Rheological Properties of Water-Soluble Methacrylate Block-Copolymers

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ABSTRACT

Rheological properties as function of temperature of several block polymers containing poly(2-(dimethylamino) ethyl methacrylate), poly(ethylene oxide) and poly(propylene oxide) were studied. Effect of each block on rheological properties is discussed. Wood fiber sheets were prepared using these polymers as additive. Dynamic mechanical properties of these sheets were compared with rheological behaviour of corresponding polymer.

INTRODUCTION

Block polymers have potential to be used for different applications. Block co-polymers enable combination of monomers with different molecular characteristic in tailored regions of the polymer chain. In block co-polymers, hydrophilic and hydrophobic regions can be present in the same molecule. Also ionic sequences can be combined with neutral sequences (Fig. 1).

Block polymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are commercially available and widely studied, especially in water solution[1] Also poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) block co-polymers have been studied, and they exhibit interesting organization behaviour with pH.[2] Since these polymers usually are used in water environment, rheological properties of water solutions of these polymers have been reported earlier. Since these block polymers are mostly used as water applications, no attention is paid on melt properties[3] of the structures.
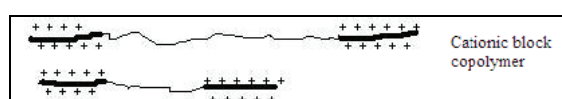

Figure 1. Schematic structure of studied block co-polymers.

In this paper, thermal behaviour of block polymers of PDMAEMA, PEO and PPO are presented. Molecular structures of all of the blocks are shown in Fig. 2. Effect of each block on the rheological properties is discussed.
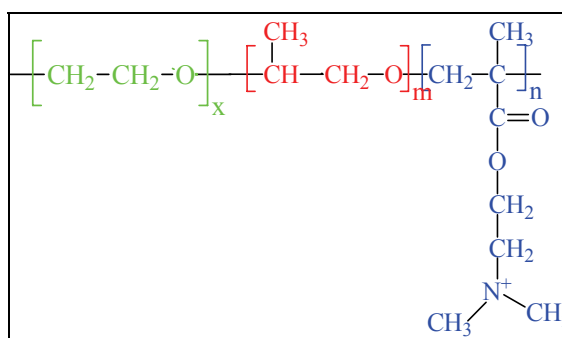

Figure 2. Block structures of PEO, PPO and PDMAEMA.

MATERIALS AND METHODS

Polymers used in the study were prepared with potassium hydride from PEO and PPO macroinitiators according to a method reported first by Nagasaki et. al.[4] Block structures of the co-polymers are listed in Table 1. Block co-polymers used in

this study were of form DED, DEPED and DPD, where D identifies poly(2-(dimethylamino) ethyl methacrylate), E identifies poly(ethylene oxide) and P identifies poly(propylene oxide).

Table 1. Block length of the used polymers.

Polymer	Block structure (kg/mol)				
	D	E	P	E	D
DED-10	10	10	-	-	10
DEPED-14	10	6	2.5	6	10
DEPED-5	10	0.85	4.1	0.85	10
DPD-2	10	-	2	-	10

Rotational Reometry

The measurements were done with Anton Paar Physica MRC 310 strain controlled rheometer. Temperature was controlled with peltier heating element at lower plate, and cooling was done with water circulator. Used geometry was 25 mm plate geometry. Gap size was controlled with TruGap induction sensor. Gap size was optimized to be 150 μm to minimize possible temperature gradient. Measured temperature ramp was cooling from 100 °C to -30 °C at 5 °C/min followed by heating up to 100 °C with same ramp. Oscillatory measurement was done at 0.1 % strain within linear viscoelastic region at 10 Hz frequency. Moduli and viscosity were recorded.

Differential Scanning Calorimeter (DSC)

Melting temperatures (T_m) and glass transition temperatures (T_g) were determined with a Mettler Toledo DSC 821e differential scanning calorimeter with heating rate of 10 °C / min.

Preparation of fiber sheets

1 % suspension of beaten wood fibre was mixed with 1 % solution of polymer. Resulting mixture was stabilized in fridge for three hours, filtered through polytetrafluoroethylene filter, washed with distilled water and dried in room temperature.

Dynamic Mechanical Analysis (DMA)

DMA measurements were done with TA Instruments DMA Q800 equipment. The measurements were done in ambient humidity. Dimensions of the samples were approximately: w * t * l = 3 mm * 0.15 mm * 12 mm. Length was measured automatically by the equipment, whereas other dimensions were measured manually before each run. Measured temperature ramp was of 5 °C / min from -30 °C to 150 °C. Amplitude used was 2 μm and the measurement was done at 10 Hz frequency.

Table 2. Melt behaviour of block co-polymers based on rheological measurements.

Polymer	Transition temperatures (°C)			Melt viscosity
	$T_g{}^a$	$T_m{}^a$	$T_m{}^b$	$|\eta^*|$ 90°C
DED-10	< -30	56	47	200
E-10	< -30	65		1.9
DEPED-14	< -30	52	47	180
EPE-10	< -30	61		3.2
DEPED-5	< -30	27	7.1	5.9
EPE-5	< -30	41		0.32
DPD-2	-8	65		87
P-2	< -30	< -30		0.076
PDMAEMA	12	~50		43

[a] Rotational Rheometry
[b] Differential Scanning Calorimetry (DSC)

RESULTS

Melt behaviour

Transition temperatures of block co-polymers are listed in Table 2. T_g of PDMAEMA reported in literature is 5 °C[5] When transition temperatures of DSC and rheometry are compared, some deviation is detected. Values are systematically about 10 °C higher from rheometry than the values measured with DSC. That delay is typical when rather high amount of sample is rapidly heated.

DMAEMA block increases melt viscosity of the polymers remarkably (Figs. 3 and 4). As the lowest the increase is one decade (EPE-5), but it can also be as high as three decades (P-2) (Table 2). As opposite, it also decreases viscosity at so called rubbery region, and it can be seen in Figs. 3 and 5.

Crystallinity of PEO is dominant also in EPE block polymer, and further modification with DMAEMA does not decrease this behaviour remarkably. Still, crystallinity of block polymers seems clearly to be smaller when DMAEMA block is present (Figs. 3 and 4). Characteristic for pure PDMAEMA is that it has practically no melting point, but has glass transition temperature at 5 degrees.[5]
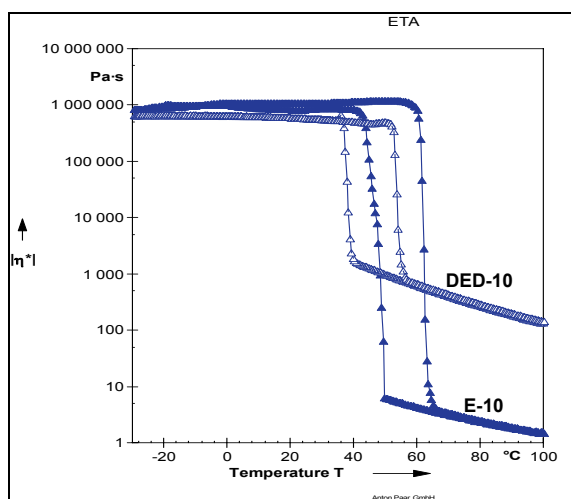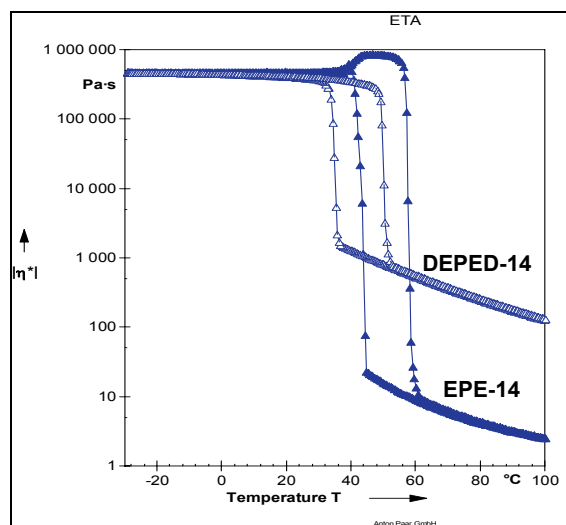

Figure 4. EPE-14 and DEPED-14 block polymers - viscoelastic behaviour.

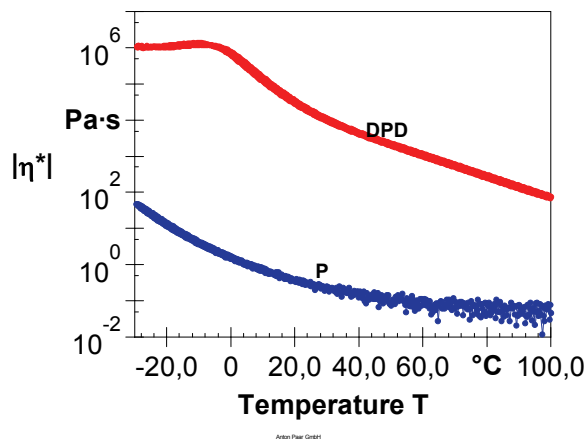Figure 5. Viscoelastic behaviour of DEPED-5 and EPE-5 block co-polymers.

Figure 3. Viscoelastic behaviour of DED-10 block co-polymer and E-10 pre-polymer.

Figure 6. Thermomechanical behaviour of DPD-2 block polymer.

Figure 7. Viscoelastic behaviour of PDMAEMA homopolymer.

Just like in other polymers, addition of D-block increases melt viscosity of DPD polymers (Fig. 6). The material properties are clearly changed, and transformation point (T_g) can be seen at temperature near room temperature.

When three block systems are present, structure seems to have tendency to organize before melting (Figs. 3 and 4). When homopolymer is formed to block co-polymer, increase in viscosity before melting is seen only in block polymer DED-10 (Fig. 3) whereas same kind of behaviour is seen in unmodified block polymer EPE-14 (Fig. 4) but not in modified polymer DEPED-14. That behaviour indicates that modification of three-block polymer onto penta-block disturbs ability to form organized structures.

Temperature ramp of pure DMAEMA homopolymer is presented in Fig. 7. PDMAEMA exhibits clear transition point at 12 °C, which. Also melt viscosity of the homopolymer is rather high (Table 2). Therefore, it can be concluded, that DMAEMA block is the reason for higher melt viscosity of the block polymers.
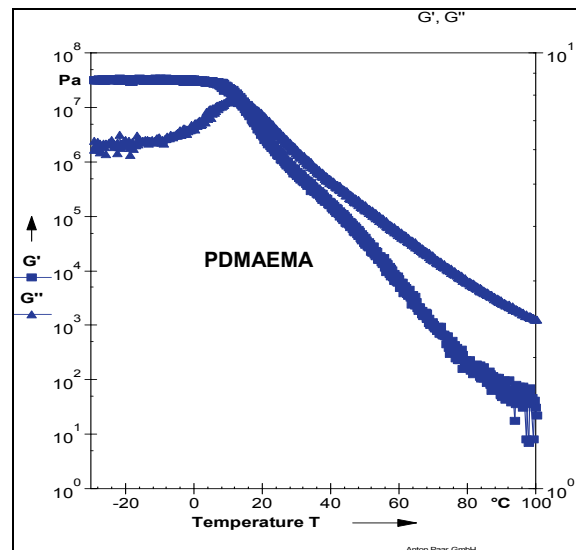
Behaviour as fibre additive

Some of the polymers were used as additive in fibre sheet. Dynamic mechanical properties of prepared sheets are presented in Fig. 8. Different transition temperatures can be seen in fibre sheet when non-ionic polymer was used as additive. It indicates that unmodified polymer forms so strongly organized structure that it does not form homogeneous structure with fibres. Instead, the modified ionic polymer is evenly distributed since no transition peaks can be seen.
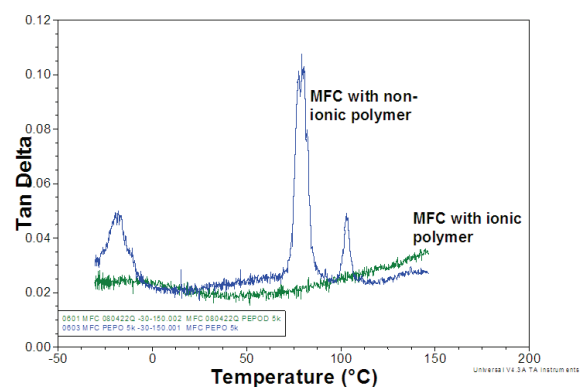

Figure 8. Temperature ramp of sheets prepared from polymer and wood fibre measured with DMA.

CONCLUSION

DMAEMA sequence clearly increases melt viscosity of measured block polymers. It also weakens strongly crystalline character of PEO block. Based on this study, it can be concluded that three block structures are more organized than penta-block structures independent on the block composition. When DMAEMA block polymer is used as an additive in wood fiber, homogeneous structure is formed, and no temperature transitions are present.

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