhesion between PA66 and PP-g-MAH compared to the adhesion between PA66 and non-modified PP. The strengthening effect due to the modification is reduced during analysis at 25 °C. At 170 °C, above the melting temperature of the matrix, the difference of extensional stress between the two laminates disappears totally. This decrease of the strengthening effect by increasing temperature is illustrated in Fig. 11. At room temperature (25 °C) the adhesion between PA66 and PP-g-MAH is stronger compared to the adhesion between PA66 and PP-control. At lower degrees, this difference becomes even more visible. The

increased stiffness of the polymers at lower temperature may be involved causing this increase of extensional stress. At higher temperatures (170° C), just above the melting temperature, the difference disappears. Thus, the more liquid the matrix is, the more the interfacial strengthening effect due

to the matrix modification is eliminated.

Independent of what matrix is used in the textile composite there is a decrease of extensional stress by increasing temperature (Fig. 12). It seems that the more liquid the matrix is, the weaker the laminar adhesion.

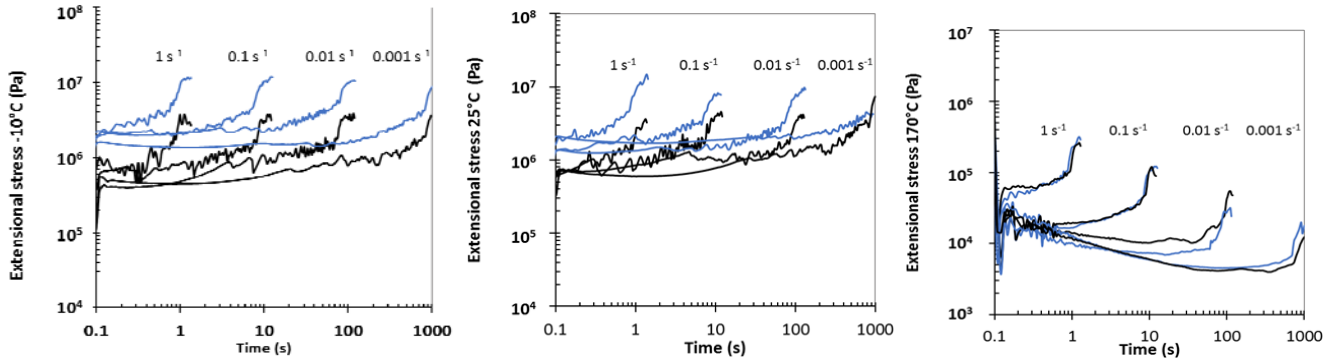


Fig. 10 Extensional T-peel stress of PA66 – PP-control laminates (black) and PA66 – PP-g-MAH laminates (blue) at different temperatures -10 °C, 25 °C, and 170 °C. Data are obtained with DMTA using in rheometer at extensional strain rates as indicated

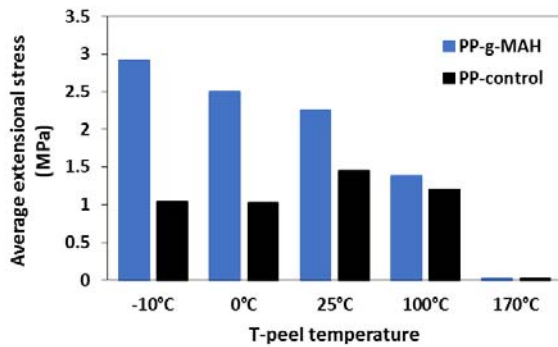


Fig. 11 Decrease of laminar adhesion strength by increasing temperature. T-peel tests were performed using the DMTA system of a rheometer at an extensional strain rate 0.1 s⁻¹ and at -10 °C, 0 °C, 25 °C, 100 °C and 170 °C. The average extensional stress from 1 – 7 seconds of the T-peel test

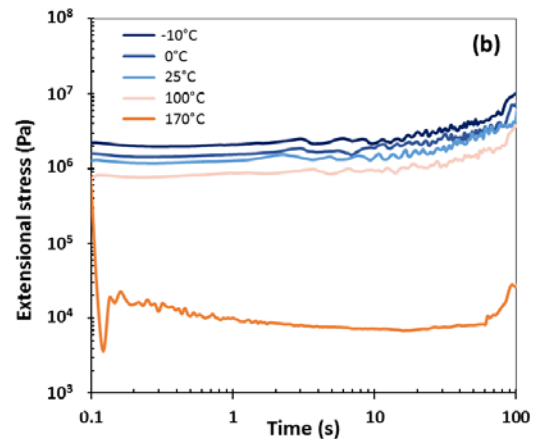
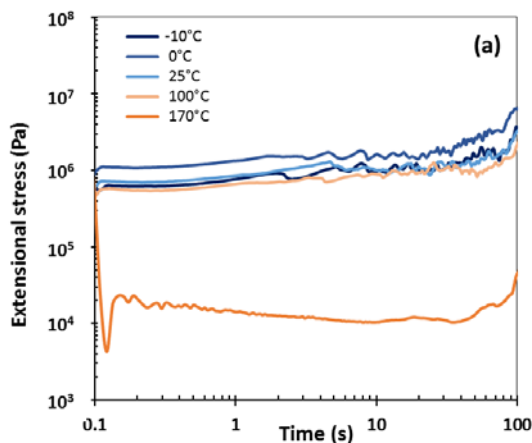


Fig. 12 T-peel test PA fabric laminate with PP non-treated (a) and PP-g-MAH (b) at -10 °C, 0 °C, 25 °C, 100 °C and 170 °C. At extensional strain rate of 0.01 s⁻¹

IV. CONCLUSION

Method development for analysis of polymeric composites is needed to obtain more basic understanding of interfacial mechanisms within the composites. Using a rheometer in DMTA mode, is a sensitive tool to investigate the temperature-dependent flow behavior of polymers and polymeric composites. In this study, we have found that modification of the PP by MAH grafting strengthens the adhesion to PA66, compared to non-modified PP having a similar viscoelastic behavior. This strengthening effect seems to be even stronger at lower temperatures. The increased stiffness of the material at lower temperatures may influence the measurement. However, at temperatures just above the melting temperature of the PP matrix, the increased laminar strength due to the matrix modification disappears. Thus, the modification plays a limited role in the adhesion to the textile if the matrix is in molten state. It seems in general that there is an increase of extensional stress by decreasing temperature

during the measurement, independent of what matrix is used in the composite. Additional analysis with AFM, nano-IR and LCR are useful methods to characterize the textile composite at microscopic level. Also, ATR-FTIR and contact angle detection gives more chemical information about the composite components and their possible chemical interactions. In conclusion, the T-peel analysis by DMTA is a technique that can be applied for polymeric textile composite characterization at a range of temperatures. The rheological model could be elaborated with micro bond tests and T-peel tests in an oscillation mode. This would simulate a more dynamic situation, in which composites may be once they are in use.

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REFERENCES

- [1] C. Heinzmanns, C. Weder, and L. M. de Espinosa, "Supramolecular polymer adhesives: advanced materials inspired by nature," *Chemical Society Reviews*, vol. 45(2), pp. 342-358, 2016.
- [2] M. Dasdemir, B. Maze, N. Anantharamaiah, and B. Pourdeyhimi, "Reactive compatibilization of polyamide 6/polyethylene nonwoven based thermoplastic composites," *European Polymer Journal*, vol. 63, pp. 194-206, 2015.
- [3] B. Smith, X. Zhang, G. Jiang, H. Wu, and S. Guo, S., "Effect of the temperature gradient on the interfacial strength of polyethylene/polyamide 6 during the sequential injection molding," *High Performance Polymers*, vol. 26(2), pp.135-143, 2014.
- [4] J.R. Büttler, T. Pham, "Characterization of Polyamide 6 - Polypropylene Laminates," *AIP publishing*, for publication accepted, May 2018.
- [5] M. Kelchtermans, M. Lo, E. Dillon, K. Kjoller, and C. Marcott, "Characterization of a polyethylene-polyamide multilayer film using nanoscale infrared spectroscopy and imaging," *Vibrational Spectroscopy*, vol. 82, pp.10-15. 2016.