

Article

On the Effect of Recycled Polyolefins on the Thermorheological Performance of Polymer-Modified Bitumen Used for Roofing-Applications

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Abstract: In order to meet the technical specifications in roofing applications, the bitumen used for this purpose is standardly modified by polymers. This, in general, allows the re-use of recycled polymer during the production of polymer-modified bitumen (PmB), simultaneously reducing the amount of polymeric waste. Recycling processes, however, may degrade or contaminate polymers, leading to reduced crystallinity and lower melting temperature. Six different recycled polyolefins (high crystallinity: iPP, HDPE; reduced crystallinity: APP, PP Copolymer; waxy polyolefins: Wax 105, Wax 115) were assessed on their suitability for roofing applications. Mixing characteristics, polymer distribution and thermo-mechanical properties of the PmB samples were determined, employing fluorescence microscopy, modulated temperature differential scanning calorimetry (MTDSC) and dynamic shear rheometry (DSR). Depending on mixing properties, two levels of polymer content (5 and 16 wt% or 16 and 30 wt%) were considered. High crystallinity polymers exhibited the biggest increase in $|G^*|$ and lowest phase angle. Reduced crystallinity polymers were more easily dispersed and showed improved $|G^*|$ and phase angle. Waxy polyolefins improved bitumen similarly to reduced crystallinity polymers and are easily dispersed. The results suggest, that a reduced crystallinity or lower melting temperature of the recycled polymers resulting from degradation or contamination may be beneficial, resulting in improved mixing behavior and a more homogeneous distribution of the polymer within the bitumen.

Keywords: polymer modified bitumen; polymer crystallinity; polymer recycling; polyolefins; roofing; HDPE; PP; PE



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1. Introduction

Bitumen is readily available as a by-product of the crude oil refining process. Since it exhibits convenient mechanical properties, it is widely used as a binder material for paving and sealing applications. However, the high temperature performance of bitumen is insufficient in hotter climates and can lead to rutting of roads or dripping on roofs and bridges [1]. It is commonly known, that synthetic polymers can be used to enhance the thermal and mechanical properties of bitumen [2,3]. For roofing applications, polymer modification levels are typically high and thermoplastics, such as LDPE have been used in concentrations up to 20% [4]. Classically, virgin polymers are used for this application. This requires petroleum-based resources and results in a potentially higher cost of production [5].

Simultaneously, the amount of waste plastic has risen continuously throughout the last decades and conventional ways of disposal such as land-filling and incineration have a negative effect on the environment [6]. The use of this waste plastic in the manufacturing of polymer-modified bitumen (PmB) reduces the ecological cost of waste disposal, while also reducing the manufacturing cost of PmB. This is achieved through reusing the over-

abundant waste plastic. Additionally, the creep resistance of PmB is generally increased, which results in a longer lifespan of the bitumen felt [7].

The performance of virgin polypropylene-based polyolefins and polyethylene has been intensively studied by Fawcett, McNally et al by means of differential scanning calorimetry (DSC), dynamic shear rheometry (DSR) and fluorescence microscopy [8,9]. They found improved high-temperature properties of PmB as well as swelling of the polymer rich phase and a limited miscibility of the polymer-rich phase in the bitumen. Also the suitability of a variety of recycled polymers for engineering applications has been demonstrated by DSC, DSR and fluorescence microscopy [10–15]. However, the compatibility of polymers is dependent on the composition of the underlying base bitumen, which varies depending on the origin and processing parameters during crude oil refinement [2]. Also the recycling process may change the polymers by degradation and contamination [16,17]. To account for these two factors, within the presented work the applicability of six recycled polyolefinic polymers to modify bitumen are studied, using bitumen with a different chemical composition compared to Fawcett et al. The aim of this paper is to assess the suitability of these recycled polymers for roofing applications, since these applications typically require especially high proportions of polymer and the use of recycled polymers would provide the greatest benefit.

2. Experimental

2.1. Methods

Blend preparation: For an optimal dispersion of the polymer in the bitumen, the following routine was applied. After preheating in an oven (160 °C), the bitumen was transferred to a heating plate and continuously stirred with an IKA T50 digital Ultra Turrax running at 2000–3000 rpm. At 20 °C above the melting temperature of the polymer, the polymer was added. In order to avoid the decomposition of bitumen components [18], the temperature did not exceed 200 °C. After adding the target amount of polymer, the polymer was dispersed at 190 °C for 30 to 90 min. Mixing was deemed complete, when the polymer phase was homogeneously distributed in the bitumen or no change in structure was observed in fluorescence microscopy for 15 min.

Fluorescence Microscopy: The polymer distribution in PmB was measured with an Axio Imager A.2m fluorescence microscope from Zeiss optics equipped with a 100-watt high-pressure mercury plasma arc-discharge lamp (HBO 100). The objective used was a Zeiss EC Epiplan 40x. For better contrast, a green color filter was applied. The samples shown in the results section were taken and analyzed directly after dispersing the polymer in the bitumen. The suitability of this method was demonstrated by Handle et al. [19].

Modulated Temperature DSC (MTDSC): The thermal transitions were measured by MTDSC (NETZSCH DSC 214 Polyma), using a heating rate of 3 K/min and *heat-only* conditions (0.40 K amplitude, 50 s period). The measuring range was from −65 to 200 °C. All properties were obtained from the second heating cycle to eliminate the influence of the thermal history. For polymers, samples were obtained by cutting them into flat pieces of approximately 10 to 15 mg. Sample preparation for bitumen and PmB was done by dripping the bitumen into the measurement pan and shortly heating it to ensure the complete coverage of the bottom of the pan. In case dripping was not possible due to high viscosity the bitumen was cooled down, cut and finally heated in the same way. DSC was used to determine the degree of crystallinity of the PmB blends according to Naskar et al. [20].

DSR: For the thermo-mechanical characterization of the polymers, bitumen and PmB a HAAKE MARS III parallel plate rheometer in forced oscillation mode was used. Due to the difference in force required to measure the rheological properties of bitumen in high and low temperature ranges two different measurement geometries had to be applied. For the low temperature range (−10 to 40 °C) a geometry with 8 mm in diameter and for the high temperature range (30–100 °C) a geometry with 20 mm in diameter was used. The

amplitude of the maximum strain was set to 0.001 and the angular frequency was 10 Hz. Samples were obtained by casting the sample geometry in silicone molds.

2.2. Materials

Polymers: The investigated recycled polymers can be divided into three classes: (a) High crystallinity, high viscosity polyolefins (iPP, HDPE), (b) reduced crystallinity, low viscosity polyolefins (APP, PP Copolymer) and (c) waxy polyolefins (Wax 105, Wax 115). The considered iPP, HDPE and PP Copolymer were reclaimed packaging materials, while the APP was a by-product of an iPP synthesis and the waxy polyolefins were chemically cracked, recycled polyethylenes. Since very little information on the properties of these polymers apart from their origin was available, MTDSC (see Figure 1 and Table 1), FTIR-ATR and DSR experiments (see Figure 2) were performed.

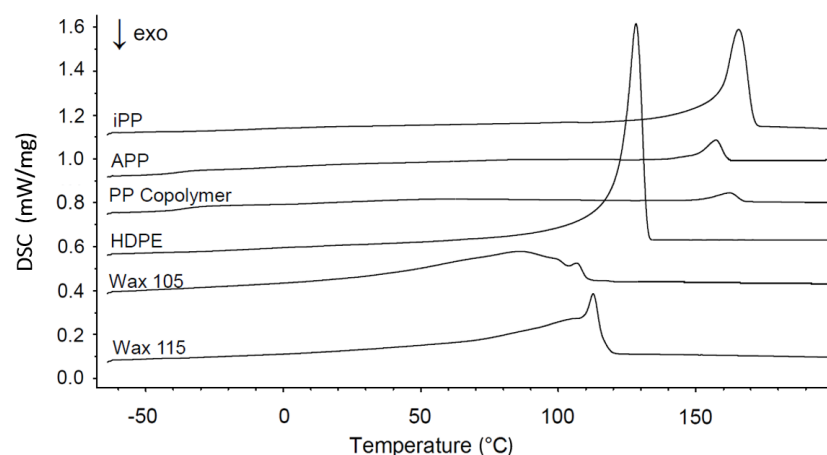


Figure 1. Total heat flow of the recycled polymers measured by MTDSC.

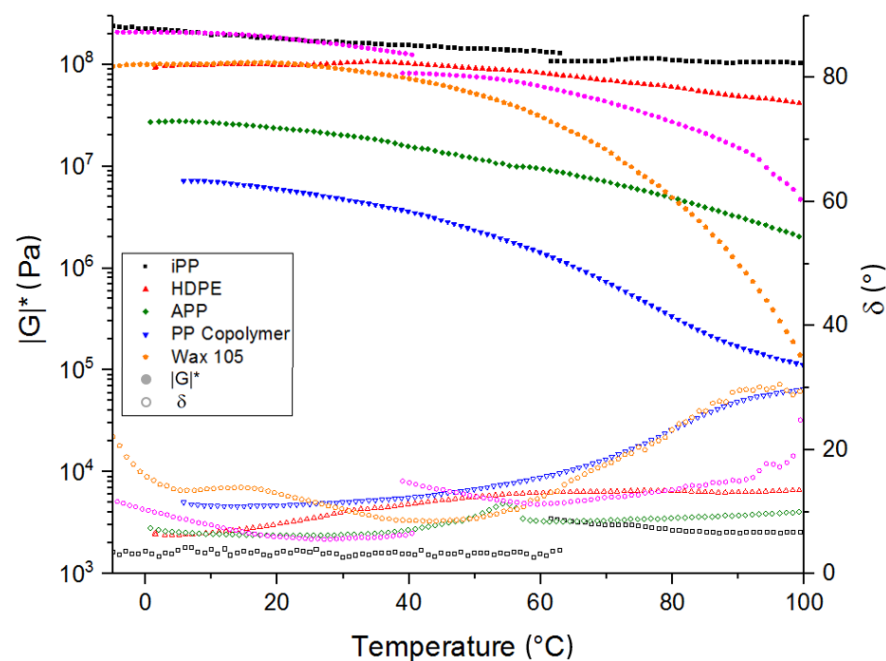
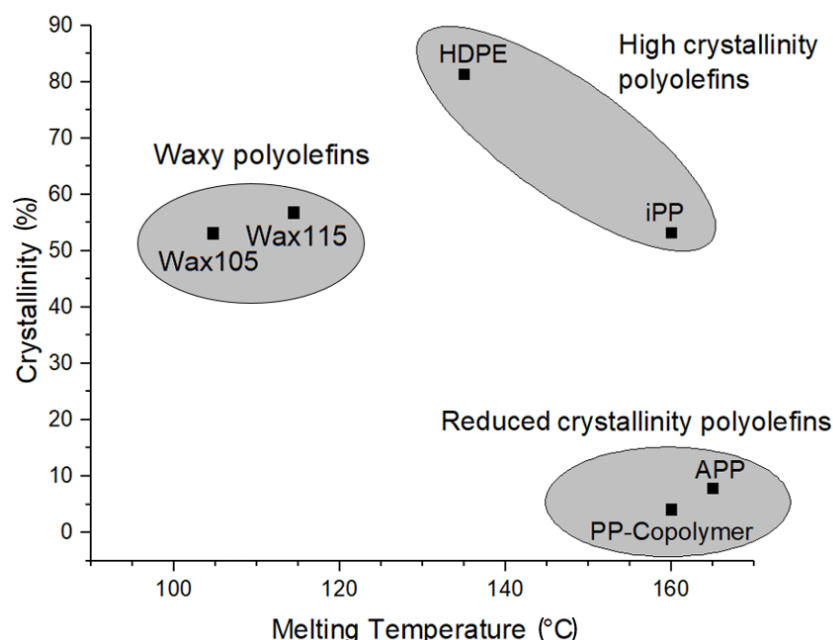


Figure 2. Rheological properties of the considered recycled polymers: Complex modulus $|G^*|$ and the phase angle δ determined from DSR measurements.

Table 1. List of polymers used, their identity and important thermal transition points.

Name	Identity	T_m /°C	T_g /°C
HDPE	HDPE	135	-
iPP	iPP	160	-
APP	APP	82/165	−35
PP Copolymer	Poly-alpha-Olefine, PP based	51/160	−31
Wax 105	Recycled waxy polymer, PE based	89–105	-
Wax 115	Recycled waxy polymer, PE based	50–115	-

The PP Copolymer is a random copolymer of propylene and alpha-olefins. The glass transition may be related to low-order regions similar to APP. Also the melting peak of heterotactic polypropylene segments is clearly visible. Wax 105 and 115 show broad melting transitions with very low onset temperatures and no glass transitions. The numbers 105 and 115 correspond to the melting temperatures of these polymers. For iPP, HDPE and APP the transitions described in the literature were found. Of the polypropylene based polymers iPP exhibits the highest melting enthalpy followed by APP. The PP Copolymer is the least crystalline of the polypropylenes. The high crystallinity polyolefins exhibited the highest complex modulus $|G^*|$ at 100 °C. The lower crystallinity polyolefins (APP, PP Copolymer) exhibited the lowest $|G^*|$ at 0 °C. The waxy polyolefins exhibited the steepest decent in $|G^*|$ in the high temperature region and a similarly high $|G^*|$ at 0 °C as the high crystallinity polyolefins. Furthermore, the degree of crystallinity was determined by comparison of the heat of fusion of the polymer melting peaks determined by DSC with the theoretic energy of fusion for 100% crystallinity, which is available in literature [21]. In Figure 3 the crystallinity is plotted versus the melting temperature, clearly showing the groups of investigated polymers.

**Figure 3.** Crystallinity versus melting temperature of the investigated polymers.

Bitumen: B160/220 bitumen provided by Orlen Litvinov was used in this study. SARA fractioning by thin-layer chromatography coupled with a flame ionization detector (TLC-FID) yielded a composition of 7.5% saturates, 42.7% aromatics, 30.3% resins and 19.5% asphaltenes with an instability colloidal index of 0.37. It exhibited a broad glass transition centered at −22.1 °C. The total, reversing and non-reversing heat flow of the employed bitumen can be found in Figure 4.

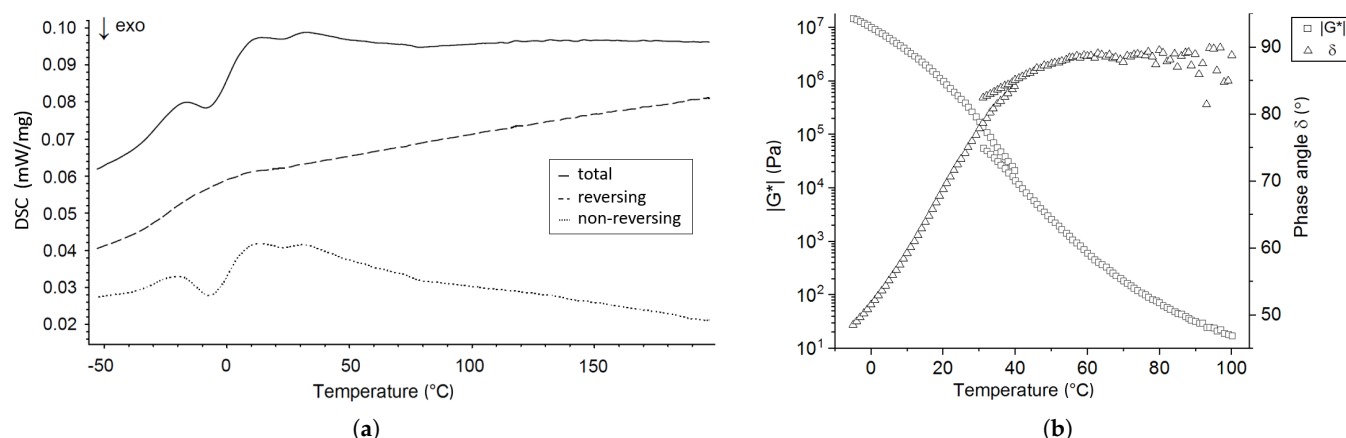


Figure 4. Characterization of B160/220 crude bitumen from Orlen Litvinov. (a) Total, reversing and non-reversing heat-flow curves (top to bottom) determined by MTDSC. (b) Complex modulus $|G^*|$ and phase angle as determined by DSR measurements.

Remarks on mixing properties: PmB has to fulfill two opposing requirements regarding viscosity: High viscosity at temperatures possible during application (-20 – 100 °C) and low viscosity at processing temperatures (up to 200 °C). This poses a problem for polymers, that exhibit a higher melt viscosity such as the studied higher crystallinity polyolefins. Accordingly, the iPP and HDPE blends at 16 wt% (percentage by weight) exhibited high viscoelastic properties causing the PmB to creep up the disperser shaft and limiting the flow of the sample. To ensure a homogeneous temperature and dispersion of the polymer, the blend was additionally stirred manually. The 5 wt% blends posed no problem during mixing. This suggests, that these high crystallinity polymers can only be applied in low percentages with this experimental setup regarding the mixing properties. The reduced crystallinity polyolefins have weaker self-interaction than the high crystallinity polyolefins and were expected to be more easily dispersible. This was the case for the APP and the PP Copolymer, which can therefore be added in higher percentages. The mixing properties of the polypropylenes were largely consistent with the ones found by A.H. Fawcett and T. McNally for the virgin polymers [8]. The waxy polyolefins were easily dispersible at 16 and 30 wt% and modifications with high percentages without impairing the processing characteristics of the bitumen are possible.

List of blends: For all types of polymers, 16 wt% blends were considered in the experimental program. Depending on the mixing behavior and the high temperature $|G^*|$, either 30 wt% or 5 wt% blends were additionally prepared. The list of the so-obtained blends are given in Table 2.

Table 2. List of blends considered in the experimental program.

Name	5 wt% Blend	16 wt% Blend	30 wt% Blend
HDPE	X	X	
iPP	X	X	
APP		X	X
PP Copolymer		X	X
Wax 105		X	X
Wax 115		X	X

3. Results and Discussion

3.1. Phase Distribution

PmB typically exhibits either two phases (a polymer-rich phase consisting of mainly polymer swollen with light components of the bitumen and a bitumen-rich phase consisting

mainly of the residual part of the bitumen) or one homogeneous phase containing both the polymer and the bitumen. The phase distribution within the considered PmB blends can be seen in Figure 5 as obtained by fluorescence microscopy, with the polymer-rich phase being green. The distribution of the polymer-rich phase may be categorized as accumulated, loosely distributed, lamellar and continuous in case two phases are present (see Table 3).

Table 3. Categorization of polymer-rich phase as obtained by fluorescence microscopy.

Polymer	5 wt% Blend	16 wt% Blend	30 wt% Blend
iPP	accumulated	lamellar	-
HDPE	loosely distributed	continuous	-
APP	-	loosely distributed	continuous
PP Copolymer	-	continuous	continuous
Wax 105	-	continuous	continuous
Wax 115	-	homogeneous	homogeneous

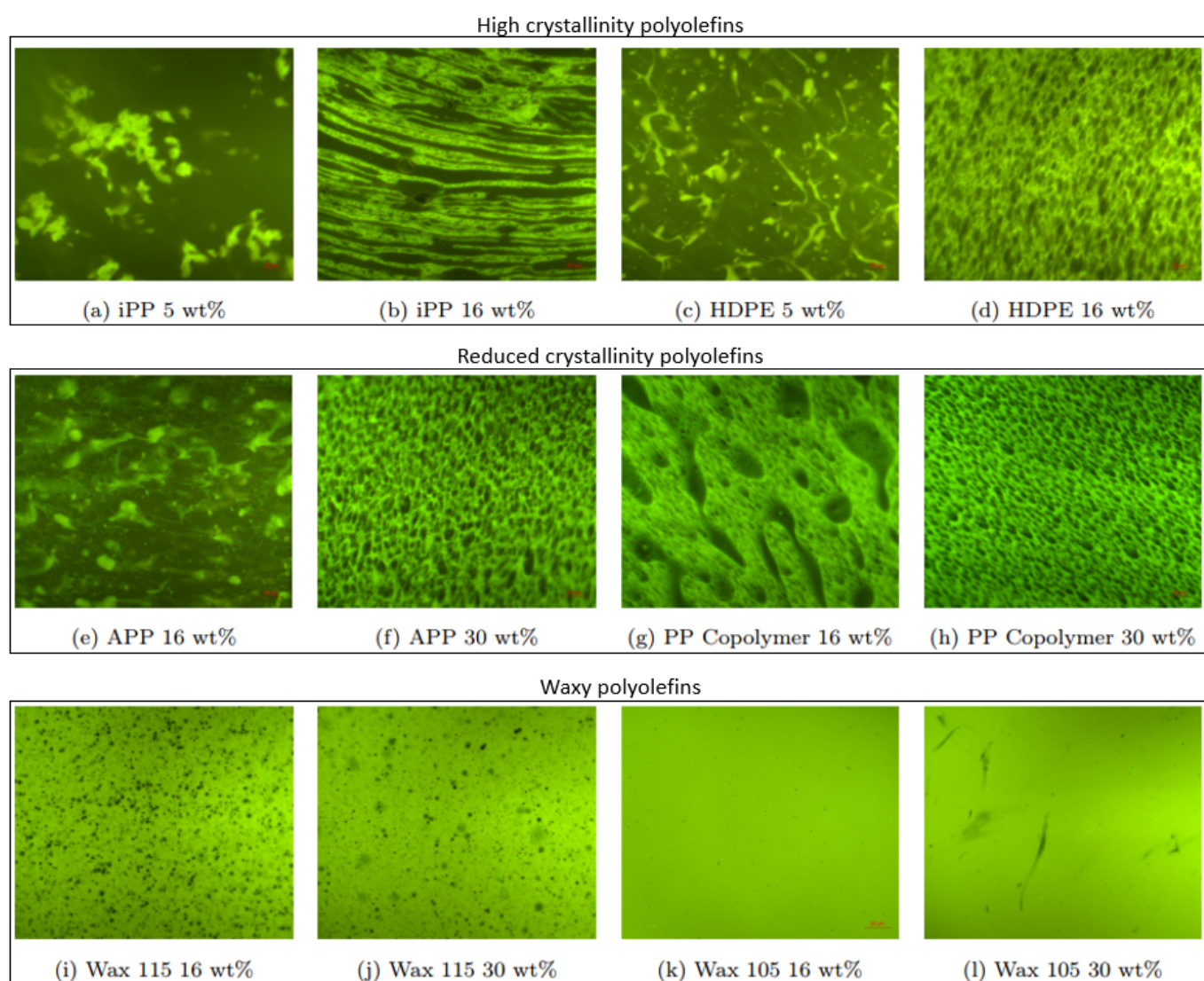


Figure 5. Fluorescence micrographs of the polymer distribution of various polyolefins at 40× magnification (image dimensions represent an area of 420 μm $\times$ 350 μm ; the polymer-rich phase is green).

Influence of polymer melting temperature: For the high crystallinity polyolefins (iPP, HDPE) it was observed, that the polymer-rich phase of the higher melting iPP ($T_m = 160$ °C)

is less uniformly distributed than the one of HDPE ($T_m = 135\text{ }^{\circ}\text{C}$) at both additive concentrations (Figure 5a–d). The waxy polymers (Wax 105, Wax 115) exhibited the lowest melting point ($T_{m,Wax105} = 105\text{ }^{\circ}\text{C}$, $T_{m,Wax115} = 115\text{ }^{\circ}\text{C}$) of the considered polymers and showed the most evenly distributed polymer-rich phase (Figure 5i–l). Accordingly, a lower polymer melting point seems to improve the distribution of the polymer within the bitumen, with the lower melting point indicating weaker polymer-polymer interactions within the crystalline regions and hence facilitating the dissolution of the crystalline regions or the swelling of the polymer.

Influence of the degree of crystallinity: Although the polypropylene-based polymers (iPP, APP, PP Copolymer) show roughly the same polymer melting point, they differ in their degree of crystallinity, which is reflected in the area of their polymer melting peak (see Figure 1). iPP shows the highest relative crystallinity, followed by APP, while PP Copolymer exhibits the lowest crystallinity. Lower crystallinity implies a higher proportion of less ordered and amorphous polymer regions, improving the distribution of the polymer-rich phase. Accordingly, the reduced crystallinity polypropylenes (APP—loosely distributed, PP Copolymer—continuous) are more evenly distributed than e.g., 16 wt% iPP (see Figure 5b,e,g). As can be seen in Figure 5e,g at 16 wt% modification, the polymer-rich phase of the lower crystallinity PP Copolymer is more evenly distributed than in case of APP modification.

These findings are consistent with results reported in A.H. Fawcett and T. McNally, where no continuous polymer distribution has been found for iPP contents of up to 28.6 wt% [8,9]. In addition to the distribution of the polymer within the bitumen (see Table 3), four basic morphologies can be identified:

1. Polymer-rich phase (accumulated, loosely distributed) in bitumen-rich matrix (Figure 5a,c,e)
2. No distinct matrix phase (lamellar, Figure 5b)
3. Bitumen-rich phase in polymer-rich matrix (continuous) (Figure 5d,f,g,h,i,j)
4. Only one phase (homogeneous) (Figure 5k,l)

Both the distribution of the polymer-rich phase and the established phase morphology influence the rheological properties, as will be addressed in the following chapter.

Rheology

The performance of PmB at high temperatures is strongly linked to its elastic behavior at these temperatures, with an improved performance being indicated by a higher complex shear modulus $|G^*|$ and a phase angle below 45° . In this paper, $|G^*|$ and the phase angle of the investigated polymers, the crude bitumen and the PmB-blends were determined by DSR measurements with the obtained results shown in Figure 6.

The polypropylene and polyethylene-based blends, where the polymer-rich phase was distributed in a bitumen-rich matrix, (iPP 5 wt%, HDPE 5 wt%, APP 16 wt%) show a rheological behavior closer to the crude bitumen than the pure polymer, with the phase angle exceeding 45° in some temperature regimes. However, beneficial effects of the polymeric network can be seen for temperatures higher than $50\text{ }^{\circ}\text{C}$, resulting in a lower phase angle and a slower decrease of $|G^*|$ with increasing temperature compared to the crude bitumen. On the other hand, the polypropylene and polyethylene-based blends with no distinct matrix phase (iPP 16 wt%) or with the bitumen-rich phase being distributed in the polymer-rich matrix (HDPE 16 wt%, APP 30 wt%, PP Copolymer 16/30 wt%) exhibited a behavior closer to the pure polymer, with lower phase angles and an even smaller decrease of $|G^*|$ for increasing temperature than observed for the aforementioned blends where the polymer-rich phase was distributed in a bitumen-rich matrix.

The waxy polymer based blends exhibited a continuous decrease of $|G^*|$ and phase angles below 45° up to temperatures of $80\text{ }^{\circ}\text{C}$. For temperatures above $80\text{ }^{\circ}\text{C}$, $|G^*|$ continues to drop and the phase angle increases sharply, which is attributed to the polymer melting at 105 and $115\text{ }^{\circ}\text{C}$, respectively.

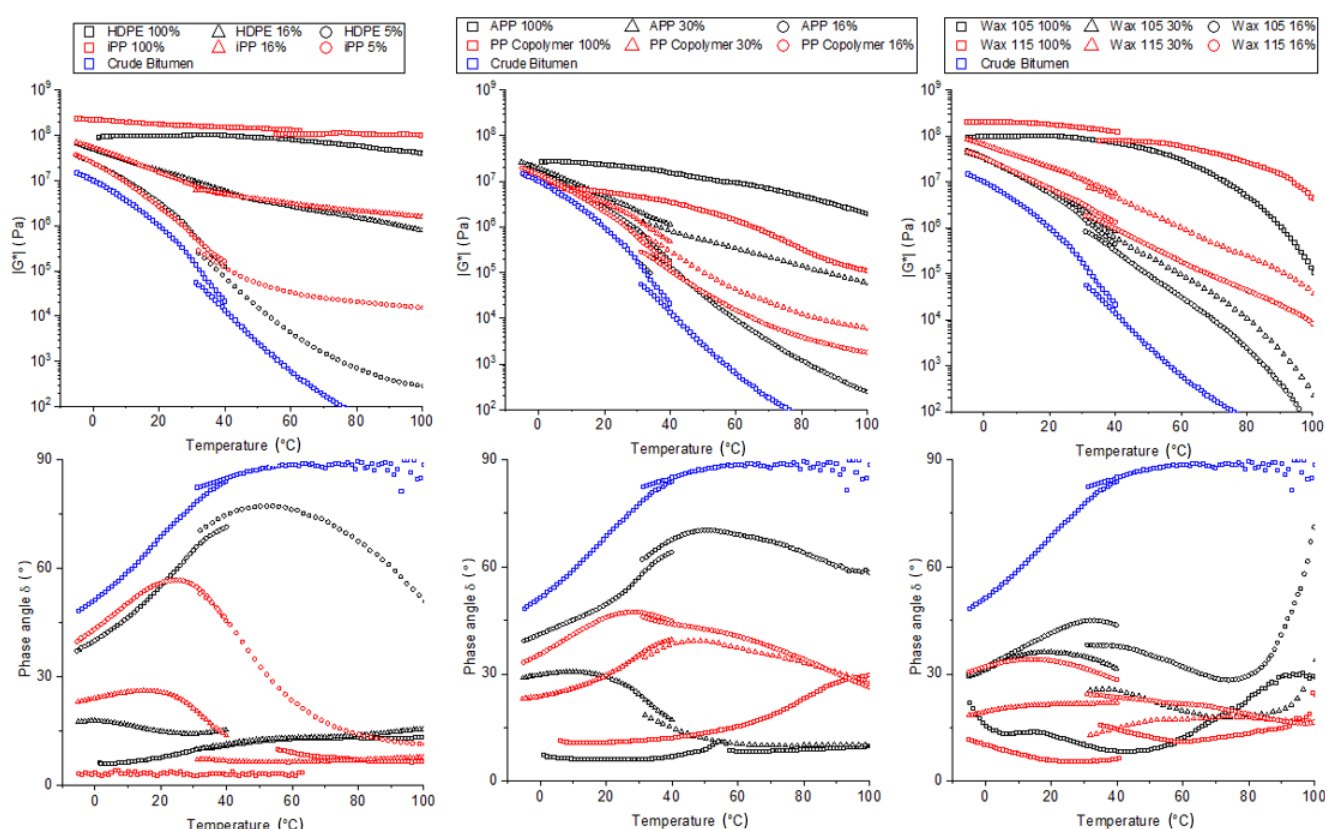


Figure 6. Complex shear modulus $|G^*|$ and phase angle δ of the polymers, crude bitumen and PmB-blends determined by DSR experiments. **Left:** High crystallinity polyolefins. **Middle:** Reduced crystallinity polyolefins. **Right:** Waxy polyolefins.

During application roofing felts, dark materials such as PmB-blends can reach temperatures of up to 70 °C during hot summer days. Therefore, $|G^*|$ and phase angle at this temperature of the considered types of PmB are compared in Figure 7a. Higher phase angles and lower $|G^*|$ are observed for lower polymer concentrations. The polypropylene-based polymers exhibited higher $|G^*|$ values depending on the percentage of crystalline polymer in the blend, see Figure 7b. This suggests, that the crystalline fraction of the polymer-rich phase determines the $|G^*|$ of the blend since its structure remains relatively unchanged and therefore retains the rheological properties of the polymer. The crystallinity was determined by MTDSC with the results given in Appendix A (see Figures A2–A4).

Considering the temperature range from 0 to 70 °C, the morphology at room temperature identified by fluorescence microscopy is plotted versus the maximum phase angle obtained in this temperature range (see Figure 7c). For the blends, where the polymer-rich phase is distributed within the bitumen-rich matrix phase, phase angles above 60° are observed for APP (16 wt%), HDPE (5 wt%) and iPP (5 wt%), whereas morphologies characterized by a dominant polymer-rich phase with (i) no distinct matrix phase, (ii) bitumen-rich phase in polymer-rich matrix phase and (iii) homogeneous distribution of the polymer show lower phase angles. This can be explained by the high phase angle of the employed bitumen (close to 90° starting at 40 °C), which has a higher impact on the properties of the PmB blends when the bitumen-rich phase is the matrix phase. The limited improvement of the maximum phase angle in case of homogeneous blends, which is consistent with literature (see [2]), is likely due to the disruption of the crystalline structure of the polymer due to the interaction with bitumen components and therefore resulting in a performance more similar to crude bitumen. For MTDSC measurements see Figure A5 in Appendix A.

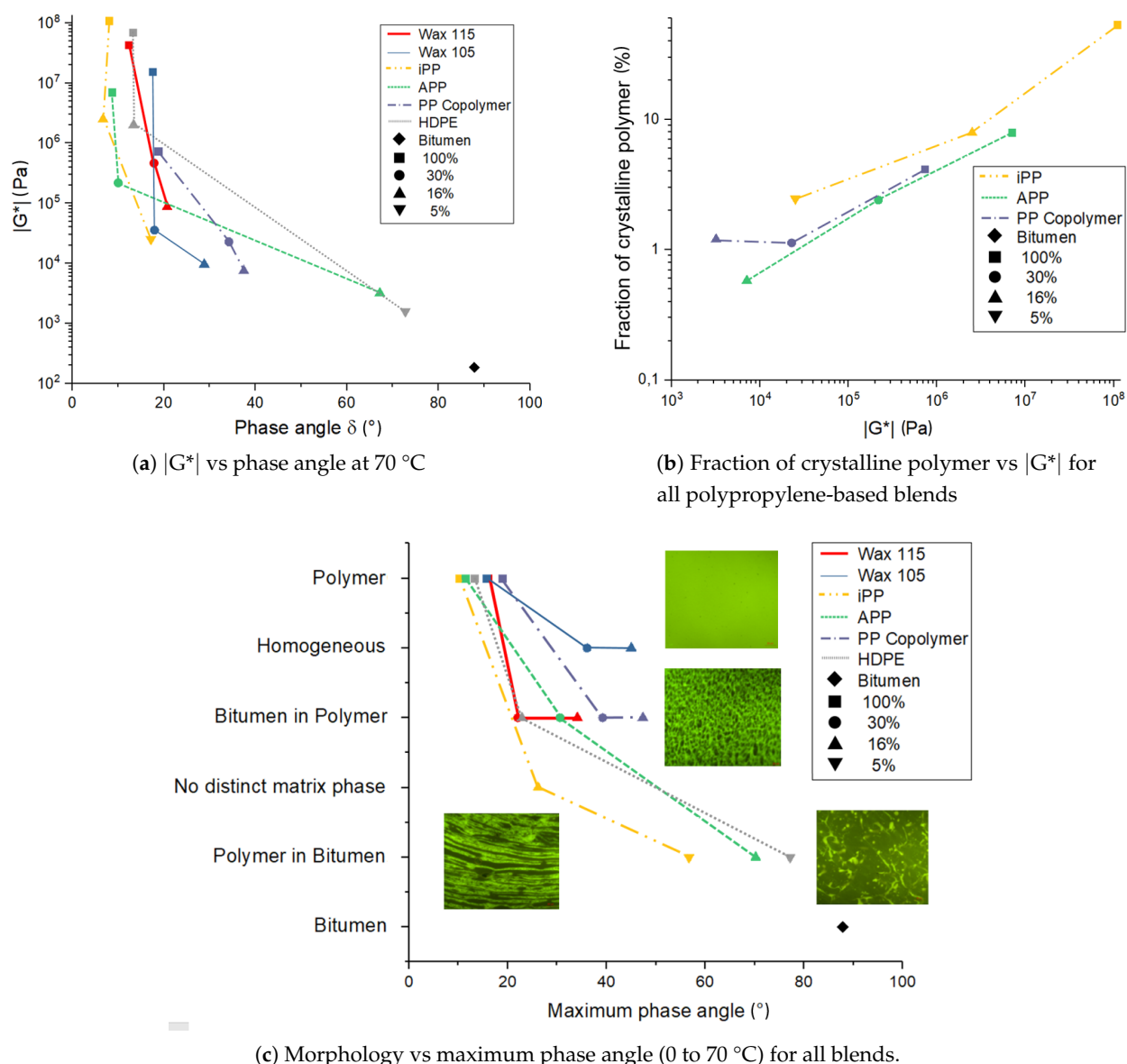


Figure 7. Morphology, $|G^*|$, phase angle and crystallinity as obtained by DSR, MTDSC and fluorescence microscopy.

4. Conclusions

In the course of this study one base bitumen (Orlen Litvinov 160/220) and six recycled polymers were tested for their suitability to be used for polymer modified bitumen felts. The investigated recycled polymers can be divided into three classes:

- High crystallinity, high viscosity polyolefins (iPP, HDPE)
- Reduced crystallinity, low viscosity polyolefins (APP, PP Copolymer)
- Waxy polyolefins (Wax 105, Wax 115)

A 16 wt% modification was prepared for all polymers. Additionally, depending on the mixing behavior, either a 5 wt% or a 30 wt% modification were considered in the experimental program. The base bitumen and the blends were characterized by fluorescence microscopy, MTDSC and DSR.

Based on the obtained results, following conclusions can be drawn:

- High crystallinity polyolefins show the highest improvement considering high temperature $|G^*|$ and phase angle, given that the polymer-rich phase is the matrix phase.

Additionally, they are generally less evenly distributed than the other investigated polyolefins and are more difficult to process due to their highly viscous behavior.

- Reduced crystallinity polyolefins improve high temperature $|G^*|$, although not as much as the high crystallinity polyolefins, generally exhibit higher phase angles at the same modification level and are more evenly distributed when compared to high crystallinity polyolefins.
- Waxy polyolefins improve high temperature phase angle and $|G^*|$ similarly to reduced crystallinity polyolefins, are easily dispersed and exhibit the most uniform polymer distribution. However near their melting temperature, they exhibit a sharp phase angle increase and $|G^*|$ decrease, which may be relevant during application.

Considering both $|G^*|$ and the phase angle at 70 °C and the maximum phase angle in the temperature range of 0 to 70 °C, polymer modifications using HDPE (16 wt%), iPP (16 wt%), Wax 105 and 115 (16 and 30 wt%), APP (30 wt%) and PP Copolymer (30 wt%) were found to be acceptable for engineering applications such as roofing. For temperatures above 90 °C, Wax 105 does not improve the performance of the PmB due to its low melting temperature resulting in a high phase angle and low $|G^*|$.

Consequently, based on our results, there is potential for the use of recycled polyolefins in highly modified PmB roofing applications. Furthermore, the results even suggest, that a reduced crystallinity or lower melting temperature of the recycled polymers resulting e.g., from degradation or contamination may even be beneficial, resulting in an improved mixing behavior and a more homogeneous distribution of the polymer within the bitumen. For other engineering applications it may be necessary to test lower modification grades and to conduct tests such as creep recovery and PmB temperature stability.

Author Contributions: Conceptualization: A.S. and S.H.U.; methodology: M.W., A.S., S.H.U. and R.L.; formal analysis: M.W., A.S., S.H.U. and R.L.; investigation: M.W. and A.S.; resources: S.H.U. and R.L.; data curation: M.W.; writing—original draft preparation: M.W.; writing—review and editing: M.W., A.S., S.H.U. and R.L.; visualization: M.W.; supervision: A.S. and S.H.U.; project administration: S.H.U. and R.L.; funding acquisition: R.L. All authors have read and agreed to the published version of the manuscript.

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Appendix A

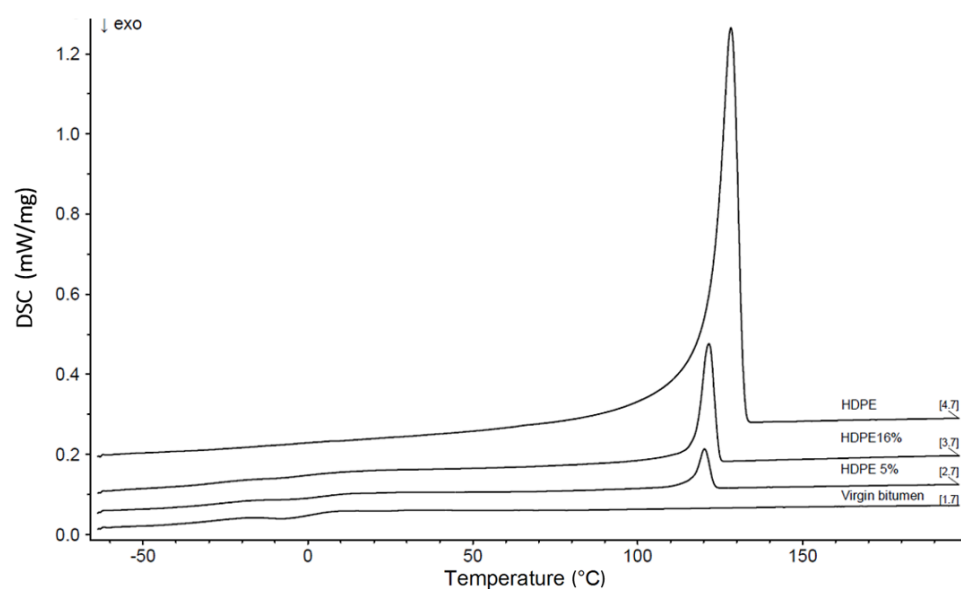


Figure A1. Total heat flow of the HDPE blends measured by MTDSC.

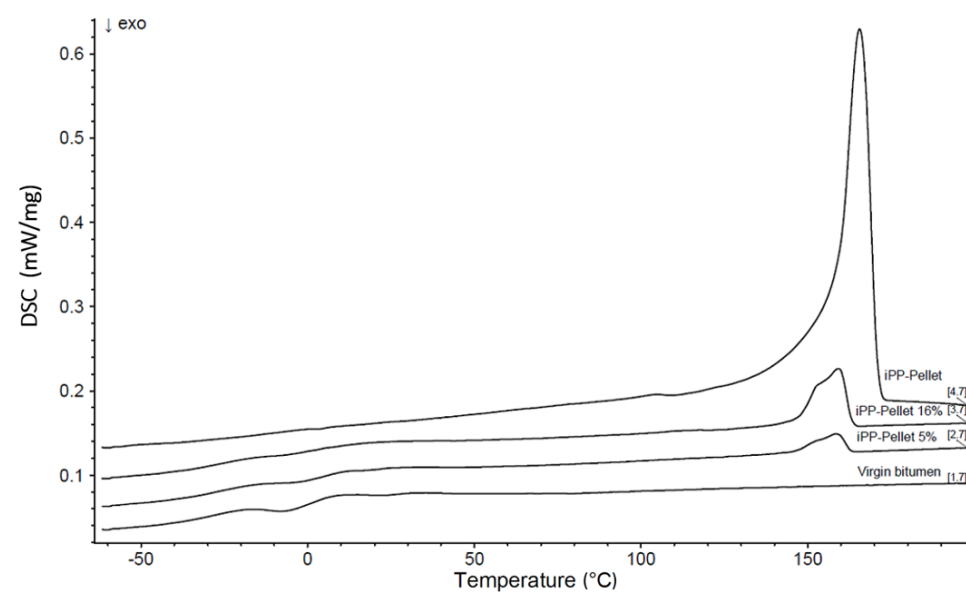


Figure A2. Total heat flow of the iPP blends measured by MTDSC.

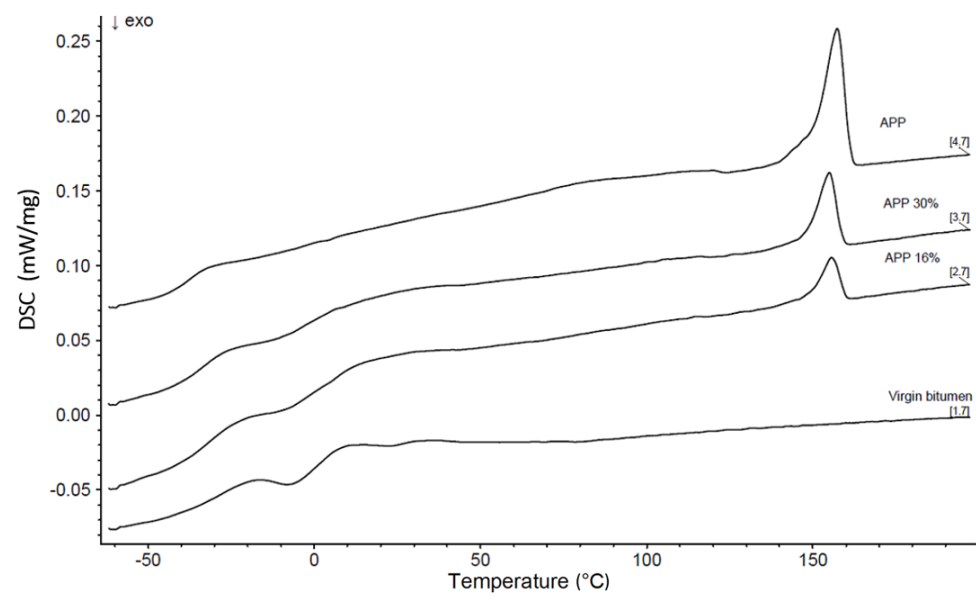


Figure A3. Total heat flow of the APP blends measured by MTDSC.

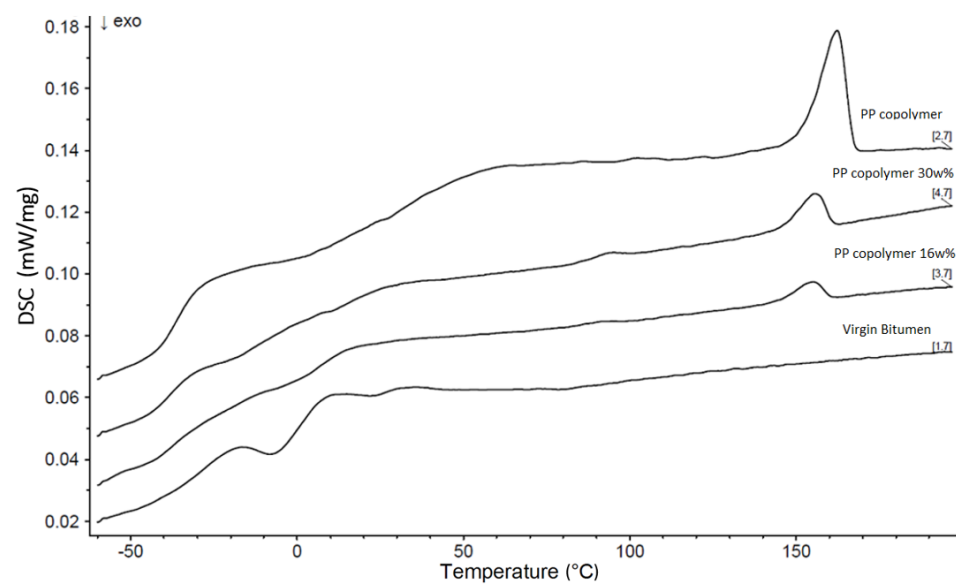


Figure A4. Total heat flow of the PP Copolymer blends measured by MTDSC.

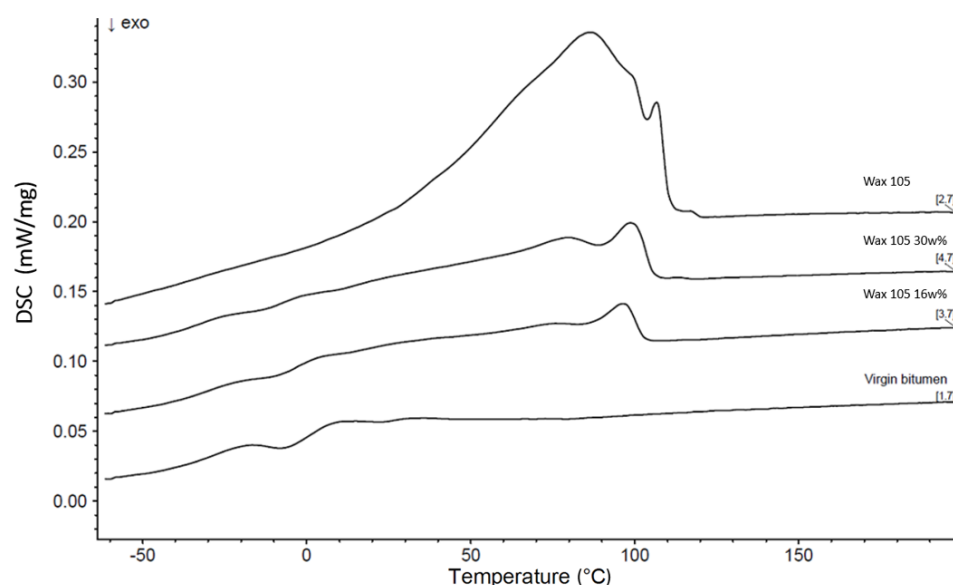


Figure A5. Total heat flow of the Wax 105 blends measured by MTDSC.

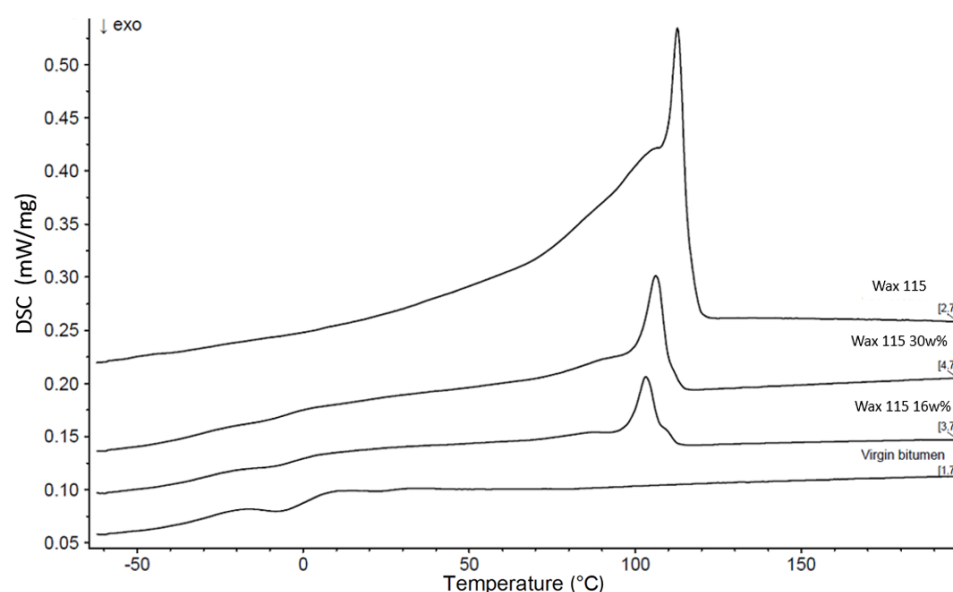


Figure A6. Total heat flow of the Wax 115 blends measured by MTDSC.

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