A-P100. Influence of Ester Diluents and Chain Extension on Polyurethane Viscosities

Dalia Bražinskienė, Sandra Mačiulytė, Paulina Nemaniutė, Tadas Matijošius, Svajus J. Asadauskas

Center for Physical Sciences and Technology (FTMC), Saulėtekio 3, Vilnius
dalia.brazinskiene@ftmc.lt

Polyurethanes are often used as adhesives in laminated packaging, where viscosity is critical. Poly diethylene glycol adipate macrodiol was chain-extended with hexamethylene diisocyanate at 1:0.3 mol [1] to produce a polyurethane prepolymer [2]. Then it was diluted with ethyl acetate 1:1 (w/w) to produce the first adhesive component. As the second adhesive component, aromatic tri-isocyanate CAS 53317-61-6 was used at 1.4 mol excess to assure eventual gelation.

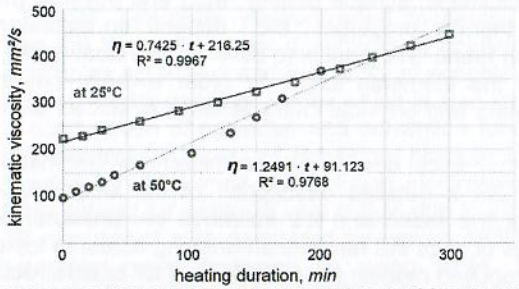

Fig. 1. Viscosity increase during polyurethane addition to tri-isocyanate in ethyl acetate

Right after mixing the blend viscosity η was periodically measured per ASTM D445. The narrow capillary of the Cannon-Fenske viscometer minimized the vaporization of ethyl acetate. Polymerization-induced thickening was gradual, Fig. 1, with stronger non-linearity observed at 50°C than 25°C. Catalytic effects of the ester linkage in ethyl acetate could be responsible for the acceleration of the carbamate formation, since chemical reactivity generally intensifies at higher temperatures. Eventually, the adhesive formulation was fortified with nanoparticles and successfully used to laminate multilayer plastic films and Al foils.

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Keywords: *adhesive, rheology, gelation, prepolymer.*
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2. S. Mačiulytė et al. *Proc. Chemistry & Chem. Tech.* p. 88 (2019)

B-P101. Enhancement of the Compatibility between Natural Rubber and Pineapple Leaf Microfibers for Better Stress Transfer in Their Composite

Karine Mougin[1], Budsaraporn Surajarusarn[1,2], Nuttapong Hariwongsanupab[2], Gautier Schrodj[1], Samar Garreau[1], Taweechai Amornsakchai[2]

[1]Institut de Science des Matériaux de Mulhouse, IS2M-CNRS - UMR 7361, Université de Haute Alsace, F-68100 Mulhouse, France
[2]Mahidol University, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Nakhon Pathom, Thailand
Karine.mougin@uha.fr

The compatibility between natural rubber (NR) and pineapple leaf microfibers (PALMF) in NR-PALMF composites were improved by two methods. One method was carried out by the addition of nitrile rubber (NBR) during mixing [1]. The other method was by chemically treating PALMF surface with silane and/or a compatibilizer. Modulus at low strain of NR-PALMF composites increased in both cases. Composite prepared with silane modified PALMF has however higher modulus than that containing NBR indicating better compatibility between NR and PALMF. Modulus at high strain of NR-PALMF composites has also been increased by addition of carbon black filler. This system has been compared to natural rubber reinforced by aramid fibers (see Fig. 1) and has shown better mechanical properties.

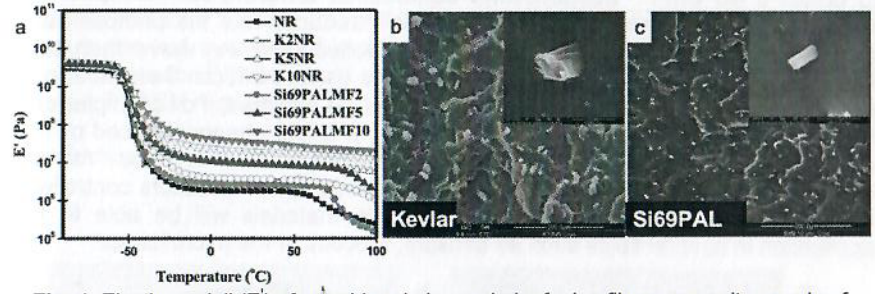

Fig. 1. Elastic moduli (E') of aramid and pineapple leaf microfiber composites made of natural rubber (b) SEM micrographs of cryogenic fractured natural rubber composites at low and high magnifications for b) aramid composite, c) PALMF treated composite

Keywords: *natural rubber, pineapple leaf fibers, composite, reinforcement.*

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Influence of ester diluents and chain extension on polyurethane viscosities

*D. Bražinskienė *, S. Mačiulytė , P. Nemaniutė , T. Matijošius, S. J. Asadauskas*
Center for Physical Sciences and Technology (FTMC), Saulėtekio 3, LT-10257, Vilnius, Lithuania
** dalia.brazinskiene@ftmc.lt*

INTRODUCTION

Polyurethane (PU) plastics are widespread in various areas such as adhesives, coatings, synthetic leather, etc. [1]. Frequently, PU plastics are obtained from two components: 1) macrodiols and 2) isocyanates, whose reactions form urethane linkages [2]. The macrodiol must contain two OH groups with a polyether, polyester, hydrocarbon, polycarbonate or other spacer chain in between. Quite often, the macrodiol is pre-reacted with diisocyanates for chain extension, diluted with ethyl acetate and only then cross-linked with multifunctional isocyanates into the final PU plastic. Polyurethanes are often used as adhesives in laminated packaging, Fig, 1. Viscosity is critical in such adhesive application. In this study, effects of dilution with less viscous polyols on viscosity are investigated using two types of viscometers: rotary and capillary.

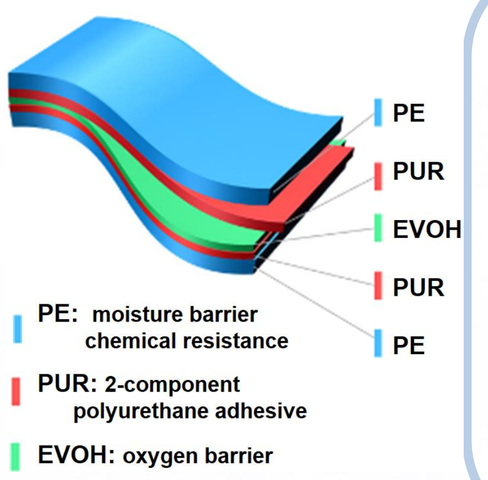
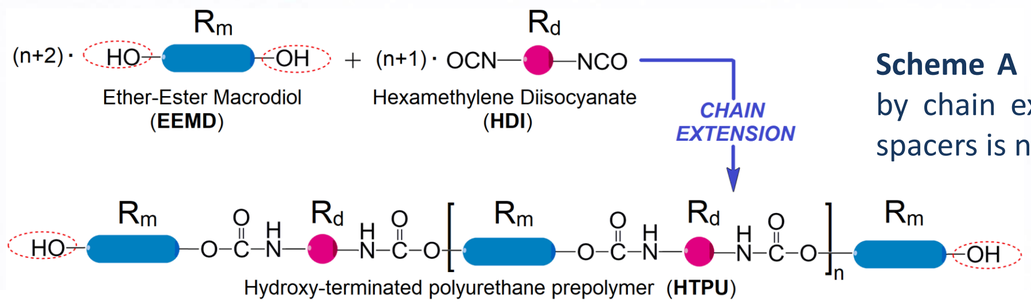


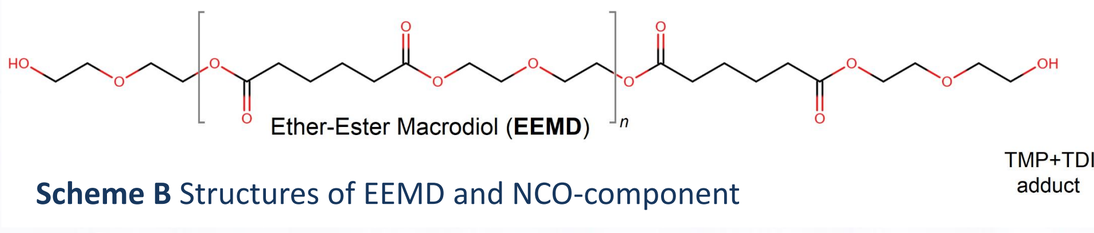
Fig. 1 Multilayer film for food packaging [7]

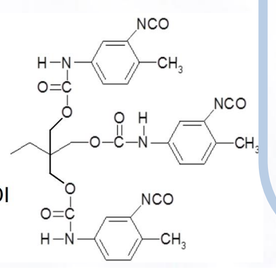
EXPERIMENTAL

Synthesis of hydroxy-terminate PU (HTPU) was described previously [4], as this study focuses on viscometry. Viscosity of EEMD blends was measured by rotary viscometer Lamy CP-2000 Plus using a 1° cone spindle RM100, see Fig. 2. A 1 mL sample was placed onto a clean bottom plate, the spindle was lowered, and temperature was equilibrated for 5 min to ±0.2°C accuracy before the automatic measurement of dynamic viscosity. Viscosity increase during polymerization was measured using capillary viscometer. Right after mixing of HTPU, ethyl acetate and TMP-TDI adduct, the sample was placed into the viscometer bulb and kinematic viscosity η was periodically measured per ASTM D445. Viscosity of PEG 400 was measured using both techniques.



Scheme A HTPU preparation by chain extension. Scale of spacers is not respected





Scheme B Structures of EEMD and NCO-component

MATERIALS

In a previous study [3], several hydroxy-terminated PU (HTPU) prepolymers were obtained for use as an OH-component in two-component PU adhesives, see Scheme A. In this investigation, an Ether-Ester Macrodiol (EEMD) was represented by a copolymer of diethylene glycol and adipate at 2700 g/mol, see Scheme B. Initially, chains were extended with hexamethylene diisocyanate (HDI). Resulting HTPU was then diluted with ethyl acetate at 1:1 (w/w) to produce the first adhesive component. As the second adhesive component, aromatic tri-isocyanate CAS 53317-61-6 was used at 1.4 mol excess, represented by an adduct of trimethylol propane (TMP) and toluene diisocyanate, see Scheme B. An attempt was made to avoid usage of volatile ethyl acetate. EEMD viscosity was reduced by blending it with polyethylene glycol of 400 g/mol (PEG 400) or a multifunctional ester-based polyol (EMP).

RESULTS

A narrow capillary of the Cannon-Fenske viscometer minimized the vaporization of ethyl acetate. Polymerization-induced thickening was gradual, see Fig. 3. The trend appeared somewhat linear with stronger non-linearity observed at 50°C, than 25°C. Catalytic effects of the ester linkage in ethyl acetate could be responsible for the acceleration of the carbamate formation, since chemical reactivity generally intensifies at higher temperatures.

Dilution effects were investigated by blending EEMD with PEG 400 or EMP. Higher amounts of EEMD increased viscosity of EMP blends nearly exponentially, see Fig. 4. The semilog correlation was close to excellent. Dilution with PEG 400 also followed the semilog correlation very well, see Fig. 5.

Fig. 5 also includes PEG 400 viscosity of 29 mPa·s at 50°C from elsewhere [6]. In addition, kinematic viscosities of PEG 400, measured by capillary viscometry, are multiplied by respective densities, resulting in 28.92 mPa·s. This value was much closer [6], than 33.1 mPa·s, measured by the rotary viscometer. Viscosity at 75°C was calculated using ASTM D341 interpolation and deviated from that of rotary viscometer, 13.33 [6] and 13.84 (capillary) vs 17.8 mPa·s (rotary). This shows the advantages of capillary viscometry.

Fig. 2 Rotary rheometer (left) and capillary viscometer (right) [5] used in the study

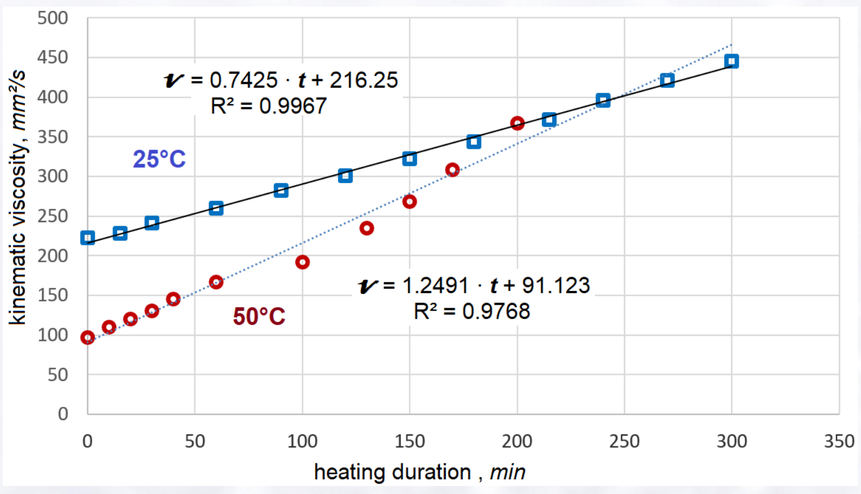


Fig. 3 Viscosity increase due to HTPU addition to the TMP-TDI adduct in ethyl acetate, as measured by capillary viscometer

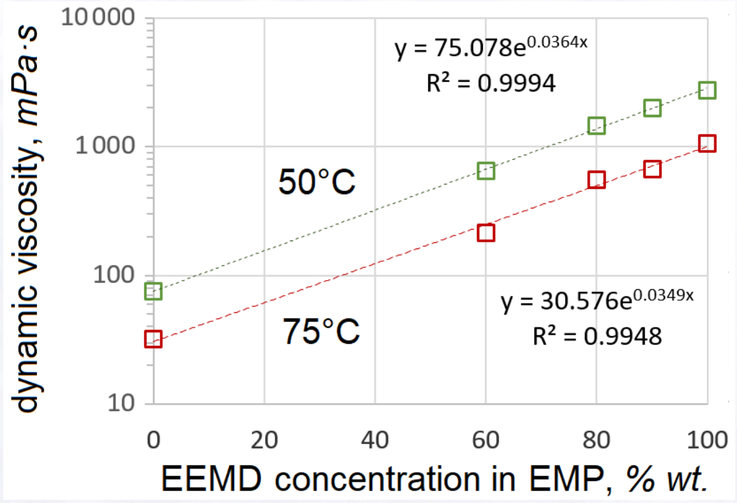


Fig. 4 Influence of EMP diluent on dynamic viscosity of EEMD blends at 50°C and 75°C

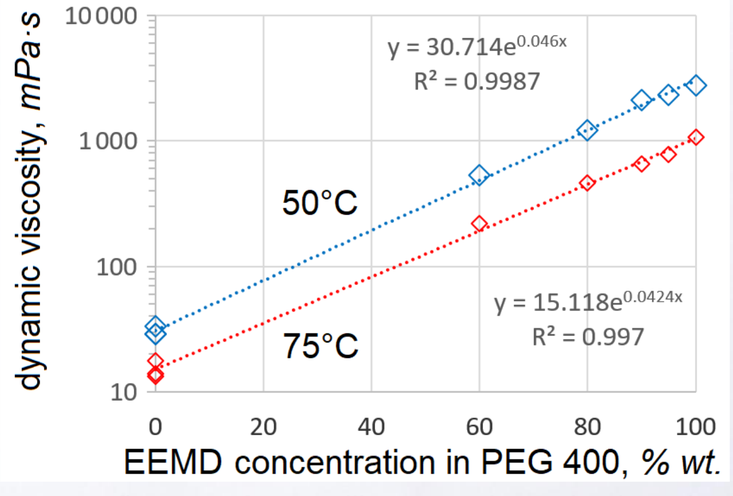


Fig. 5 Influence of EMP diluent on dynamic viscosity of EEMD blends at 50°C and 75°C

CONCLUSIONS

- Viscosities of PEG and adipate copolymer blends often follow semilog correlation quite closely
- Viscosity of polymerization blend in ethyl acetate may increase linearly with time, but catalytic effects of the solvent can accelerate the reaction.
- Accuracy of rotary viscosity measurements is usually lower than those of capillary viscometry.

ACKNOWLEDGMENTS

This study was carried out under project TERMINUS, funded by the European Union under Horizon 2020. Call: H2020-NMBP-ST-IND-2018. Grant Agreement: 814400. The technical concept and advices of J. Buechner, T. Fait (Covestro) and A. Strakšys (FTMC) are cordially appreciated.

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