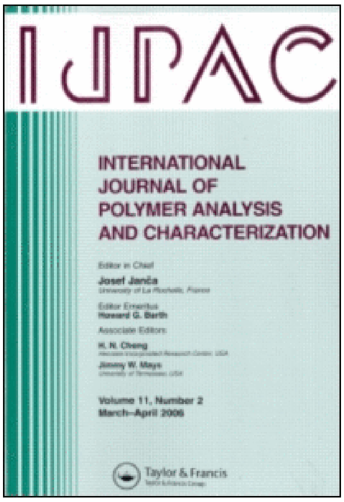

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Non-isothermal Crystallization Behavior of Lignin-Filled Polyethylene Terepthalate (PET)

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Abstract: The important role of lignin can be understood from the interesting properties of the natural composite, wood. Lignin, which has a cross-linked phenyl propane skeleton containing some active sites as well as an aromatic stable structure having a potential of providing dynamic compatibility with polyethylene terepthalate (PET), is a low-cost chemical constituent material available in large quantities as a waste from pulp and paper industries.

On account of these properties as well as biodegradability, conventional inert filler materials such as mica or metal oxides may be replaced by alkali lignin to produce a material with better thermal characteristics, exploring a new way of utilizing lignin. These objectives have been studied through the non-isothermal crystallization behavior of purified alkali lignin-filled PET blends with varying compositions. Analysis by DSC and TGA showed the modification in a nucleation process, the steady acceleration of the crystallization process with increasing lignin proportion. Besides significant decrease in the glass transition

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temperature, decreasing melting temperature with increasing lignin concentration should account for the processibility of PET at lower temperature.

Keywords: Lignin; PET; Filler; Non-isothermal crystallization; DSC; TGA

INTRODUCTION

Wood is a naturally occurring polymeric composite made up of cellulose, hemicelluloses, lignin, and extractives. It is a most versatile and widely used structural material due to its abundance, renewability, desirable mechanical strength, and other properties.

During pulping processes, black liquors, mainly containing degraded lignin in a soluble form, are obtained. Isolated lignin is burned to produce energy and to recover inorganic chemicals required for the pulping process. However, lignin when not recovered constitutes an environmental pollution problem that needs to be remediated.

Several applications of lignin such as additives for concrete, surfactants, adsorbents, dispersants, adhesives, fertilizers, and reinforcing agents for rubber and in the production of phenol-formaldehyde, urea-formaldehyde, epoxy resins, and biodegradable polymers are on record.[1–5]

Some researchers[6] have used lignin in an aliphatic skeleton polymer as filler. It was decided to prepare lignin-polyethylene terepthalate (PET) composites, because of their low density, low cost, and low abrasive character. In addition to these properties, lignin provides considerably stable inert bulk mass, and its aromatic content may simultaneously offer dynamic compatibility due to some typical functional groups. These chemical features of lignin were considered of significant interest to be exploited to replace conventional inorganic particulate fillers like talc, mica, calcium carbonate, etc.

Similarly, a new class of renewable, biodegradable, "green" materials, having a wide range of applications due to their unique physical and fundamental properties, provides newer manufacturing opportunities that minimize energy consumption, waste generation, and cost in comparison to synthetic petrochemical-based polymers.[7] Lignin structure is dependent on wood species and processing conditions.[8] Some industrial processes consistently produce standard well-defined lignins. Extensive cross-linking and strong intramolecular interactions of polymeric lignin limit the utilization of polymeric lignin in solid material systems.[8,9] These interactions can be disrupted through polymer blending, thus altering the lignin's viscoelastic properties.[8] However, there have been few studies of miscible polymer blends with lignin.[10]

Polymer blending is a more promising and convenient method to develop products with desirable properties. Chemical and physical properties of the polymer blends are dependent on monomer type(s), molecular weight, and composition of the respective polymers. Most polymers, however, are immiscible due to low entropy of mixing.[11] Favorable polymer blending can occur only due to specific intermolecular interactions and thus composite materials with desirable properties may be produced. However, the properties of the lignin-polymer blends depend on the synthetic polymer incorporated and the corresponding intermolecular interactions.[12] There are several examples of the use of lignin as an additive or as a prepolymer in several polymeric systems.[13–15] Studies on blends containing lignin or lignin derivatives have shown that in some cases the mechanical and/or thermal properties of the polymeric material are improved with the lignin addition.[16]

EXPERIMENTAL SECTION

Purification of PET and Lignin

Polyethylene terepthalate was purified by using phenol and tetracholoroethene (TCE) (60 : 40 w/w) and by acetone as solvent/non-solvent system. A 2% solution was prepared in phenol + TCE (60 : 40). The solution was heated to 90°C for complete dissolution. The polymer solution was then transferred to a separating funnel, and the solution was added dropwise to 200 mL acetone, which was vigorously stirred mechanically. The precipitated polymer was filtered and dried under vacuum. The dried polymer was then transferred to watch glass and placed in an oven at 50°C for one hour. It was then weighed again, dried in an oven, and reweighed until the weight remained constant. The polymer was finely powdered and meshed through a 300-micron sieve.

Purification of Lignin

Solid lignin was obtained from industrial waste black liquor after acidification. This crude lignin was dissolved in 1, 4-dioxane, and the solution was filtered to remove the undissolved impurities. Excess of cold water was poured in a filtrate to precipitate out pure lignin. The solution was filtered to obtain pure lignin. The same purification process was repeated several times to remove all minute traces of impurities to obtain a purer form of the lignin. Finally, the lignin precipitate was dissolved in 1, 4-dioxane, and the dioxane was allowed evaporate to get a dark brown powder of the lignin in purest form. It was dried in an oven at 100°C for one hour.

Polyblend Preparation

Different homogeneous polymer blends of composition by weight percent of purified PET with purified lignin were prepared by dry mixing. The dry mixed powder was homogenized by grinding with an agate pestle and mortar for about 20 minutes and was then meshed through a 300-micron sieve for uniform particle size. By using this method 2, 4, 6, 8, and 10 weight percent lignin-PET blends were prepared.

Polyblend Analysis

Non-isothermal crystallization studies were carried out on a differential scanning calorimeter (DSC). DSC measurements were conducted on a Mettler DSC 821 STAR^{e} Thermal System. The instrument was calibrated with an indium standard, and a nitrogen atmosphere was used throughout the experiment. All measurements were performed at a scanning rate of 10°C /min.

The glass transition temperatures (Tg), melting temperatures (Tm), enthalpies of fusion, cold crystallization temperatures (Tcc), and enthalpies of cold crystallization were obtained from the corresponding transitions in the DSC curves. The Tm and Tcc were taken as the peak values of the respective endotherm and exotherm in the DSC curves. The Tg was taken as the midpoint of the specific heat increment. Non-isothermal crystallization was performed by heating the pure lignin as well as all polyblend samples (weight 10 mg) to 300°C, holding them there for 5 min (first run), and then quenching them in an ice-acetone freezing mixture. The quenched sample was dried under vacuum and then heated up to 300°C with a heating rate of 10°C/min, cooled to 150°C with a rate of – 10°C/min, and again heated up to 300°C with a heating rate of 10°C/min. The thermal parameters were obtained from cooling and reheating scans for the crystallization and melting behavior.

Thermogravimetric Analysis of Lignin-Filled PET Blends

Thermogravimetric analysis of pure PET and lignin-filled PET blends was carried out on a Mettler Toledo Star^{e} system to observe the effect of blending on decomposition temperature of PET.

RESULTS AND DISCUSSION

Non-isothermal Melt Crystallization of PET

DSC non-isothermal melt crystallization scans for pure PET as well as for different blend compositions are shown in Figure 1. Normal temperature range for crystallization of PET from melt is 203° to 223°C. A shift in the temperature at the onset of crystallization would signify a modification in the nucleation process of PET in the presence of lignin. The change in the crystallization peak width (see Figure 2), the heat of crystallization, relates to the composition of the blend, the effect of blending on the rate of crystal growth, and the degree of crystallization. The heat values of crystallization parameters for PET-lignin blends are given in Table I. The degree of supercooling (Degree of Supercooling = Peak Melting Temperature – Onset of Crystallization) for PET is given in Table I(a). It is evident from the data that the degree of supercooling decreases with increasing lignin content in PET (i.e., maximum 34.5°C for 2% lignin and minimum 30.6°C for 8% lignin in PET), suggesting enhanced crystallization of PET with increasing content of lignin up to 8% and thereafter a rising trend with increasing lignin content in PET.

It is observed (see Figure 2) that crystallization width first increases with 2% lignin in PET, but afterwards it decreases with increasing lignin content in PET. Similarly, the crystallization peak temperature for pure PET is found to be 215.7°C, which steadily decreased with increasing

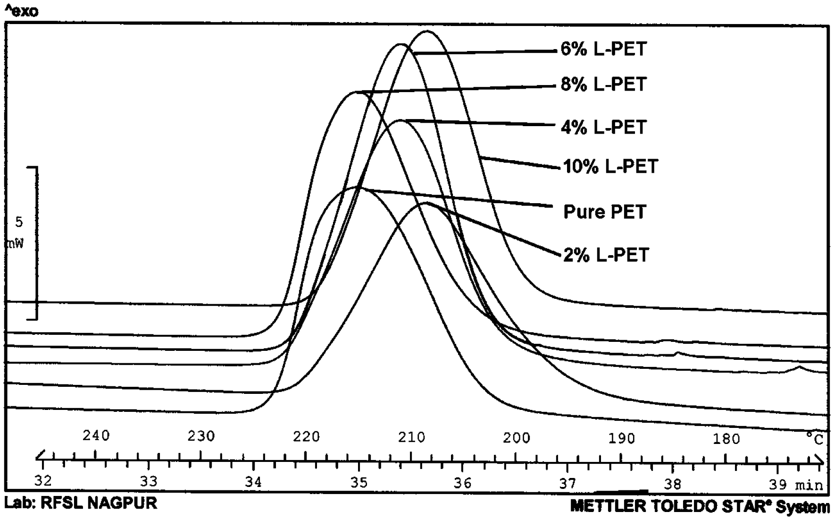

Figure 1. Melt crystallization behavior of lignin-PET blends.

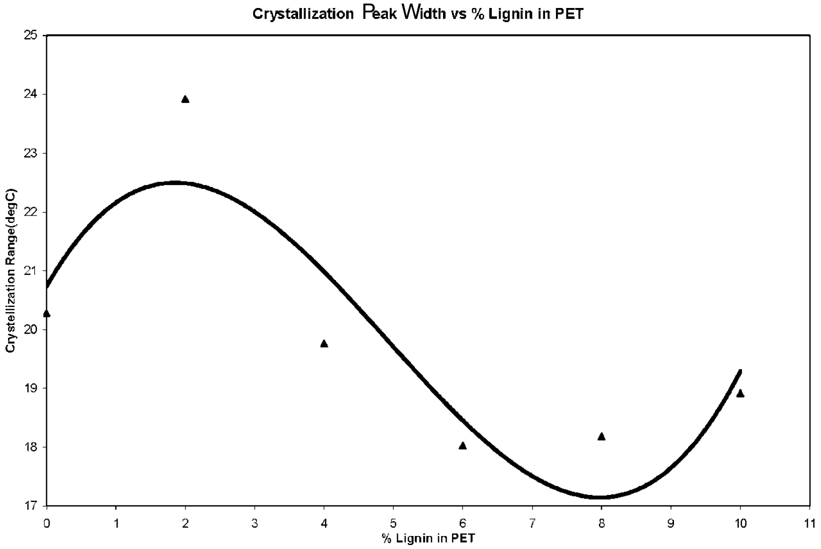

Figure 2. Crystallization peak width of lignin-PET blends.

lignin. Both these phenomena suggest an acceleration of crystallization of PET in the presence of lignin. The average heat of crystallization for PET-lignin blends is found to be slightly higher than that of pure PET, indicating that the crystallization of PET is enhanced. As a result of blending, the degree of crystallinity also increased.

Melting Behavior of Blends

DSC melting scans for pure PET as well as for different blend compositions are shown in Figure 3. The melting range for pure PET is found to

Table I. Crystallization parameters of PET + lignin blends

Blend details		Crystallization temperatures (°C)			Crystallization parameters	
%PET	%Lignin	Onset	Peak	End	Hexo (J/g)	Peak width
100	0	223.2	215.7	202.9	58.3	20.3
98	2	220.3	209.0	196.3	56.3	23.9
96	4	221.7	211.7	201.9	58.4	19.8
94	6	221.0	211.7	203.0	66.4	18.0
92	8	222.8	215.7	204.6	55.5	18.2
90	10	218.7	209.3	199.8	63.7	18.9

Table I(a). Degree of supercooling in PET + lignin blends

Blend details				
%PET	%Lignin	Melting peak temperature (°C)	Crystallization onset temperature (°C)	Degree of supercooling (°C)
100	0	254.5	223.2	31.3
98	2	254.7	220.3	34.5
96	4	253.8	221.7	32.1
94	6	252.6	221.0	31.6
92	8	253.4	222.8	30.6
90	10	251.5	218.7	32.8

be 240.2° to 263.5°C. A significant shift in the temperature at the onset of melting of blend samples is observed. With 2% lignin, the onset temperature was 240.5°C and dropped to 234.4°C. Similarly, a significant depression in peak melting temperature is also observed. The peak melting temperature for pure PET was 254.5°C and dropped to 251.5°C for 10% lignin in PET. The heat of fusion of PET (Table II) increases with increasing lignin content. This may be due to morphological changes with the composition such as crystallite size and also due to the nature of the interfacial structure between PET and lignin. It was also observed that the melting peak width increased with the increasing percentage of lignin in a blend. This implies the slowing down of the process of melting over little wider range of temperature.

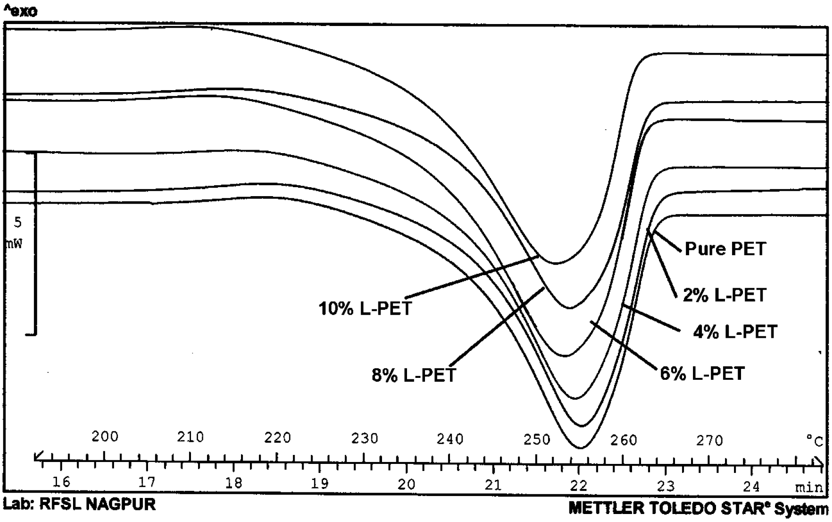

Figure 3. DSC melting scans of lignin-PET blends.

Table II. Melting parameters of PET + lignin blends

Blend details		Melting temperatures (°C)			Melting parameters	
%PET	%Lignin	Onset	Peak	End	Hexo (J/g)	Peak width
100	0	240.2	254.5	263.5	60.0	23.3
98	2	240.5	254.7	263.7	60.8	23.2
96	4	239.2	253.8	263.1	62.4	23.9
94	6	236.6	252.6	262.3	64.6	25.7
92	8	238.3	253.4	262.6	57.5	24.3
90	10	234.4	251.5	261.3	67.5	26.8

Glass Transition and Cold Crystallization of Blends

The changes occurring in glass transition and cold crystallization parameters are shown in Figures 4 and 5 and Table III. It is observed that there is a significant decrease in glass transition as well as cold crystallization peak temperatures of blend samples as compared to pure PET.

Decomposition Temperature

The 2% lignin-filled PET showed decrease in decomposition temperature but subsequently showed a steady rise. At around 8 and 10% lignin,

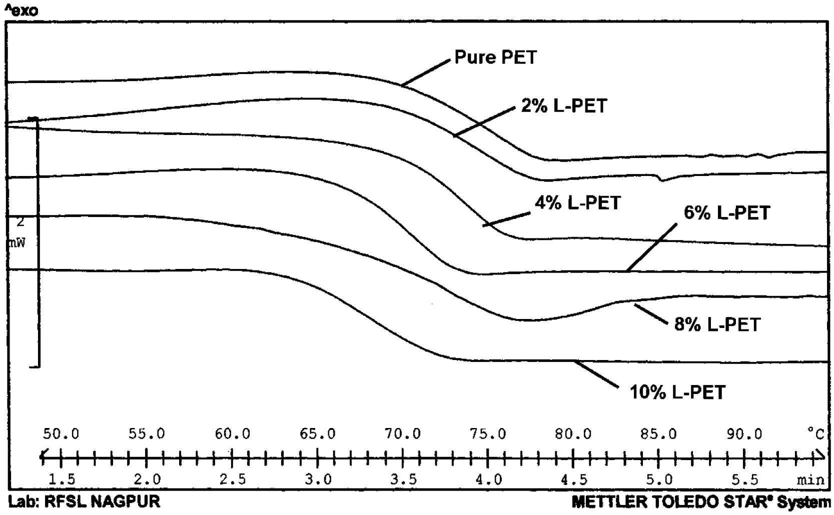

Figure 4. DSC glass transition scans of lignin-PET blends.

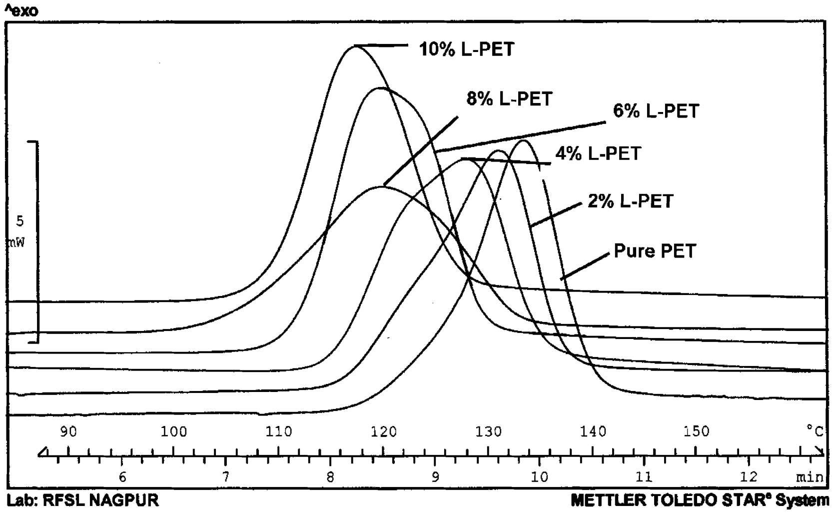

Figure 5. DSC cold crystallization scans of lignin-PET blends.

the decomposition temperatures reach close to the same values as shown by pure PET (see Figure 6).

CONCLUSION

The crystallization rate of PET component increases slightly and the degree of crystallization also increases with the increasing amount of

Table III. Glass transition and cold crystallization parameters of PET + lignin blends

Blend details		Glass transition temperatures (°C)		Cold crystallization temperatures (°C)			Cold crystallization parameters	
%PET	%Lignin	Onset	Midpoint	Onset	Peak	End	Hexo (J/g)	Peak width
100	0	69.0	73.1	124.2	133.7	139.9	42.5	15.7
98	2	68.6	72.7	119.2	131.3	137.3	40.5	18.1
96	4	69.4	72.4	115.1	128.1	135.3	44.8	20.2
94	6	66.3	69.7	111.8	120.0	129.6	47.2	17.8
92	8	65.0	71.9	106.1	119.9	133.1	36.5	27.0
90	10	63.8	67.7	109.3	117.8	126.9	43.8	17.6

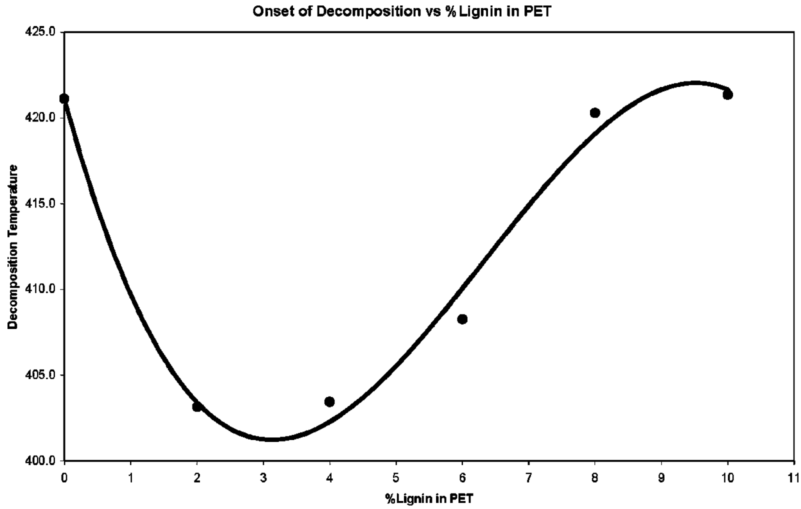

Figure 6. Thermal decomposition of lignin-PET blends.

lignin in PET. The melting peak temperatures for all compositions are found to decrease with increasing amount of lignin, showing processability of lignin-filled PET at lower temperatures.

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