

CHAPTER V

MORPHOLOGY & PROPERTIES
OF BLENDS OF STARCH -
CAPROLACTONE BLEND
AND LIGNIN DERIVATIVES.

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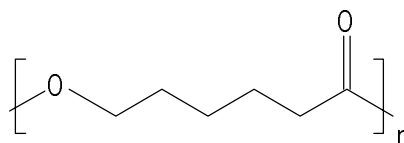
MORPHOLOGY & PROPERTIES OF BLENDS OF STARCH –CAPROLACTONE BLEND AND LIGNIN DERIVATIVES.

ABSTRACT

A binary blend of polycaprolactone and starch in 70:30 weight ratio (known under the tradename “Envar”) was blended in various weight ratios with organosolv lignin (L) and organosolv lignin butyrate (LB) by solvent casting and melt blending. The thermal transitions observed by DSC revealed behavior resembling that of native polycaprolactone (PCL). Depression in melting temperatures obtained by DSC revealed interaction between SCL and L or LB. Also dynamic mechanical measurements indicated some measure of polymer-polymer interaction by revealing shifts in the glass and melting transitions of PCL. Crystallinity in PCL was found to increase probably due to nucleation initiated by the lignin particles. An increased degree of crystallinity was observed in the case of higher- T_g lignin compared to lower T_g lignin butyrate. Modulus and tensile properties increased up to about 20 % incorporation of lignin components.

INTRODUCTION

Poly (ϵ -caprolactone) (PCL) has attracted considerable attention as a potential replacement for conventional polymers due to its biodegradability, favorable miscibility characteristics with other polymers, and low temperature adhesiveness [Huschen et.al, 1981]. The structure of the PCL repeat unit is



Poly (ϵ -caprolactone)

Various studies have been carried out on modifying PCL by blending or copolymerizing it with other polymers such as starch [Griffin (1987)]. Multiphase starlike copolymers have been prepared using PCL as the hard segment arm and hydroxypropyl lignin as the core [Oliveira and Glasser, 1994 a]. It was found that significant T_m -depression of PCL resulted when copolymers of lignin with T_g 's greater than the T_m of caprolactone were added, whereas lignin cores having lower T_g 's did not depress the T_m . Also the melting point of PCL increased as the arm length of the star copolymer rose to a degree of polymerization of 50.

PCL is a crystalline polymer which reveals three thermal transitions: a first order transition at 60 °C corresponding to a melting endotherm; a second order glass transition at ca. -60 °C; and an exothermic crystallization peak at around -25 °C. Crystallinity has also been observed for copolymers with very small segments of caprolactone [Oliveira and Glasser, 1994 a]. Therefore, miscibility of PCL with other polymers has also been of interest from its application point of view. Among the cellulose esters considered in blends with PCL, highest miscibility was observed for blends with cellulose butyrate having a DS \geq 2.0 [Nishio et al., 1997].

The starch-caprolactone blend (SCL) considered in this study has been developed in the Michigan Biotechnology Institute, Michigan State University, East Lansing, USA [Narayan and Krishnan (1995)]. SCL is a blend and composite of starch and poly (ϵ -caprolactone) and it is prepared in a twin screw extruder. The term 'blend' refers to the condition where starch is in plasticized form, whereas 'composite' refers to compositions in which starch is granular in structure [Narayan and Krishnan (1995)]. It has been reported that distinct phases were observed in the fractured surfaces of SCL, thereby indicating little or no interfacial adhesion between the starch and PCL components in the blend. Further details on SCL can be obtained from other literature [Narayan (Patents)]. SCL is available in the form of granules under the tradename "Envar". This study is aimed at improving the properties of a binary blend of PCL and starch by blending with a high- T_g organosolv lignin (L) and a relatively lower- T_g organosolv lignin butyrate (LB). The effect of the lignin component on the crystalline behavior of PCL component and the glass transition behavior of the blends will be discussed.

EXPERIMENTAL

MATERIALS

The thermoplastic starch-caprolactone blend (SCL) was obtained as commercially available prototype (tradename ENVAR) in the form of pellets from Prof. Ramani Narayan, Biomaterials Research Center, Michigan State University. The approximate starch content of this material is 30%. The polycaprolactone has a M_n of 148,000 and a M_w of 473,000. Other specific details of SCL are available in literature [Narayan and Krishnan (1995); Narayan (Patents)].

Organosolv Lignin (L) was obtained from Aldrich Chemical Company, WI, USA (Catalog #: 37,101-7). The glass transition and thermal decomposition temperatures are 107°C and 308°C, respectively. The average molecular weight M_w and M_n are 3,140 and 820 respectively with a MWD of 3.8. Organosolv lignin butyrate (LB) was prepared by esterification of organosolv lignin as mentioned in chapter II of this thesis. The glass transition temperature of lignin butyrate and thermal decomposition temperatures are 54°C and 308°C, respectively. The average degree of substitution by butyryl groups is 0.69. The molecular weight, M_w , is 7,730 with a MWD of 3.3.

METHODS

Blend Preparation

SCL/L blends of 100/0, 95/5, 90/10, 80/20, and 70/30 were prepared by melt extrusion. Corresponding amounts of SCL in pellet form and L in powder form were melt extruded in a CSI-MAX Mixing Extruder from Custom Scientific Instruments Inc., USA, at 170°C to produce a homogeneous blend of the two components. The extrusion mixing was repeated for higher amounts of L content so as to disperse the two polymers homogeneously. The extrudate was then transferred to a preheated Mini-Max Injection Molder from Custom Scientific Instruments. The injection molder fixture temperature was maintained at 175 to 190°C, or at lower temperatures for blends with L, depending on the amount of L present. It was observed that the melt processing of the blends required less injection pressure with the addition of the lignin component. This permitted a reduction of the molding temperature by 10 to 15°C, which also reduced the possibility of decomposition of the components to a certain extent. The L powder was placed inside the cavity of the molder where it was melted and blended. The polymer was blended in the melt for approximately one minute before it was injected into the mold. The injection plunger was manually raised and lowered during this time to improve mixing. The mold cavity was heated through conduction from the fixture during the injection process and so can be considered as a preheated mold. The cooling rate was not controlled after injection. The molds were allowed to cool for a few minutes at room temperature and then quenched in cold water to reduce the temperature to below 50°C. Consequently, the specimens should be considered to have been quenched.

For preparing of the blends with LB, the blend components were stirred in chloroform (blend concentration of approximately 15% by weight of the solution) at room temperature until all the material was totally dissolved. The solution was then cast in teflon molds and kept in a dessicator at room temperature for 72 hours so as to evaporate

the solvent (chloroform) in a controlled manner. The solvent-cast blend was then placed in a vacuum oven at 35°C for 12 hours to remove any remaining solvent. This method of solvent casting was adopted to achieve greater dispersion of the LB component in SCL. Portions of these solvent cast blend films were then transferred to the Mini-Max Injection Molder and molded into the specimens described earlier.

Two types of specimens were molded: rectangular DMTA specimens and dog bone Minimat specimens. Rectangular specimens had average dimensions of 38 mm x 12.6 mm x 1.6 mm. Dog bone specimens, had a nominal length of 15 cm long with a gage section measuring 10 mm x 3.3 mm x 1.67 mm.

Differential Scanning Calorimetry (DSC)

The thermal analysis of the samples was determined on a Perkin-Elmer Model DSC-Series-4 equipped with a Thermal Analysis Data Station (TADS) using standard aluminum pans. Nitrogen was used as a sweeping gas. Measurements were made on ca. 10 mg samples in the temperature range between -40 and 130 °C at a scanning rate of 10°C/min. Nitrogen was used as a sweeping gas. The instrument was calibrated with an indium standard. The heat of crystallization and crystallization temperature were reported from the first cooling scan from melt at a scanning rate of 10°C/min. The heat of fusion was reported from the second heating scan. The glass transition temperature (T_g) was well below the initial temperature of the scan and this was not noted in any of the DSC scans. The melting temperature (T_m) is reported as the peak value of the melting endotherms. Crystallinity was calculated according to the following relation :

$$X_c (\%) = (\Delta H_f / \Delta H_f^0) \times 100$$

where ΔH_f is the measured heat of fusion for the sample, and ΔH_f^0 is the heat of fusion for 100% crystalline PCL. According to the work published by Crescenzi et.al., ΔH_f^0 of crystalline PCL is 3.69 kcal/mole or 135 J/gm[Crescenzi *et al.* 1972]. Here the other two blend components (starch in SCB and L/LB) are amorphous and so it is assumed that the crystallinity is only from the PCL component. Normalized values were obtained by dividing the observed ΔH_f by the actual weight fraction of the PCL component present in the ternary blend (considering 70% by weight of PCL in SCL).

Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical properties of the blend samples were determined using a dynamic mechanical thermal analyzer (DMTA) by Polymer Laboratories Ltd., Shropshire, England. The samples were loaded horizontally in DMTA standard medium size clamps. Measurements were performed in the single cantilever-bending mode. The spectra were collected from -80°C to 60°C at a heating rate of 4°C/min and a frequency of 1.0 Hz.

Mechanical Properties

The mechanical properties (modulus, strength and ultimate strain) of the blends were determined on a Miniature Materials Tester (Minimat model # SM9-06) by Polymer Laboratories Ltd., Loughborough, England. Tests were conducted at room temperature with a 1000 N load cell using a strain rate of 5 mm/min. The calculation of modulus and

strength was based on the initial cross sectional area. The data represent the average of four measurements for each composition.

RESULTS AND DISCUSSION

THERMAL ANALYSIS

• Differential Scanning Calorimetry (DSC) Results

The DSC scan of the SCL sample reveals an endothermic peak at 63⁰C (Fig. 5.1 and Table 5.1) which is due to the melting of the PCL component. Since the DSC-scans were obtained from a lower temperature of -40⁰C, and the glass transition temperature (T_g) of PCL is reported to be -60⁰C, no glass transitions corresponding to PCL component were observed in the temperature range. Crystallization of the PCL component in SCL was so spontaneous that not even a trace of cold crystallization was observed in any of the heating scans (even after quenching from melt). Cooling scans of SCL at 10 deg/min revealed a sharp exotherm at 33⁰C (Table 5.1). This represented crystallization with a ΔH_c value of -49 J/gm of SCL (compared to ΔH_f value associated with crystalline melting of SCL of ca. 58 J/gm of SCL) (Table 5.1). The normalized heat of fusion of PCL component (assuming no crystallinity from the starch component) is approximately 81 J/gm of PCL as compared to 135 J/gm reported for 100% crystalline PCL [Crescenzi *et al.* 1972]. The value of T_m for the SCL cast in chloroform and melt extruded are comparable to that of the original SCL. Also, the ΔH_f -values are close to that of original SCL and not much difference was noted from the samples prepared by different methods (Table 5.1).

DSC thermograms of blends of SCL with L or LB revealed crystallinity at all compositions with sharp single endothermic peaks corresponding to the crystalline melting of the PCL component (Figures 5.1, 5.2, 5.3). The cooling scans for SCL/L or SCL/LB blends (not shown) revealed a subsequent decrease in the crystallization temperatures (T_c) with addition of the lignin component (Figure 5.4). However, the effect of different lignin components (L or LB) and different processing conditions (melt vs. solvent cast) are noted in Figure 5.4. The LB component has a greater effect on the T_c -decrease than the L component. The corresponding results from the heat-of-crystallization data normalized to the PCL component in the blend reveals an increase in ΔH_c from -69 to -77 J/gm of PCL at a 10% by wt. of L in the blend (Table 5.1 and Fig. 5.5). Similarly, the highest normalized crystallinity of PCL in SCL/L blends (66%) is more than that in SCL/LB blends (60%) (Table 5.1). However, the ΔH_c -values decrease when LB is present and the values are significantly reduced at high LB contents. Therefore, the crystallinity in PCL is higher when L is present than when LB is present. This reveals that the formation of crystallites in the PCL phase is hampered more when LB is present than when L is present in the blend; and that shifts the crystallization peak towards lower temperatures when the sample is cooled from melt. Similar results are observed from the melting endotherm data. The melting temperatures (T_m) shifts towards lower temperatures as the amount of lignin component in the blend increases (Figure 5.6). This depression of the melting points of PCL phase indicates some form of interaction between PCL and L or LB. However, the melting point depression is more pronounced in case of solvent cast SCL/LB blends and less for SCL/L blends. This is expected since in general crystals formed at lower temperatures (i.e. possessing lower T_c 's) melt at lower temperatures.

Similar to the heat of crystallization data, the heat of fusion data (normalized to the amount of PCL present) reveal an increase in ΔH_f for the SCL/L blends at 10% concentration (Figure 5.7). The normalized ΔH_f values for SCL/LB blends show lower increases with higher LB contents in the blend. This reveals that LB interacts more with SCL than L. Therefore, greater interactions (possibly due to hydrogen bonding) between PCL and LB reduces the crystallinity in the sample and the SCL/LB has lower crystallinity than SCL/L blends. However, hydrogen bonding is more probable in case of hydroxyl containing L than that of ester substituted LB and so the explanation of interaction remains unclear. Another possible interpretation might be the enhanced interaction between L and starch component in SCL, as opposed to PCL in SCL. Hence, the PCL is segregated from the starch in SCL, revealing greater crystallinity in SCL/L blends.

Another reason that can be attributed for the increased crystallinity in PCL/L blends is the nucleating effect of the lignin components, since the L has a higher T_g (107°C) than the LB (54°C). The increased crystallinity for L blends as compared to LB blends may be due to a higher spherulite concentration generated by higher- T_g lignin surfaces due to increased nucleation. Similar observations were reported earlier with lignin-polycaprolactone copolymers [Oliviera and Glasser, 1994a]. Being a small spherical molecule and having a T_g (107°C) above the temperature of crystallization (ca. 36°C), lignin acts as a hard surface, which can promote nucleation in the caprolactone phase. Lignin-PCL copolymers showed irregular shaped spherulites being formed in large numbers which was attributed to the restricted chain movements of the PCL segment and nucleating effect of the hard core lignin segment [Oliviera and Glasser, 1994a]. In this case, no restrictions to the chain movements are imposed due to lack of rigid chemical bonds between PCL and lignin molecules. Enhanced nucleation and regular growth of the spherulites is therefore expected in the PCL phase when L is added as opposed to when LB is added, which leads to a higher degree of crystallinity in the presence of L as compared to LB. Optical microscopic study is necessary to analyze the crystallization kinetics and morphology of the blends in detail.

• Dynamic Mechanical Thermal Analysis (DMTA) Results

DMTA results revealed peaks in both $\tan \delta$ as well as E'' at approximately -55°C , which corresponds to the T_g of both the PCL and starch components (Figure 5.8). As regards the DMTA data, a significant difference can be noted in the $\tan \delta$ -curves of the blends (Fig.5.9). The $\tan \delta$ -curve for pure SCL shows an early step-transition (i.e. a transition at a lower temperature) associated with the glass transition as described earlier. With the increase in temperature the curve remains constant up to around 50°C , after which it soars to higher values as the material begins to melt. When a small amount (10% by weight) of LB is present (second curve from bottom), another peak appears corresponding to the relaxations associated with the glass transition of LB (at ca. 25°C) (Fig. 5.9). This gives an indication of the existence of two separate phases, each having dimensions of more than 30 nm as explained in an earlier chapter of this thesis. This proves that the blends of SCL and L or LB are not compatible. This is also expected since one component (PCL) is crystalline and can therefore phase separate from the other two components (starch and L or LB). As the amount of LB increases, the $\tan \delta$ -curve

becomes steeper without showing any distinct transitions. Also the transitions move towards each other representing a single transition at a temperature equidistant from individual transitions. For the 50% LB composition, the transition associated with PCL component is totally eclipsed and no clear transitions are observed. This might suggest that there is some interaction between SCL and LB components in the blend. Here, the possibility of starch-LB interaction can be a possible explanation for shifting of the T_g 's. Interaction between lignin and starch (in SCL) is not revealed by the results obtained in this study. Variation in the amount of starch in SCL can lead to greater understanding of the blend properties. Further study is needed to clearly understand this phenomenon of polymer pair miscibility.

MECHANICAL PROPERTIES

Figure 5.10 describes the stress-strain behaviors of typical SCL/lignin blends. A high percentage of strain (more than 650%) is observed in almost all the samples without much effect on the stress. It was observed that the samples undergo necking after around 50% strain. Also the tensile stress increases gradually after yielding showing greater reorientation of the molecules as the polymer chains are pulled apart. It is believed that the samples undergo stress-induced crystallization due to the orientation of the polycaprolactone chains, and hence revealing greater tensile strength at higher extensions. The yield stress is found to increase in cases of blends with both L and LB till ca. 10% after which it decreases (Fig. 5.11). Greater yield stress is due to greater stress transfer between the phases. The degree of crystallinity of PCL phase has the highest value at 10% L concentration for SCL/L blends and 30% LB concentration for SCL/LB blends (Table 5.1). An increase in modulus is also observed in both the SCL/L and SCL/LB blends. This can again be attributed to the higher degree of crystallinity induced by the lignin components. The relationship between the increase in the mechanical properties and the morphology of the blends is not clearly understood since there is no information regarding the phase dimensions and structure of SCL. However, addition of L or LB up to a concentration of 10-20% by weight clearly improves the mechanical properties of SCL.

CONCLUSION

Three separate thermal transitions were observed for SCL as well as all of the blends. The crystallization and melting peaks of SCL were comparable to that of pure PCL. Depression in melting temperature for all the cases revealed interaction between SCL and L or LB. Crystallinity was promoted in the PCL phase when L was added to SCL up to a concentration of 10% by weight possibly due to nucleation from a higher- T_g lignin. When the lower- T_g lignin derivative (LB) was present in the blends with SCL, enhancement of PCL crystallinity was not so prominent as that for SCL/L blends. From DMTA-data for LB blends, shifting of the two separate transitions corresponding to the PCL and LB components were observed with increase in LB content. However, two clear transitions from the two phases reveal incompatibility between LB and PCL. The shifting of the T_g 's may be due to some interaction between the starch and LB components. As regards mechanical properties, a significant increase in both yield strength and modulus were observed for compositions till ca. 20 % with a maximum modulus increase observed for a 10 % blend of LB. Therefore, as much as 30 % of L or LB can be blended with SCL to enhance the properties of the material, though maximum enhancement in crystallinity and mechanical properties are observed for 10-20% by weight of L or LB.

FUTURE WORK

Recommendations for future work include :

- 1) Further experiments are necessary to reveal whether the SCL blends are miscible with lignin components. The crystallization studies can be performed using the well established Flory-Huggins equation and the Hoffman-Weeks plots. Moreover, in order to understand the specific interactions between lignin components and starch or PCL in SCL, nuclear magnetic resonance (NMR) or infra-red (IR) spectroscopy can be employed.
- 2) Rheological studies of the SCL blends can be performed in order to understand the melt flow characteristics of the SCL in presence of lignin component.
- 3) Morphology studies can be performed with the help of optical microscopy to obtain the crystallization growth rate data and crystallization kinetics. This might be helpful in revealing the effect of lignin component on the morphology of the PCL phase and its subsequent correlation with the observed mechanical properties of the blends considered.

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Table 5.1 : Thermal Properties of SCL blends with L and LB from DSC results.

	T_c °C	T_m °C	ΔH_c (J/gm)	ΔH_f (J/gm)	Normalized ΔH_c ⁽¹⁾ (J/gm PCL)	Normalized ΔH_f ⁽¹⁾ (J/gm PCL)	Normalized X_c (%)
SCL (original)	33.6	63.2	-49	58	-69	81	60
SCL (CHCl ₃ cast)	32.7	63.3	-49	57	-69	81	60
(Melt Extruded)	33.1	63.1	-48	54	-69	78	58
SCL/L Blends							
95/5	29.5	63.0	-49	54	-74	81	60
90/10	30.7	60.6	-48	56	-77	89	66
80/20	23.3	59.2	-40	43	-71	77	57
70/30	22.7	58.8	-36	38	-73	78	58
SCL/LB (Melt Blended)							
90/10	25.9	60.0	-43	48	-68	76	56
80/20	21.1	59.8	-40	42	-71	75	56
70/30	13.9	58.7	-33	40	-68	81	60
50/50	-0.9	57.5	-6	26	-16	76	56
SCL/LB (CHCl ₃ Cast)							
90/10	22.4	58.1	-39	43	-62	69	50
80/20	15.0	58.3	-38	42	-68	75	56
70/30	14.1	57.7	-31	38	-63	77	57
50/50	3.3	56.7	-9	26	-26	74	55

* T_c , T_m , ΔH_c , ΔH_f and X_c represent the crystallization temperature, melting temperature, heat of crystallization, heat of fusion and crystallinity in the sample respectively. The crystallization data are from the first cooling scans (from melt) (DSC results) and the melting data are from the subsequent (second) heating scans (DSC results).

⁽¹⁾ ΔH_c or ΔH_f multiplied by 1/(content of PCL in blend)

⁽²⁾ Calculation of X_c is based on $\Delta H_f^0 \approx 135$ J/gm for pure crystalline PCL (see experimental section) [Crescenzi *et al.* 1972].

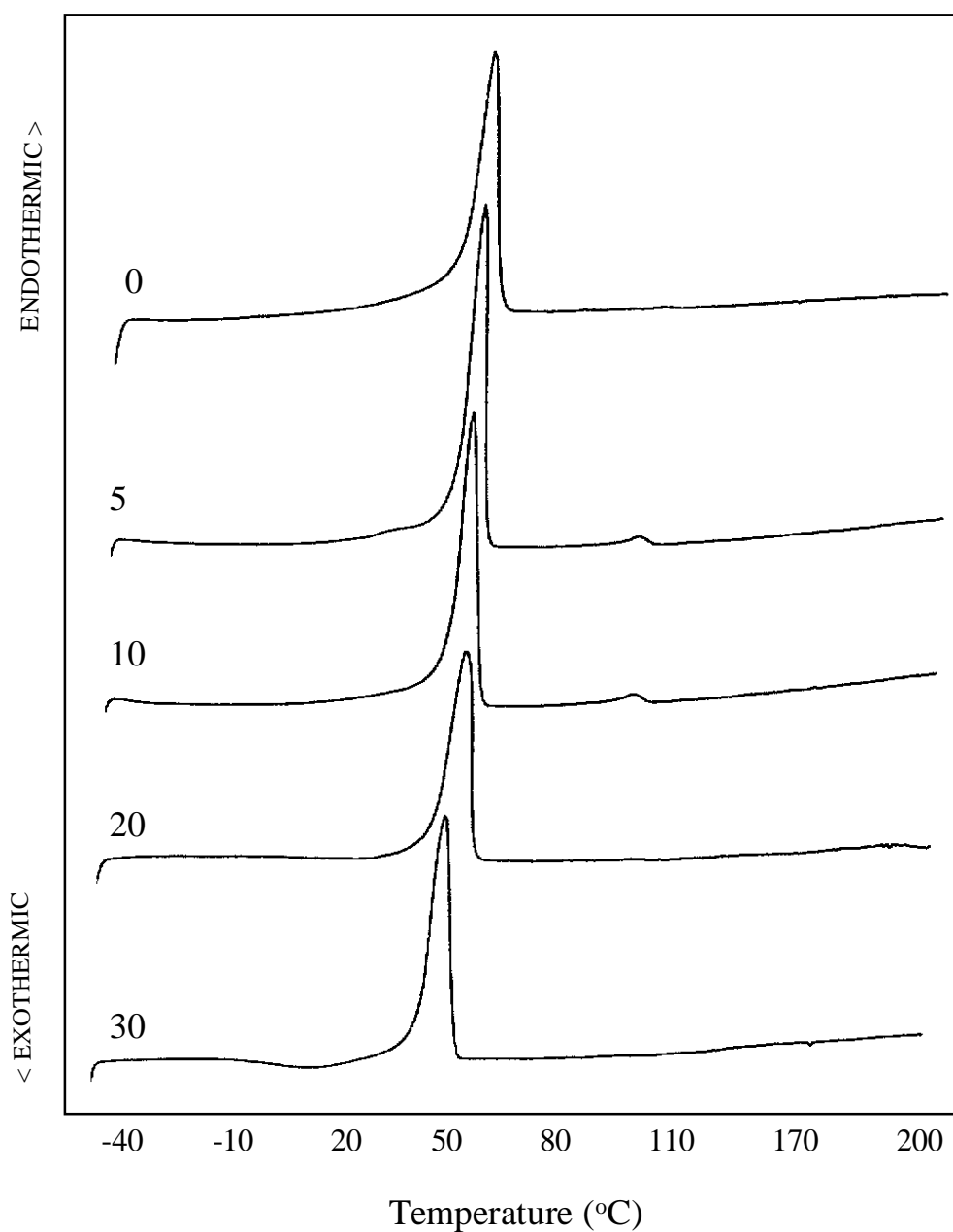


Figure 5.1 : DSC thermograms of melt blended samples of SCL and L. Numbers on each curve denote L content (wt.%) in the blend. These traces are from the second heating scan (after quenching from melt at a rate of 300 °C/min).

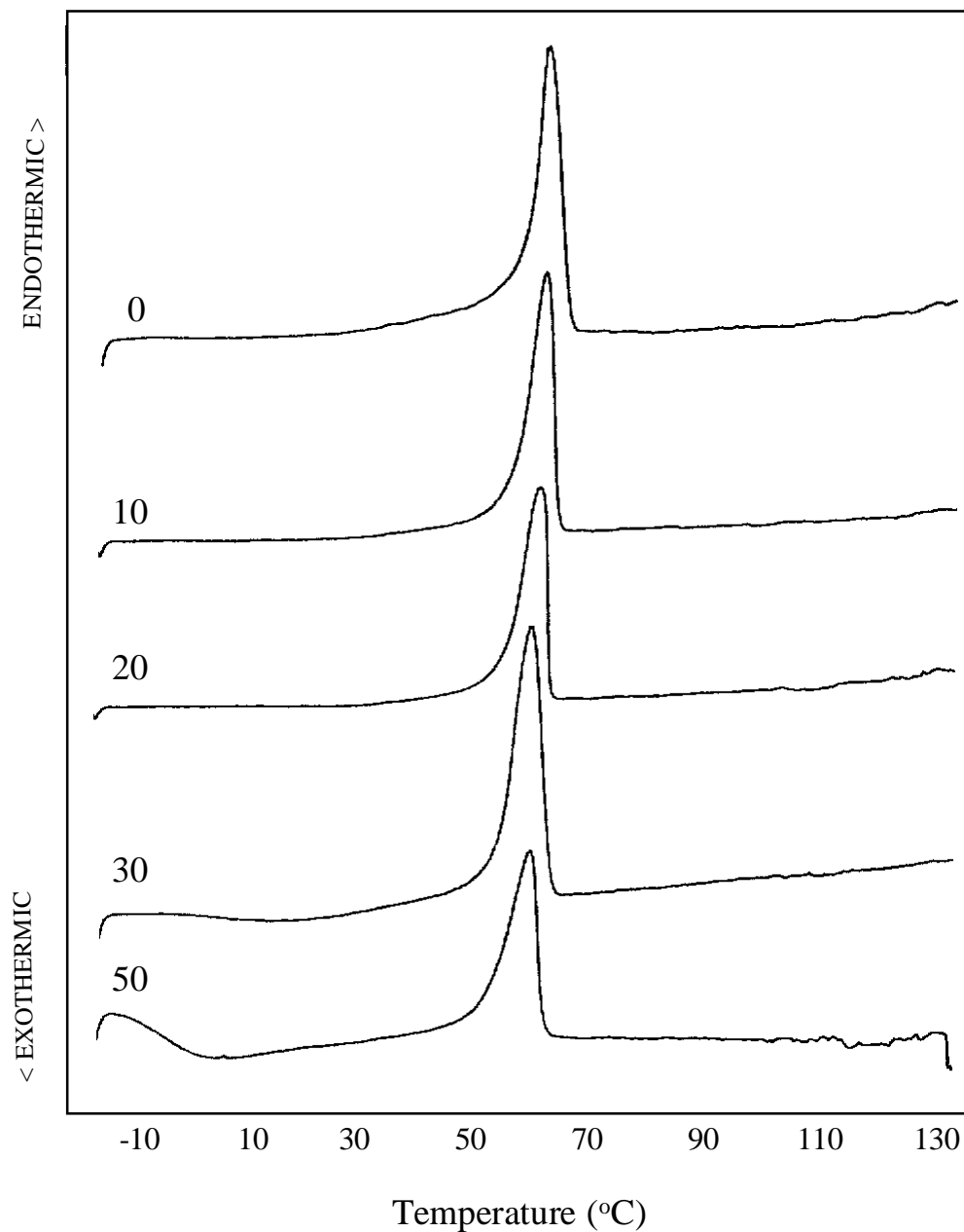


Figure 5.2 : DSC thermograms of solvent (CHCl_3) cast samples of SCL and LB. Numbers on each curve denote LB content (wt.%) in the blend. These traces are from the second heating scan (after quenching from melt at a rate of $300\text{ }^\circ\text{C}/\text{min}$).

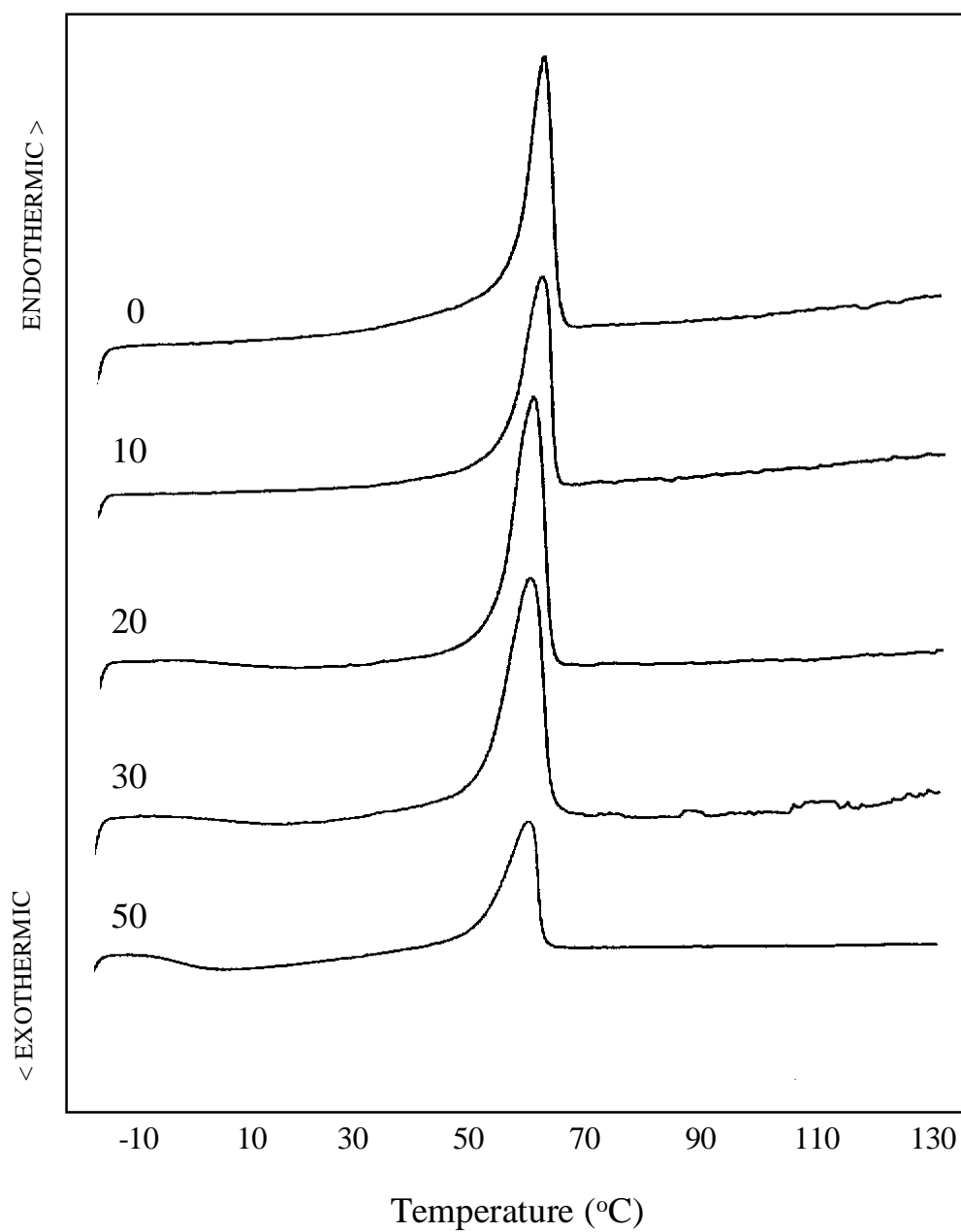


Figure 5.3 : DSC thermograms of melt blended samples of SCL and LB. Numbers on each curve denote LB content (wt.%) in the blend. These traces are from the second heating scan (after quenching from melt at a rate of 300 °C/min).

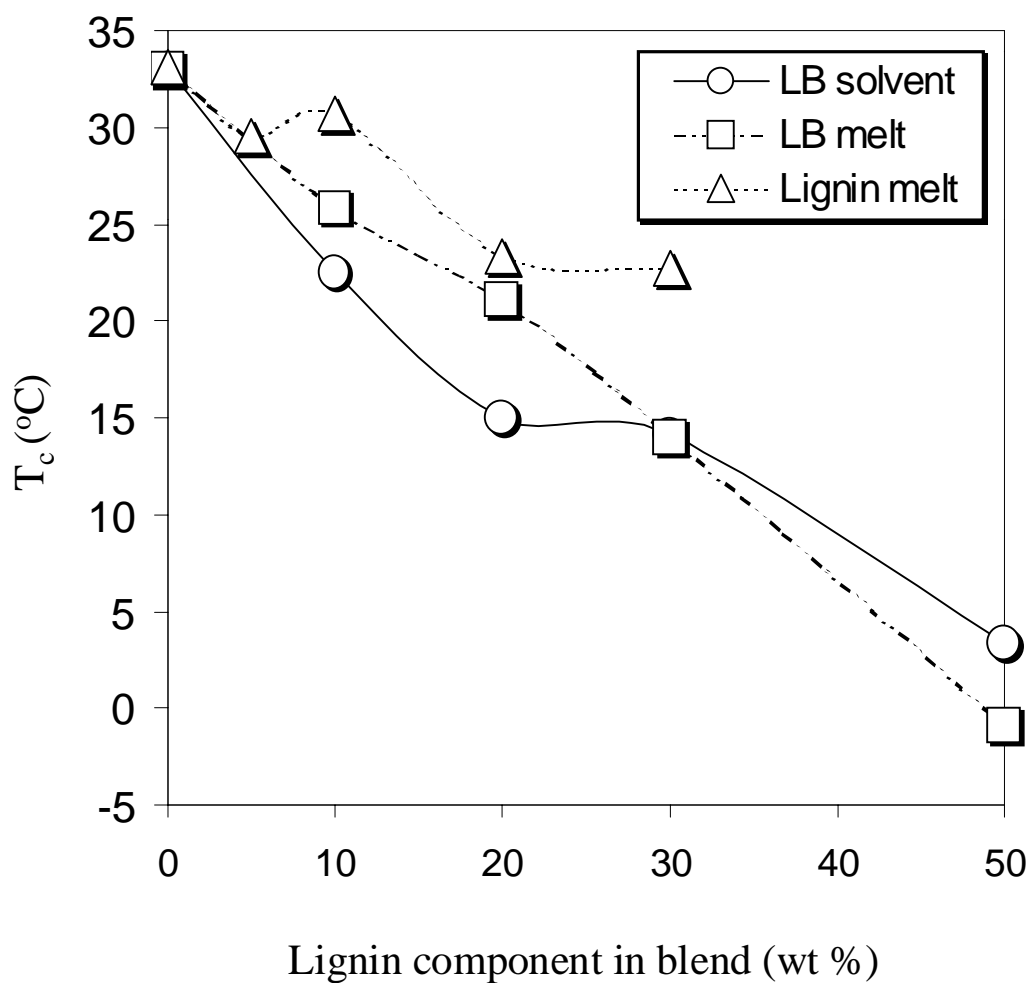


Figure 5.4: Crystallization temperatures (T_c) vs. weight percent of lignin component. The data points are from the crystallization exotherms of the DSC curves in the first cooling cycle.

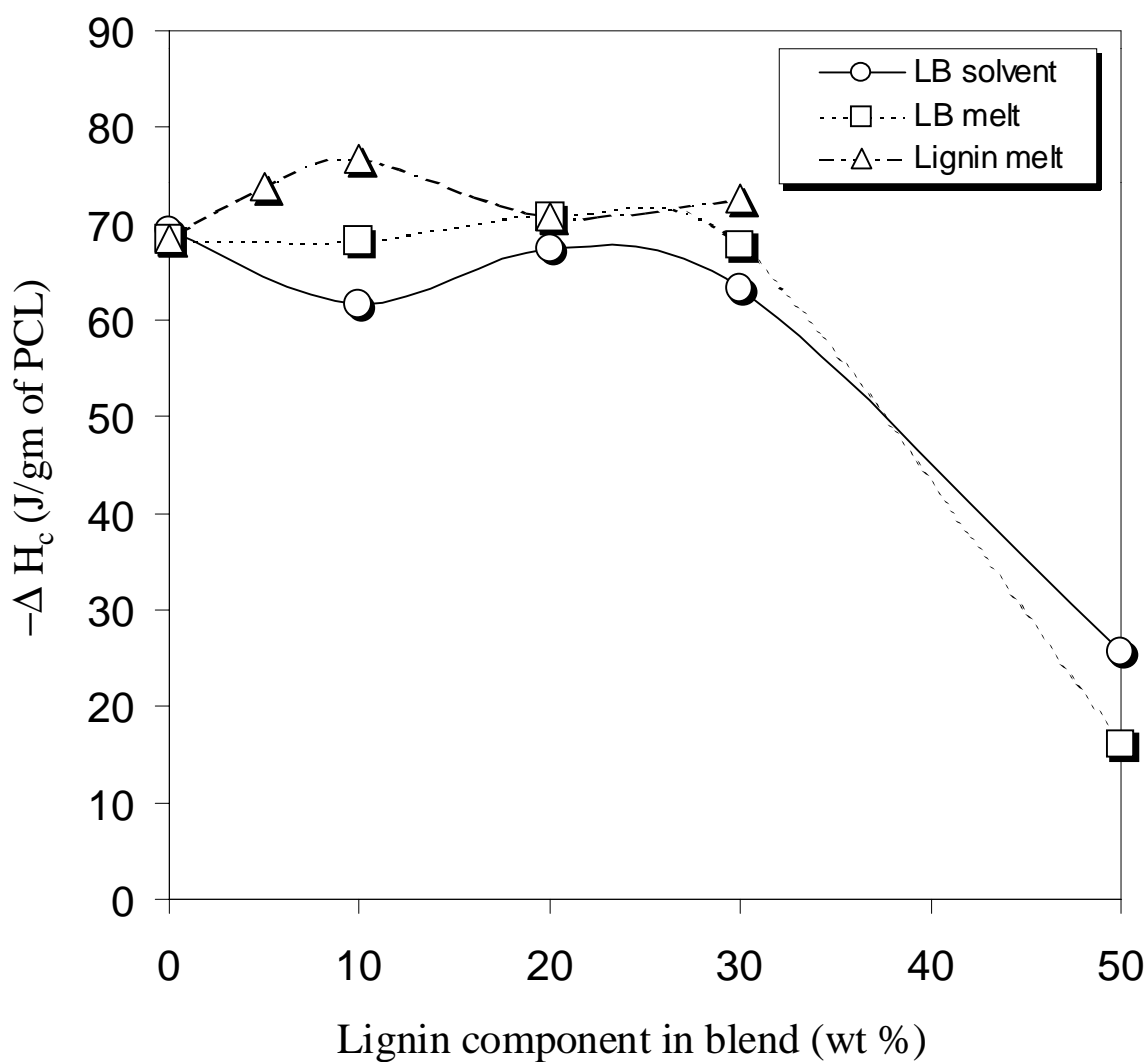


Figure 5.5 : Heat of crystallization (ΔH_c) normalized to the amount of PCL in blend vs. weight percent of lignin component. The data points are from the crystallization exotherms of the DSC curves in the first cooling cycle.

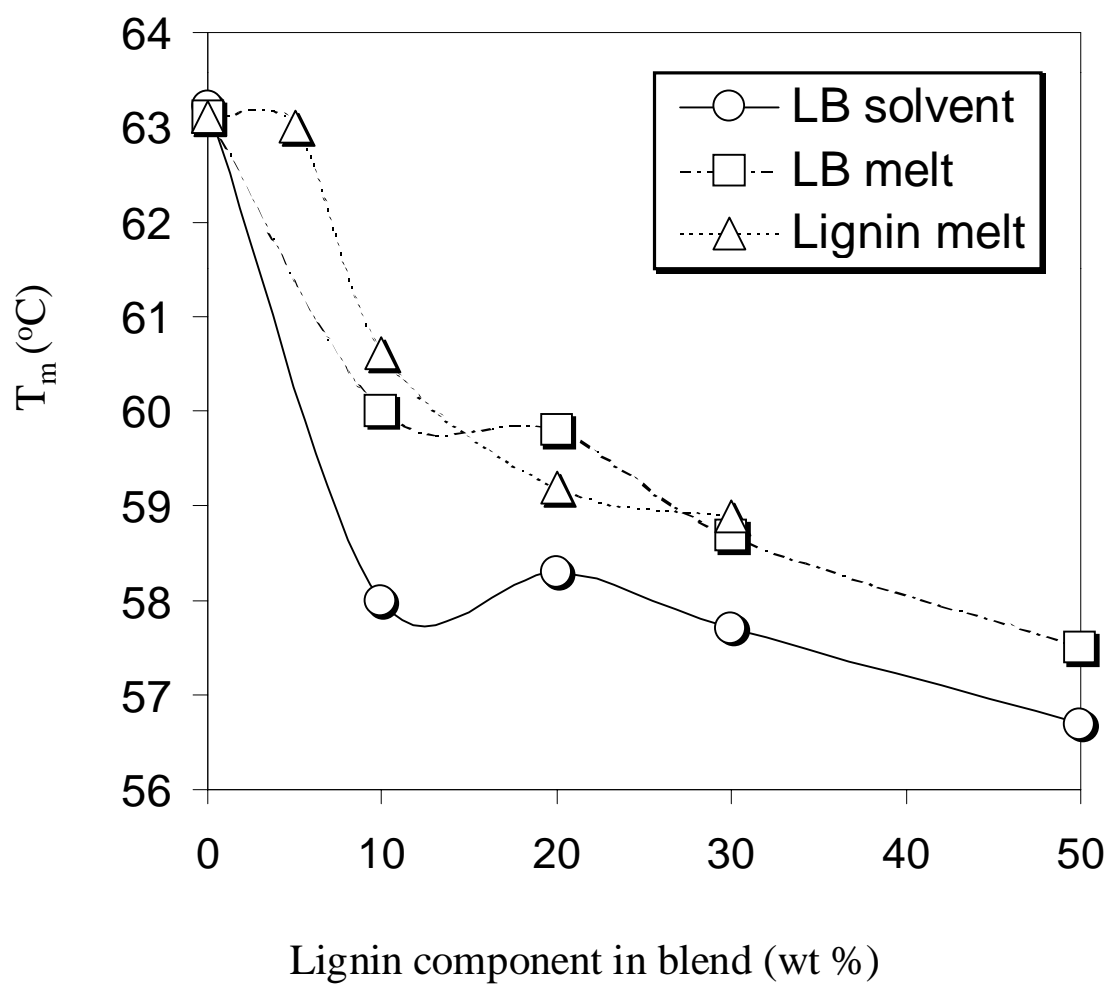


Figure 5.6: Melting temperatures (T_m) vs. weight percent of lignin component. The data points are from the melting endotherms of the DSC curves in the second heating cycle.

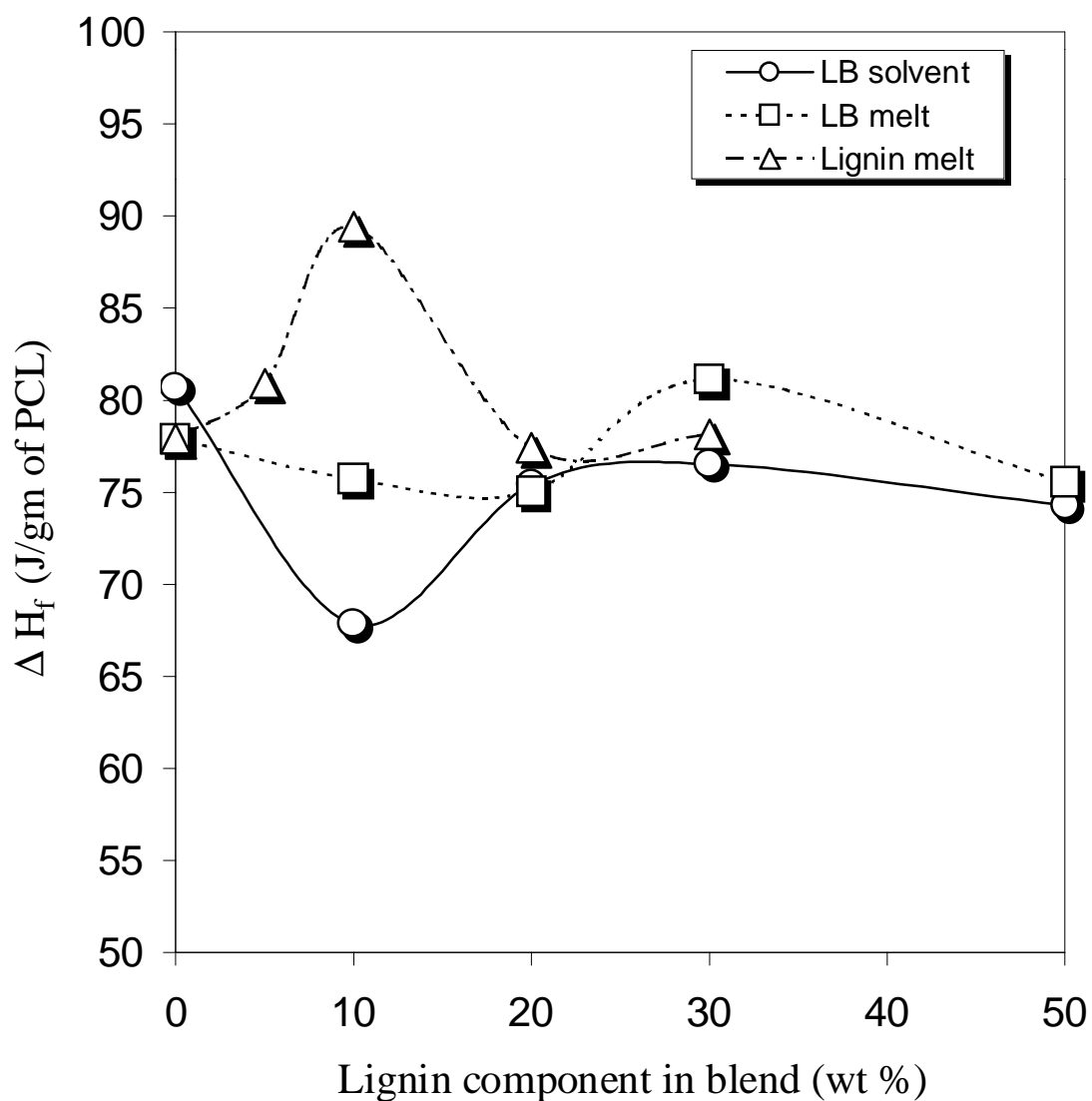


Figure 5.7 : Heat of fusion (ΔH_f) normalized to the amount of PCL in blend vs. weight percent of lignin component. The data points are from the melting endotherms of the DSC curves in the second heating cycle.

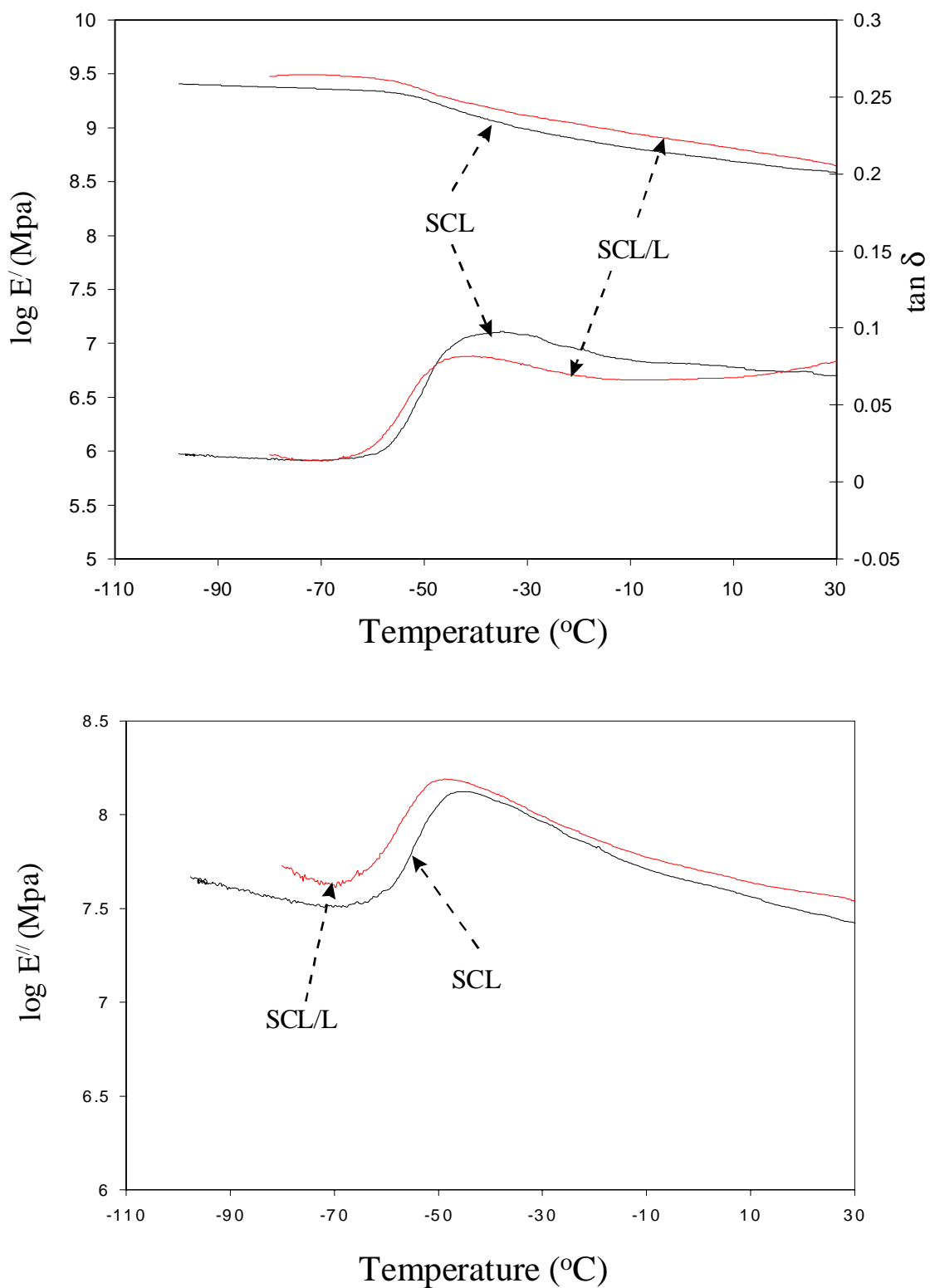


Figure 5.8 : Temperature dependence of E' , E'' and $\tan \delta$ of blends of SCL and lignin.

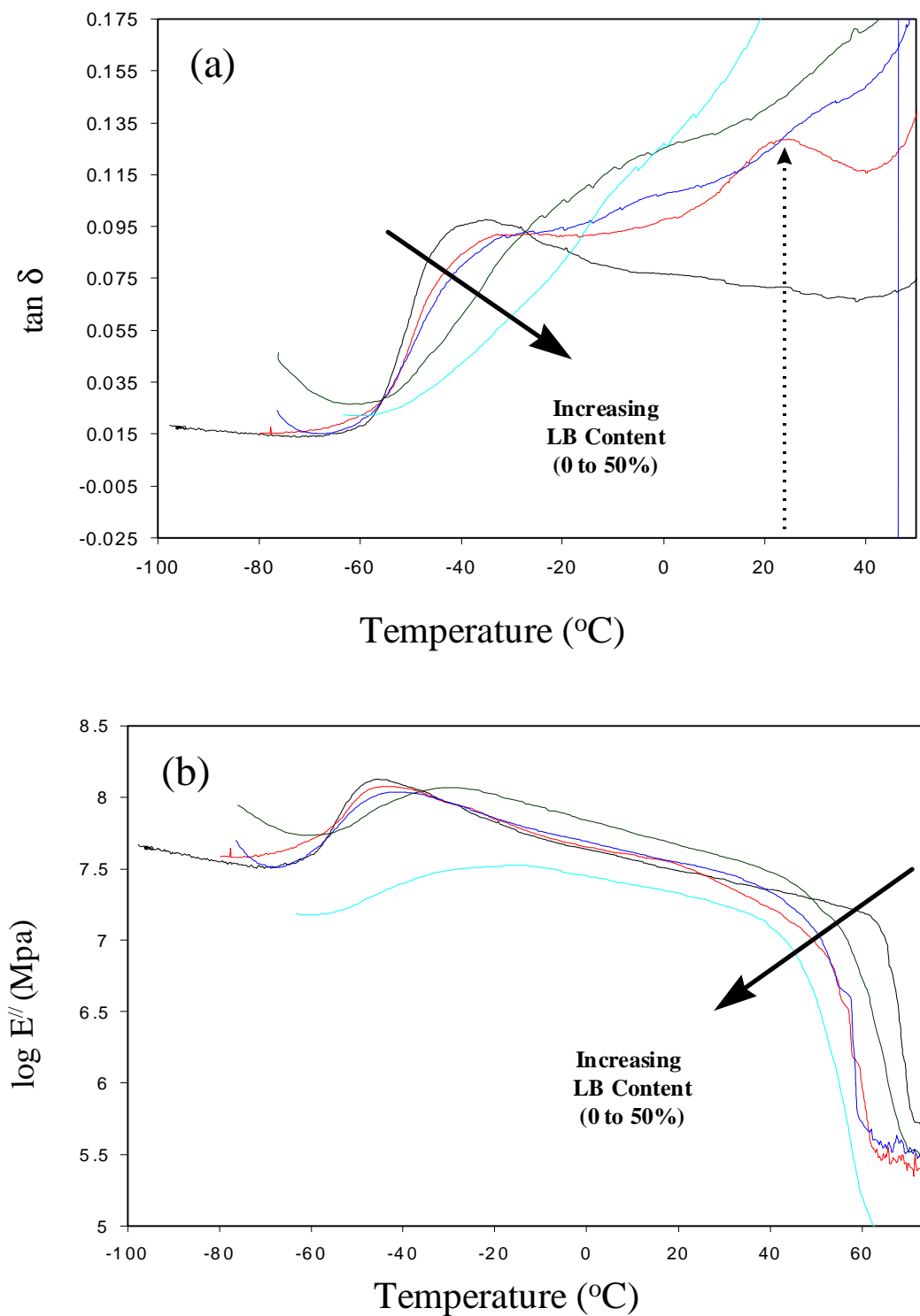


Figure 5.9 : Temperature dependence of $\tan \delta$ (a) and E'' (b) of blends of SCL and lignin butyrate (LB).

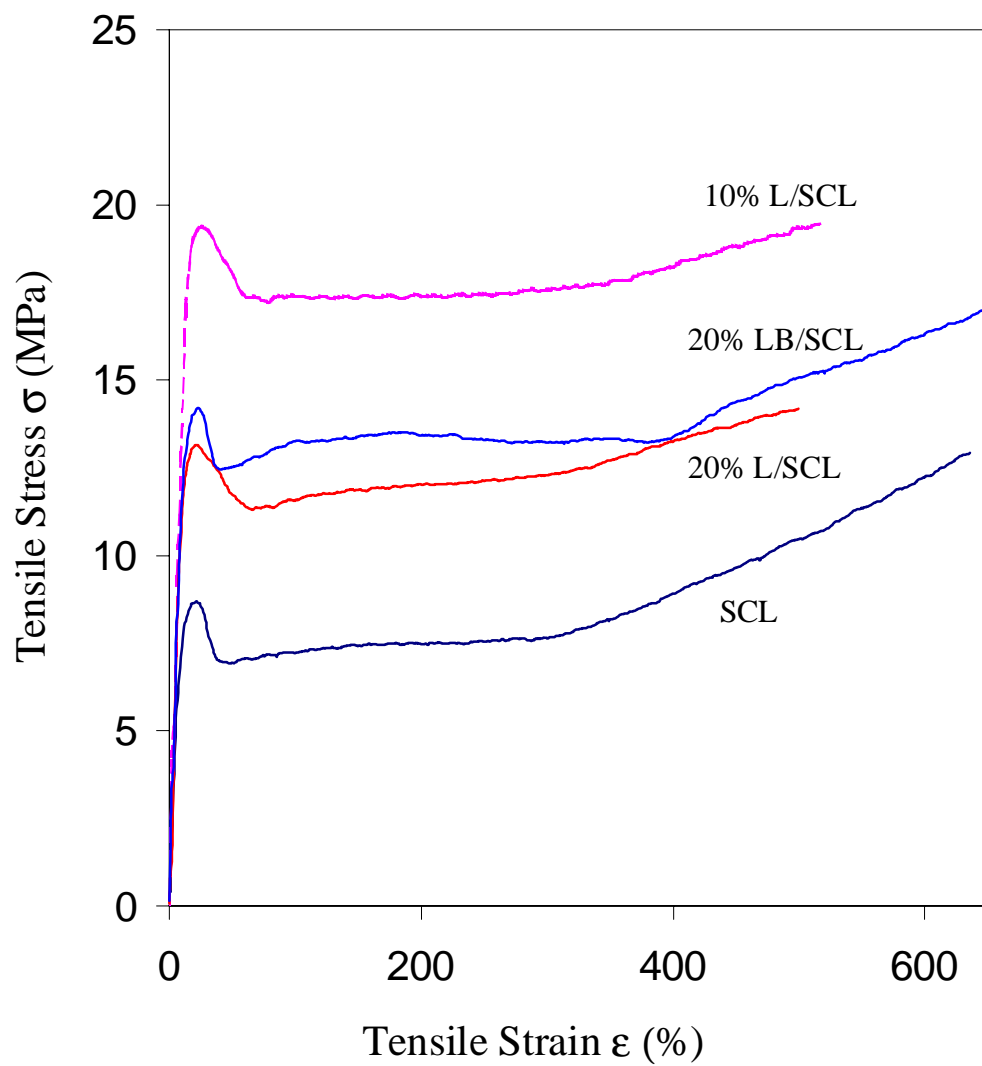


Figure 5.10 : Tensile stress vs. strain curves for SCL/L and SCL/LB blends.

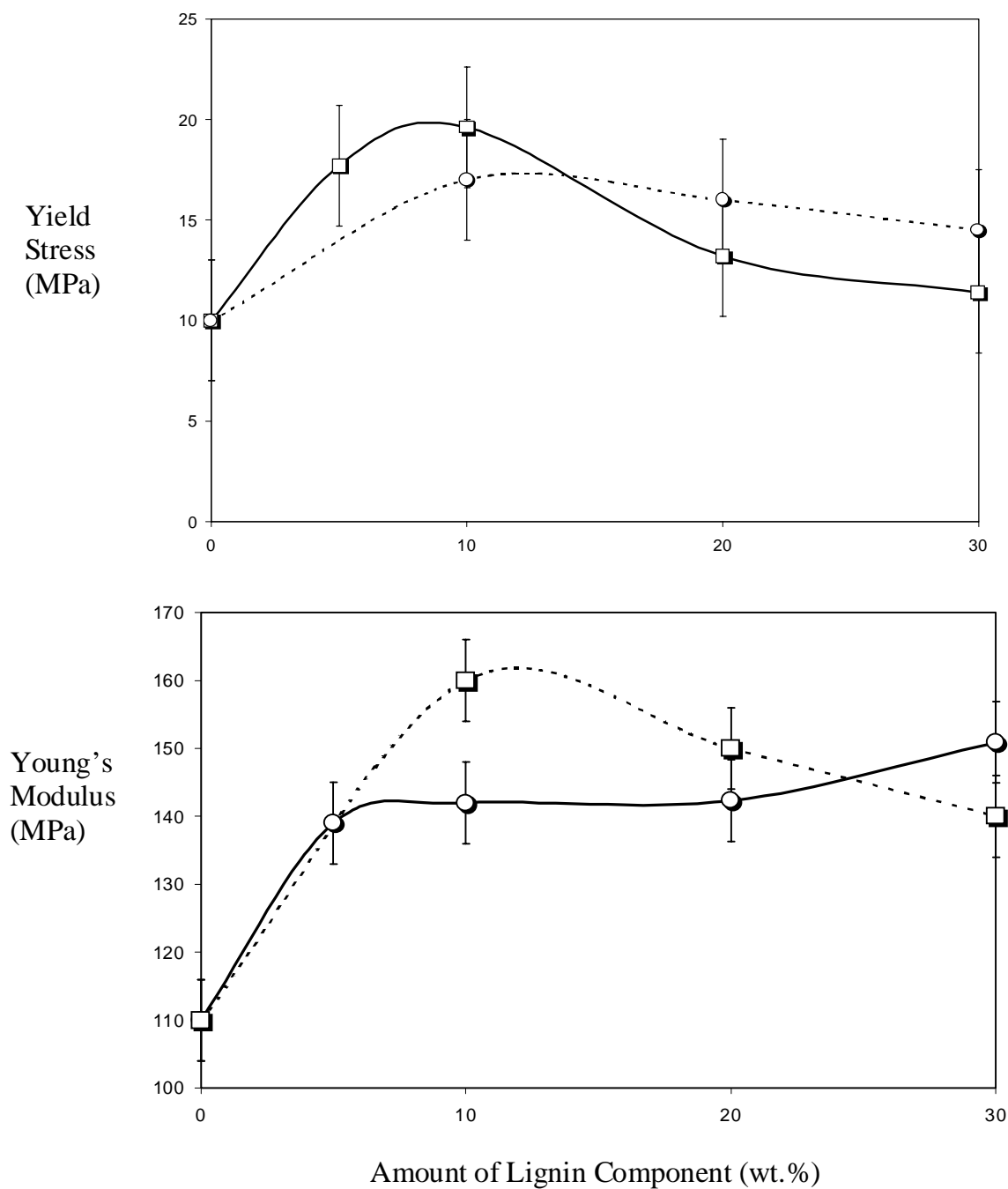


Figure 5.11 : Yield stress and Young's modulus of blends of SCL and L or LB plotted versus weight fraction of lignin component. (— SCL/L blends, - - - SCL/LB blends).