Characterization of Partially Biodegradable Poly(L-lactic acid)/Poly(methyl methacrylate) Blends as Potential Biomaterials

PAVEL KUCHARCZYK[1], VLADIMIR SEDLARIK[1*], TAKESHI KITANO[1],
MICHAL MACHOVSKY[1], MARIAN BARAK[2], MAREK KOUTNY[3], PETR STLOUKAL[3],
PETR SAHA[1]

[1] Centre of Polymer Systems
Polymer Centre
Tomas Bata University in Zlin,
nam. T.G.Masaryka 5555, 760 01 Zlin
CZECH REPUBLIC

[2]Department of Polymer Engineering
Faculty of Technology
Tomas Bata University in Zlin,
nam. T.G.Masaryka 275, 762 72 Zlin
CZECH REPUBLIC

[3] Centre of Polymer Systems
Department of Environmental Protection Engineering,
Tomas Bata University in Zlin
nam. T.G.Masaryka 5555, 760 01 Zlin
CZECH REPUBLIC
*sedlarik@ft.utb.cz, http://www.cps.utb.cz

Abstract: - This work is focused on characterization of a potential polymeric biomaterial based on poly L-lactic acid and poly(methyl methacrylate) blends. Mechanical, rheological and, thermal properties of the blends prepared in wide poly L-lactic acid concentration range were observed in order to determine morphological arrangement of the blend. In addition, hydrolytical degradation study in presence of sodium hydroxide was conducted. The results reveal a miscibility of both polymer matrices and significant non-linear influence of the blend composition.

Key-Words: poly(L-lactic acid), poly(methyl methacrylate), polymer blend, partially biodegradable, mechanical properties, thermal properties, degradation

1 Introduction

Bio-based polymers have attracted much attention over the past several decades. Their unique properties such as: biodegradability, bioresorbability, availability of renewable resources and very good potential to replace synthetic polymers make them ideal for wide use in both common (e.g. packaging, disposable daily-use items) and special applications (e.g. medical devices) [1-3]. Despite the promising features revealed above, these materials often pose significant disadvantages. Among them, poor thermal and mechanical properties and processing difficulties are often mentioned [2]. In the area of controlled release systems, such as microcapsules, undesirable release profile of a bioactive agent can

be obtained [4]. Therefore, several bio-based polymeric material modification methods have been developed [5].

Polymer blending is one of the effective ways how to obtain a material with tailored end-use properties [6]. In addition, it offers a cost-effective alternative in comparison to copolymerization or other polymer synthesis modification techniques.

Poly(L-lactic acid) (PLLA) represents one of the most promising biodegradable materials, currently available on the market. Commercial PLLA is a highly transparent and rigid material with a glass transition temperature (T_g) around 55 °C and a melting point (T_m) varying from 155 °C up to 175 °C [7]. Besides biodegradable items production, PLLA has been introduced as a biomaterial for

resorbable implants or drug delivery systems [2, 3, 5].

Poly(methyl metacrylate) (PMMA) is an amorphous polymer with T_g around 115 °C. Its properties include weathering ability and good optical properties. As well as PLLA, PMMA has been used in medicine (surgery, drug delivery systems) [8].

Blends of PLLA and PMMA have been studied by several authors. Zhang *et al.* studied a miscibility of the blend prepared by solution precipitating and solution casting methods. It was concluded that the blends can be both miscible and immiscible, depending on the preparation method and stereo regularity of PLLA phase [3]. In another paper, Kim-Phuong Le *et al* investigated morphologies of thermoplastically blended PLLA/PMMA and concluded that the unique morphology, potentially useful for a biomaterial application, can be achieved [9]. On the other hand, Li *et al.* in his papers revealed and described the miscible behaviour, characterized by the upper critical solution temperature at temperatures between 230 – 250 °C [5, 10].

On the basis of the already mentioned facts, blending of PLLA and PMMA seems to be promising for preparation of a new biomaterial which could find its application in controlled release system – micro-particles [4, 11]. However, this system can be used in bulky-like items preparation as well. Thus, it is necessary to characterize the polymer blend system from the macroscopic properties point of view.

This work deals with preparation and characterization of PLLA/ PMMA polymer blends. The main attention was paid to description of morphological arrangements of the blends, which was studied in both solid as well as in molten state. Based on our best knowledge, this kind of study has never been published.

2 Experimental

2.1 Materials
PLLA (Ingeo™ 404 2D, product of NatureWorks (density 1.24 g/cm³, M_w = 115 kg/mol, *MFI* ~ 33 g/10min) and PMMA (V 046 produced by Altuglas International, France, density 1.19 g/cm³, *MFI* ~ 2g/10 min) were used for the blends preparation. Degradation studies were conducted by using NaOH (analytical grade), supplied by IPL Lukes, Uhersky Brod, Czech Republic.

2.2 Sample Preparation

The blending was carried out on Brabender Plasticoder (Brabender GmbH&Co. KG, Germany) at 180 °C and 20 rpm for 10 min. The PLLA/PMMA blends were prepared in PLLA concentration range 0, 25, 40, 45, 50, 55, 60, 75 and 100 wt. %. The resulting products of blending were pulverized (Cutting mill RETSCH SM100) and moulded into thin plate (thickness 1 mm) in a manual press at 190 °C for 10 minutes and subsequently cooled in a manual press.

2.3 Sample characterization
Differential scanning calorimetry (DSC) was used to analyze the thermal properties of the PLLA/PMMA blends. The experiments were performed on Mettler Toledo DSC1 STAR System under nitrogen atmosphere (20 cm³/min) according to the following programme: (i) first heating scan 25 – 190 °C (10 °C/min); (ii) annealing at 190 °C for 1 minute; (iii) cooling scan 190 – 25 °C (10 °C/min); (iv) annealing at 25 °C for 1 minute; (v) second heating scan 25 – 190 °C (20 °C/min). Melting point temperature (T_m) as well as exothermal response relating to crystallization temperature (T_c) was obtained from the first heating cycle. The value of glass-transition temperature (T_g) was determined in the second heating scan at the midpoint stepwise increase of the specific heat associated with glass transition.

Mechanical testing was performed on tensile testing machine Instron 8871. The speed of moving clamp was 2 mm/min. At least six dog-bone shape specimens (total length 60 mm, width 4 mm and thickness 1 mm) were tested in case of each blend.

Degradation experiment was performed on dog-bone shape specimens (see above). The samples were placed into 50 ml 1M NaOH solution and continuously shaken (100 rpm) at 37 °C. The specimens were withdrawn in the predetermined time intervals, washed in distilled water and dried at 50 °C for 24 hours up to the constant weight. The weight loss (W_l) was calculated according to Equation (1):

$$W_t(\%) = \frac{W_0 - W_t}{W_0} \qquad (1)$$

where, W_0 is initial weight of sample and W_t is weight in specific time of degradation. The degradation tests were performed in three parallel repetitions.

The viscoelastic properties of the prepared PLLA/PMMA blends were investigated in molten state by using rotational viscometer (ARES 2000, Rheometrics). A parallel-plate measuring geometry (diameter 25 mm) with the gap of about 1 mm was

used, employing a small strain (1 %) to maintain the measurements within the linear viscoelastic region. Dynamic frequency sweep tests were carried out at 190 °C to follow, storage (G') and loss (G'') moduli as a function of angular frequency (ω) from 0.1 to 100 rad/s. Another parameter describing viscoelastic behaviour, complex viscosity (η^*), was calculated by the following equation:

$$\eta^* = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} \qquad (2)$$

Scanning electron microscopy (VEGA II LMU, TESCAN) was applied to characterize the morphological arrangements of PLLA and PMMA in the prepared blends. All specimens were coated with a thin layer of Au/Pd. The microscope was operated in high vacuum mode at the acceleration voltage of 5kV. To highlight the morphology of the blend, for imaging, the specimens after 250 hours of degradation in 1 M NaOH were taken for analysis.

3 Results and Discussion

Figure 1 shows DSC thermo grams of the selected samples in the first heating scan. As can be seen, pure PLLA exhibits clear exothermic peak at around 123 °C and narrow endothermic peak at 153 °C which is connected with crystallization temperature (T_c) and melting temperature (T_m), respectively .
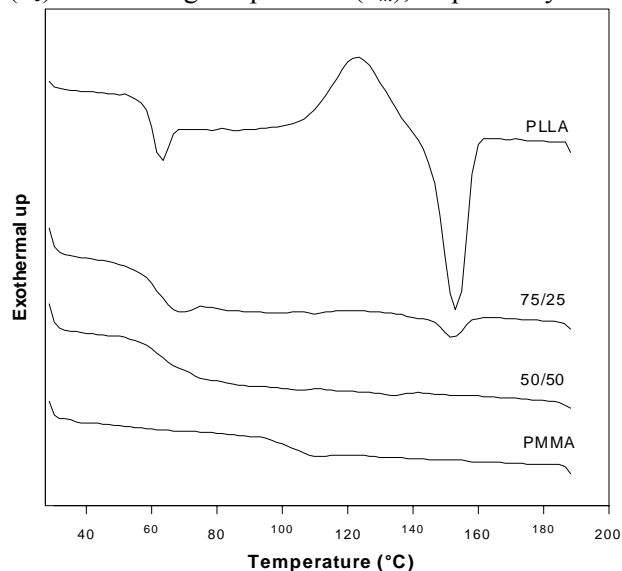

Fig. 1 – DSC thermograms of neat polymers and selected blends

It can be noticed that a presence of amorphous component (PMMA) has a negative effect on crystallization ability of PLLA phase. It was found, that only blend PLLA/PMMA (72/25) was able to crystallize and positions of T_c and T_m remained

more-less unchanged as in neat PLLA. On the other hand, DSC spectra typical for amorphous material were detected for the blends with PMMA concentration above 25%.

The values of glass transition temperatures, T_g, were taken from the second heating scan. Only one T_g was observed for all samples. As it is known, single T_g of the polymer blends indicates their miscibility [3]. On the other hand, immiscible (incompatible) binary systems are characteristic by two T_gs. Eguiburu et al. reported on miscibility of PLLA/PMMA blends prepared by precipitation and solvent cast technique [2]. On the contrary, Li et al. shows incompatibility of the PLLA and PMMA blends [5, 10]. According these data it seems that miscibility of PLLA and PMMA depends on processing conditions occurring during the blend preparation. However, occurrence of single T_g can be confirmed only by using more sensitive method such as dynamic mechanical analysis.

Dependence of T_g and the blend composition is often used for evaluation of polymer-polymer interaction. Among several models developed for the polymer interaction evaluation, Fox's and Gordon-Taylor's equations are the most discussed in the literature. The former one (Eq. 3) fits relatively well for miscible systems and predicts T_g of a blend.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (3)$$

where w_1 and w_2 represent weight fractions of the polymers with T_{g1} and T_{g2}. Later equation additionally consisted of empiric parameter k, which is often interpreted as miscibility measure due to its relation to interaction strength between blend components [3, 5].

$$T_g = \frac{w_1 T_{g1} + k(1-w_1)T_{g2}}{w_1 + k(1-w_1)} \qquad (4)$$

Figure 2 depicts values of T_g as a function of the blend composition. Since one broad T_g was detected in all blends, it is evidence of some degree of miscibility in amorphous phase. The k value, which best fits experimental results, was found to be 0.28 (Eq. 4). It reveals that although blend system is apparently miscible, interaction occurring between PLLA and PMMA is relatively weak.

Dependence of the complex viscosity (η^*) of the pure matrices and PLLA/PMMA blends on angular frequency is shown in Fig. 3. It can be seen that PLLA exhibits the lowest η^* in comparison to pure PMMA as well as their blends over the whole ω range. Moreover, PLLA exhibits low dependence on ω. On the other hand, η^* of PMMA is

significantly higher (by two orders of magnitude) at 0.1 rad/s and 190 °C. Additionally, strong shear thinning was observed in case of pure PMMA. PLLA/PMMA blends have $\eta*$ between the pure polymers at all investigated frequencies.
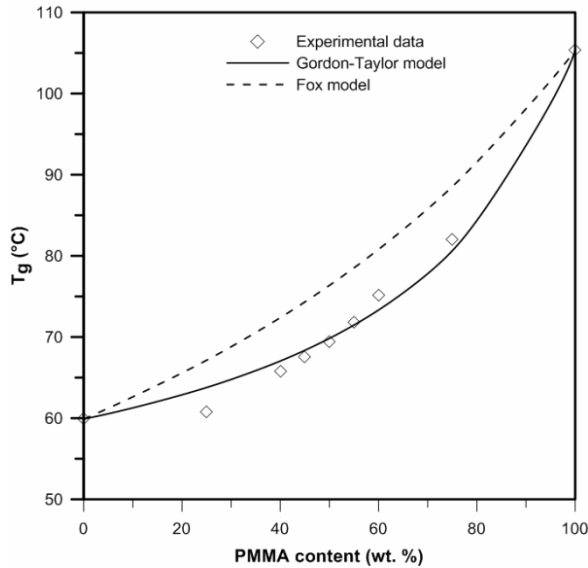

Fig. 2 – Dependence of glass transition temperatures on blend composition (2nd heating scan)

Some of the already published works report a morphological rearrangements (phase inversion for immiscible systems) detection possibility through viscoelastic properties analysis. It is determined by an occurrence of a transition between positive and negative deviations of the viscoelastic characteristics from a semi-logarithmic additive rule. [12, 13]. Only slight negative deviation was observed. This could indicate a potential miscibility of the polymer matrices (Fig. 4).
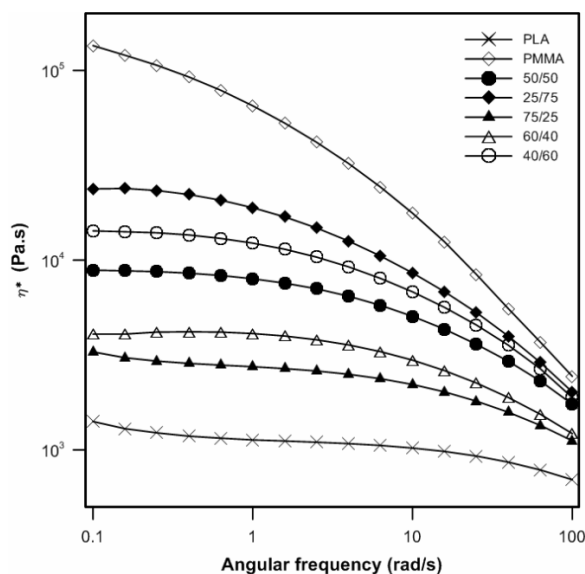

Fig. 3 - Complex viscosity ($\eta*$) versus frequency at 190 °C of PLLA/PMMA blends

Mechanical properties of PLLA, PMMA and their blends are shown in Table 1. Presented values are higher than those usually presented for PLLA and PMMA. It is connected with a specific geometry of the specimens.

An increase of E can be observed in case of the blends containing 40 wt. % PLLA (25 % enhancement in comparison to pure PMMA).
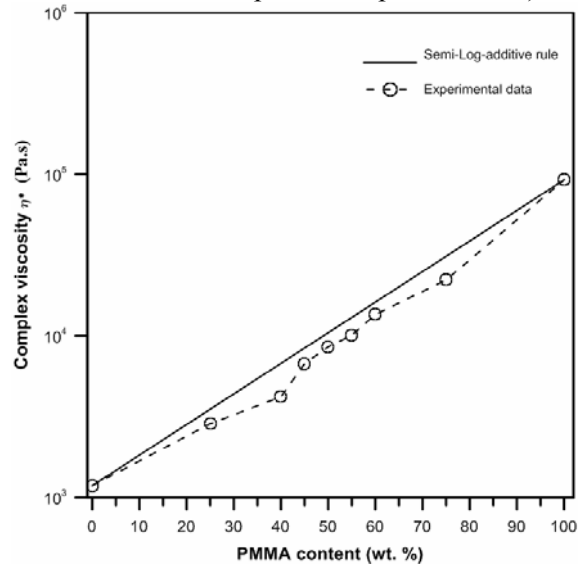

Fig. 4 – Complex viscosity versus PMMA wt. % at 190 °C and 0.3981 rad/s

Further rising of PLLA content in PMMA/PLLA blends leads to reduction of the E values, which approach value of the pure polyester matrix.

The trend of tensile strength is increasing with the concentration of PLLA up to 50 wt. %. The blend with this composition proves 21 % enhancement in comparison to pure PMMA. The PLLA rich blends show reduction of the tensile strength towards to the value of pure biodegradable matrix. These results reveal relatively good material compatibility of both polymers unlike the results presented for immiscible systems, where significant negative changes in mechanical behaviour can be detected [6, 14].

The degradation study used in this work is based on selective removal of PLLA matrix from PLLA/PMMA blend by using 1M NaOH. This method can provide information on morphological arrangements in the investigated blends. The degradation extent is presented in Fig. 5 as a time dependence of weight loss (Eq. 1). While pure PMMA is almost not affected by degradation medium, PLLA is decomposed intensively. In case of the blends, increasing PLLA content causes increased weight loss response. The experiment was finished after 250 hours when the weight losses remain more or less constant.

It can be noticed that weight losses of the blends at the end of the experiment do not correspond to the PLLA concentrations originally presented in the blends-even at 75 wt. % PLLA.

It could mean poor availability of PLLA macromolecules for hydrolysing agent, which impacts from the surface of the samples.
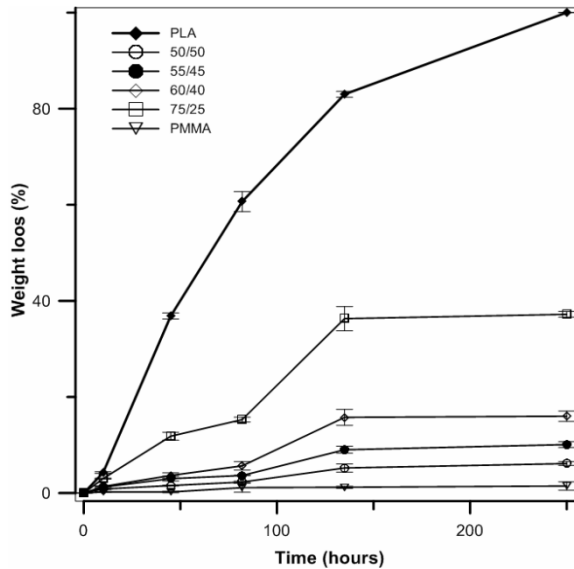

Fig. 5 – Weight loss observed during degradation experiment

The reason for such behaviour may be found either in special morphological arrangements of the PLLA/PMMA blends (entrapment of PLLA matrix in PMMA) or miscibility of both matrices.

Besides weight loss determination, degradation extent was also observed from the viewpoint of mechanical properties changes (Table 1). Generally, it can be stated that the samples become more brittle due to degradation procedure. The value of E was not determined for PLLA rich blends. The dependencies of both tensile strength and tensile strain on the blend composition have similar trend.
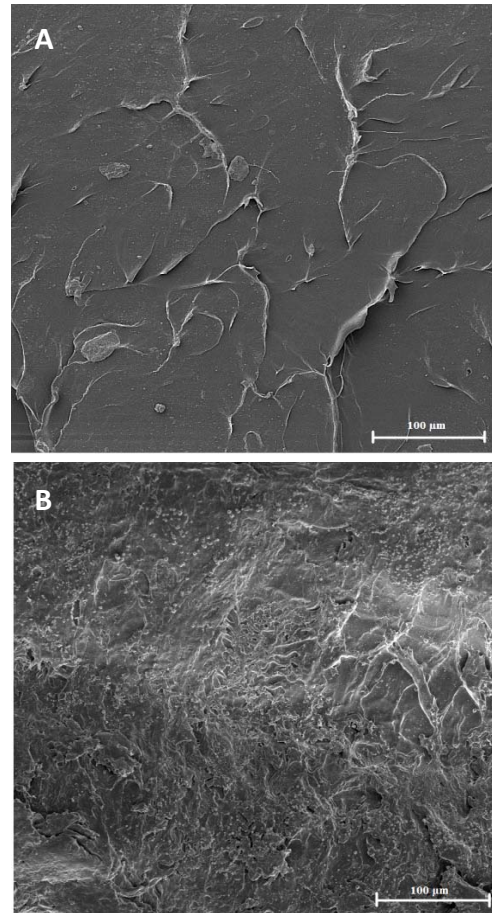

Fig. 6 – SEM micrographs of non-degraded (A) and degraded (B) samples (PLLA/PMMA 50/50)

Pure PMMA and PMMA rich blends (up to 25 wt. %) do not show a significant difference in comparison to non-degraded samples. However, steep reduction of the both characteristics occurs at higher PLLA concentrations. Removing of one of the components from the binary system can be a reason of appearance of vacancies, which are a cause of mechanical failings.

Table 1 – Mechanical properties of non-degraded samples and samples after 250 hours of degradation in alkaline medium (1M NaOH, 37 °C). (*SD – standard deviation, + Completely degraded/deteriorated*)

	As prepared			Degraded		
PMMA (wt. %)	Young´s modulus/SD (GPa)	Tensile strength/SD (MPa)	Tensile strain/SD (%)	Young´s modulus/SD (GPa)	Tensile strength/SD (MPa)	Tensile strain/SD (%)
0	6.4/0.8	61.6/1.1	1.1/0.1	+.	+	+
25	7.5/0.3	67.1/2.3	1.2/0.1	+	+	+
40	8.0/0.3	72.3/1.1	1.2/0.1	+	+	+
45	7.4/0.9	73.5/2.4	1.3/0.1	6.1/0.6	36.9/1.8	0.5/0.0
50	7.5/0.8	74.5/0.7	1.3/0.1	6.1/0.5	35.6/0.0	0.5/0.1
55	7.9/0.7	74.0/2.5	1.2/0.1	6.4/0.6	51.4/4.7	0.7/0.1
60	6.4/1.0	71.2/5.5	1.1/0.1	6.4/0.8	53.1/7.6	0.7/0.1
75	6.8/1.1	67.7/3.7	1.1/0.1	6.1/0.8	66.4/3.1	1.1/0.1
100	5.4/0.6	49.3/4.5	0.8/0.1	5.4/0.9	41.6/6.6	0.7/0.2

The discussed vacancies are clearly visible in SEM picture in Fig. 6, where comparison of virgin and degraded specimen is shown. In addition, this picture confirms the supposition of good PLLA/PMMA compatibility.

4 Conclusions

The present work deals with characterization of thermoplastically prepared blends of poly L-lactide (PLLA) and poly(methyl methacrylate) (PMMA), which can be used as a biomaterial for medical device preparation. The results of morphological, mechanical and thermal properties investigation of PLLA/PMMA blends could reveal that the given binary system proves compatibility of both components over the whole composition range. These observations are partially in agreement with some of the already published works dealing with PLLA/PMMA systems. On the other hand, it is clear that resulting morphology of the blend is strongly dependent on processing conditions in this case.

References:
[1] A. K. Mohanty, L. T. Drzal, *Natural Fibers, Biopolymers, and Biocomposites*, CRC Press, 2005

[2] J. L. Eguiburu, J.J. Iruina, M.J. Fernandez-Berridia, J. S. Román, Blends of amorphous and crystalline polylactides with poly(methyl methacrylate) and poly(methyl acrylate): a miscibility stud, *Polymer*, Vol. 39, No. 26, 1998, pp. 6891-6897

[3] G. Zhang, Z. Jianming, W. Shenguo, S. Deyan, Miscibility and phase structure of binary blends of polylactide and poly(methyl methacrylate), *Journal of polymer science: Part B: Polymer Physics* Vol. 41, 2003, pp. 23-30

[4] Z. El Bahri, J. L. Taverdet, Elaboration and characterisation of microparticles loaded by pesticide model, *Powder Technology,* Vol. 172 2007, pp. 30–40

[5] S. Li, E. M. Woo, Immiscibility-miscibility phase transition in blends of poly(L-lactide) with poly(methyl methacrylate), *Polymer International,* Vol. 57, 2008, pp. 1242-1251

[6] L. A. Utracki, *Polymer Alloys and Blends,* Hanser Gardner Pubns, 1990

[7] V. Sedlarik, P. Kucharczyk, V. Kasparkova, J. Drbohlav, A. Salakova, P. Saha, Optimization of the Reaction Conditions and Characterization of L-Lactic Acid Direct Polycondensation Products Catalyzed by a Non-Metal-Based Compound, *Journal of Applied Polymer Science*, Vol. 116, No. 3, 2010, pp. 1597-1602

[8] E. A. Stefanescu, X. Tan, Z. Lin, N. Bowler, M. R. Kessler, Multifunctional PMMA-Ceramic composites as structural dielectrics, *Polymer*, Vol. 51, 2010, pp. 5823-5832

[9] K. P. Le, R. Lehman, James D. Idol, Multiphase blends from poly(l-lactide) and poly(methyl methacrylate), *Journal of Biomaterials Science, Polymer Edition,*Vol. 17, No. 1-2, 2006, pp.121-137

[10] S. Li, E. M. Woo, Effect of chain configuration on UCTS behavior in blends of poly(l-lactic acid) with tactic poly(methyl methacrylates), *Journal of Polymer Science: Part B: Polymer Physics* Vol. 46, 2008, pp. 2355-2369

[11] M. Chorny, I. Fishbein, H. D. Danenberg, G. Golomb, Lipophilic drug loaded nanospheres prepared by nanoprecipitation: effect of formulation variables on size, drug recovery and release kinetics, *Journal of Controlled Release*, Vol. 83, 2002, pp. 389 - 400

[12] M. Schnell, V. Ziegler, B.A. Wolf, Evolution of viscosities and morphology for the two-phase system polyethylene oxide/poly(dimethylsiloxane), *Rheologica Acta, Vol. 47, No. 4, 2007, pp. 469 – 476*

[13] R. M. Li, W. Yu, C. Zhou, Phase inversion and viscoelastic properties of phase-separated polymer blends, *Polymer Bulletin*, Vol. 49, No. 4, 2007, pp. 545 – 554.

[14] I. Krupa, A. S. Luyt, Mechanical Properties of Uncrosslinked and Crosslinked Linear Low-Density Polyethylene/Wax Blends, *Journal of Applied Polymer Science*, Vol. 81, 2001, pp.973–980