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Thermal and structural studies of polypropylene blended with esterified industrial waste lignin

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Abstract Microwave-assisted chemical modification of lignin was achieved through esterification using maleic anhydride. Modified lignin (ML) was blended in different proportions up to 25 mass% with polypropylene (PP) using Brabender electronic Plasticorder at 190 °C. The structural and thermal properties of blends were investigated by thermogravometric analysis (TG), differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). TG analysis showed increased thermal stability of blends due to antioxidant property of ML, which opposed oxidative degradation of PP. DSC analysis indicted slight depression in a glass transition temperature and melting temperature of blends due to partial miscible blend behavior between PP and ML. All blends showed higher crystallization temperatures and continuously reducing percentage crystallinity with increasing ML proportion in the blends. WAXD analysis indicated that PP crystallized in β polymeric form in addition to α-form in the presence of ML. However, proportion of β-form did not show linear relation with increase in ML proportion, thus ML acts as β nucleating agent in the PP matrix. SEM analysis showed good dispersion/miscibility in PP matrix indicating modification in lignin is useful.

Keywords Modified lignin · Microwave · Polypropylene · Thermal degradation · TG · DSC

Introduction

Lignin is a complex, amorphous, polyphenolic, less reactive, natural organic polymeric material and built up from poly phenyl propane units. It is the second most abundant biopolymer on earth only next to cellulose. It is obtained as a major industrial waste material from pulp and paper industries. The Kraft/Alkaline Pulping process and Sulfide Pulping process are two main pulping processes of commercial importance. Current annual global production of lignin is approximately 50 million tones, which is increasing with the growing demand of pulp products [1]. Out of total lignin produced only, 3 MT of lignosulphonate and 0.1 MT alkali lignin are used for purposes other than fuel like [2, 3] for the production of vanillin and sulfur-containing compounds.

In the field of polymer study, inorganic fillers are being replaced by newer type of organic fillers [4–6]. Lignin being largely available and modifiable becomes a promising alternative for the purpose. Lignin has been recently used for many new products like resin [3, 7], adhesive [8, 9] for polymer blending [10, 11], and for preparation of low molecular weight fuel additives [12, 13].

Lot of work can be cited on modification of lignin to prepare suitable blends with commercial polymers. Many workers blended polyolefins using Kraft lignin to find increased thermal and photochemical stability of blends [20, 25, 26]. But the mechanical properties deteriorate with lignin proportion because of very low solubility/compatibility/miscibility of polar lignin in nonpolar polymer matrix [14–16]. This opens new area to use modified lignin (ML) (less polar) in polymer matrix which may increase solubility/miscibility of lignin in polymer matrix.

Very recently Song et al. [17] and Durmus et al. [18] have reported differential scanning calorimetry (DSC)

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studies on crystallization kinetics and melting behavior of isotactic polypropylene (PP). Wei et al. [19] showed that melting behavior and crystallization structure of PP depends on the blending material and crystallization condition. Canetti et al. [20] blended the lignin with PP and found that, increase in the thermal degradation temperature of blends as a function of lignin content. Lignin acts as a nucleating agent, which is responsible for three dimensional growths of crystalline units and enhancement of PP crystallization rate. Whereas, kinetic crystallizability is not influenced by the presence of lignin in the blends. Pouteau et al. [21–23] reported that antioxidant efficiency of lignin in PP mostly related to their solubility in PP. Indeed only the fraction soluble in PP phase can act as radical scavenger and so phase separation limits the protective action of lignin. Thus increase in lignin compatibility with polymer phase (decrease polarity) should increase its antioxidant properties. Pouteau et al. [24] modified the lignin by acid treatment and found that aliphatic content and polarity of treated lignin decreases due to modification. This decrease in polarity is responsible for increase in antioxidant property of PP compared to unmodified ones; it is only due to increased solubility of treated lignin in PP matrix. Ciobana et al. [25] prepared lignin–polymer film by casting method and found that thermal properties do not change in most cases, whereas, improvement in mechanical properties were found up to 4.2 wt% of lignin.

To increase the solubility and compatibility of polar lignin toward the nonpolar polymers, number of workers modified the lignin to decrease its polarity for different applications [26]. Esterification with several anhydrides is also on record to increase the solubility in several nonpolar solvents [27]. Sailaja and Deepthi [28] blended the esterified lignin with low density polyethylene and found some sort of intermolecular interaction between the modified lignin–polymer matrix. Xiao et al. [1] modified it using succinalysis to increase thermal stability of lignin and resultant blend when blended with commercial polymer. Fernandez et al. [29] ML using phthalic anhydride and *p*-aminobenzoic acid and blended it with commercial polymer, which showed better thermal and photochemical properties. Modifying lignin with cyclic anhydride has been pointed as a way of introducing new material properties in which carboxylate group (–COO–) can be linked through esterification or hydrogen bonding. Furthermore, the modification results in a pendant carboxylic moiety attached to lignin via covalent ester bond. Chemical modification of lignin is thus used to improve polymer lignin compatibility and to introduce reactive sites. The available hydroxyl groups on lignin molecule are reactive plentiful and become local center for high polarity capable of hydrogen bonding. The modification of these reactive nuclei results in an effective alteration of the lignin solubility behavior. Therefore further studies could be useful by using lignin in a pure form with known characteristics, because lignin composition varies from biomass to biomass and also depends on the chemical pulping process used during delignification [30, 31]. At present lesser number of significant techniques is developed for commercial utilization of industrial waste lignin.

The main goal of this article is to study the effect of ML in different proportion on the thermal degradation behavior of resultant PP/ML blends in nonoxidative atmospheres. The structural changes, morphology, and nonisothermal crystallization behavior of PPML is also investigated.

Experimental

Materials

The materials used in preparing binary blends were of commercial grade PP supplied by Bajaj Polymer, Nagpur, India, with melt flow index of 4.26 g/10 min at 210 °C and a 2.16 kg load. Lignin was isolated from the black liquor provided by Simplex Paper Mills Gondia, Maharashtra state, India. All other reagents were AR/GR grade supplied by Merck India.

Methods

Isolation and purification of lignin

Black liquor was filtered and then acidified using dilute hydrochloric acid and then it was allowed to settle down for 30 min. It was then filtered and washed with distilled water to remove acid. It was subsequently dried in oven overnight at 90 °C. Oven dried crude lignin was then dissolved in 1, 4-dioxane and filtered to remove 1, 4-dioxane insoluble inorganic impurities. 1, 4-dioxane was removed by distillation and pure lignin was obtained.

Modification of lignin

Maleic anhydride (MA) of 20 gm was placed in 250 ml round bottom flask fitted in modified microwave oven and melted by irradiation. Lignin of 10 gm was added to the molten MA in several small increments in separately setup 2RML Rotamantle set at 100 °C. Then the reaction mixture was remounted in microwave assembly and irradiated for 20 min, with intermittently controlled irradiation. The reaction mixture was then poured in excess of cold water and filtered to recover insoluble residue (ML). It was further washed successively with distilled water to remove unreacted MA. Reaction was monitored, and completion was determined using Mass Percentage Gain (MPG) formula (on oven dried basis) [32],

$$\mathrm{MPG}\ (\%) = [(\text{mass gain}/\text{original mass})] \times 100.$$

Blends preparation

Polymer blends (PP/ML) were prepared by melt mixing of ML in different proportion (i.e., mass percent 5, 10, 15, 20, and 25%) components at 190 °C for 10 min at 60 rpm in a Brabender electronic Plasticorder HAAKE AEV 153 mixer. Pure PP processed under similar condition was investigated as reference material. During the process, dry nitrogen was continuously purged into the mixing chamber to ensure minimum thermo oxidative degradation.

Analysis

Fourier transform infrared spectroscopy

The FTIR spectra was recorded on FTIR-Simadzu 100 spectrophotometer using KBr pellets in the scan range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

Thermogravometric analysis

Thermogravometric analysis (TG) was performed on Simadzu TGA-50 instrument with platinum pan, using 5–6 mg of material sample in each case. The samples were heated at 10 °C/min in nitrogen atmosphere with a flow rate of (20 mL/min) up to 800 °C.

Non-isothermal differential scanning calorimetry analysis

Non-isothermal crystallization and subsequent melting behaviors of PP and PPML blends of various compositions were investigated by DSC, using Simadzu DSC 60-A. All tests were performed in nitrogen atmosphere (nitrogen flow 30 mL/min) to avoid thermal degradation of blends during heating with a sample mass of around 4 mg. All samples were first heated from room temperature up to 250 °C at the rate of 10 °C/min and then samples were subsequently cooled down up to 40 °C at the rate of 10 °C/min and then reheated up to 250 °C at the rate of 10 °C/min.

Wide-angle X-ray diffraction

The samples of PP and PPML blends were scanned at the speed of 4 °C/min at ambient temperature using an X-ray diffractometer PANanalytical X' Pert PRO MPD with CuKα radiation at a generator voltage 40 kV and current of 45 mA. The data was collected from 5 to 30 °C interval.

Scanning electron microscopy

Morphological analysis of PP, PPML blends was done on scanning electron microscope (SEM) (JEOL JSM-6380A). The samples were coated with palladium.

Results and discussion

Fourier transform infrared spectroscopy analysis

Prior to the modification, purification of crude lignin is desirable. Esterification of purified lignin in molten MA in the presence of triphenyl antimony, as a catalyst at 100 °C takes 4–5 h for complete esterification [33], hence microwave technique was used to accelerate the process. Chemical changes occurred during esterification were determined by FTIR.

Figure 1 shows the FTIR spectra of lignin and ML. The absorbance for lignin occurs at 3400 cm^{-1} for stretching of

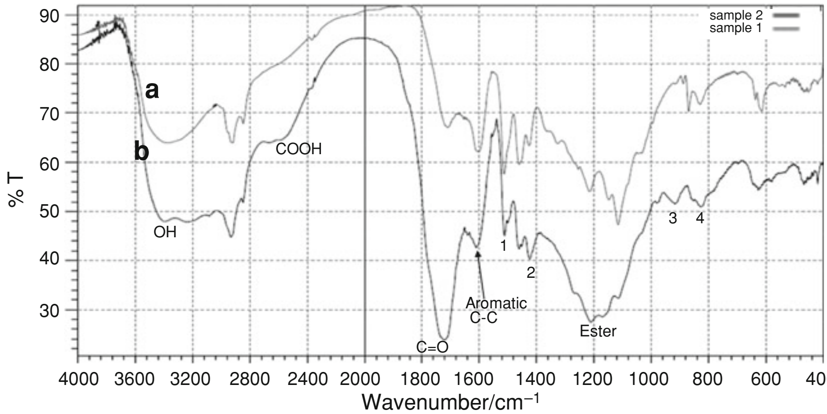

Fig. 1 FTIR spectra of *a* Pure lignin *b* Maleated lignin (ML)

1. Aromatic C-C stretch
2. Aromatic C-H stretch
3. C-O stretch Secondary alcohol & aliphatic ether
4. C-O Stretch primary alcohol Aromatic C-H in plane deformation

hydroxyl group, the absorbance at 2923 cm^{-1} arises from C–H stretching, and small absorbance at 1511, 1462, 1421, and 1327 cm^{-1} corresponds to aromatic skeletal vibrations, ß-O-4 ether bond band at 1117 cm^{-1}. Methoxy group band at 2939, 2881, 1460, and 1425 cm^{-1}, the C=C vibration of aromatic ring at 1514 cm^{-1}, the band at 1600 cm^{-1} which is characteristic of quinoid structure and carbonyl group at 1664 and 1720 cm^{-1} whereas for maleated lignin shows peak for aromatic C=O at 1771 cm^{-1} and peak at 1726 cm^{-1} for aliphatic C=O which is because of MA, for phenolic –OH at 3400 cm^{-1}, for –COOH at 2640 cm^{-1}, peak for C–O of primary alcohol at 1038 cm^{-1} and for C–O of secondary alcohol at 1097 cm^{-1}, for guaiacyl C–H 1040 cm^{-1}, ether C–O 1100 cm^{-1} at 981 cm^{-1} for C–O stretch of secondary alcohol and aliphatic ether and at 908 cm^{-1} for C–O stretch of primary alcohol, aromatic C–H in plane deformation. Increase in relative peak intensity at 1726 cm^{-1} is attributed to esterification. Whereas peak for –COOH group at 2640 cm^{-1} clearly indicated that MA linked to lignin on one side where another side is opened in the acid form as shown in Fig. 2.

Thermogravometric analysis

The effect of ML in different proportion on thermal stability of the PPML blends was studied by means of thermogravometric experiments, carried out in inert atmosphere of nitrogen. Table 1 shows the thermogravometric results corresponding to the onset, end set, midpoint, and residue (*R*) obtained at 550 °C of pure lignin, ML, and PPML blends. It indicates increased thermal stability of ML than pure lignin. Thermal degradation temperature of blends occurred at little higher temperature with increase in proportion of ML in the blends. The pure PP volatilizes in single step from 280 to 500 °C without formation of any remarkable residue. The thermal degradation behavior of lignin is completely different. It begins to degrade at lower temperature (about 200 °C) and produces remarkable char residue.

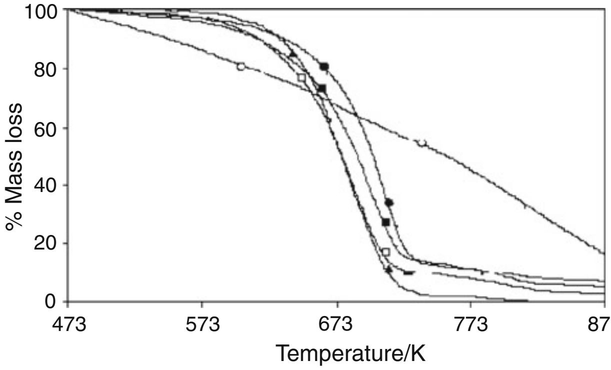

Fig. 3 TG curves under nitrogen atmosphere for PP and PP/ML blends (*filled triangle*), 90/10 (*open square*), 80/20 (*filled square*), 75/25 (*filled circle*), ML (*open circle*)

As depicted in Table 1, under nitrogen atmosphere the blends PP/ML 90/10 and 80/20 show slight increase in thermal stability whereas, PP/ML blend 75/25 show remarkable increase in thermal stability as shown in Fig. 3.

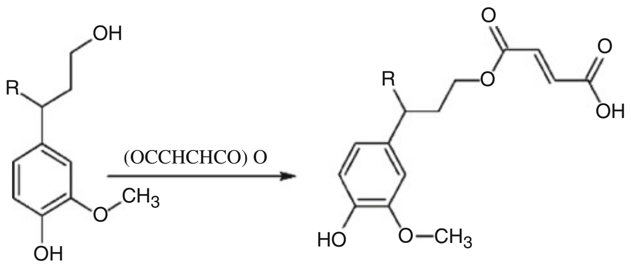

Fig. 2 Scheme for esterification of lignin by MA

Table 1 Thermogravometric results for pure lignin, modified lignin, pure PP, and PP/ML blends

Samples	Onset/°C	Mid point/°C	Residue "*R*"/mass%
Pure lignin	329.10	443.08	7.29
Modified lignin	374.24	448.70	30.38
PP	373.31	403.61	0.14
90/10	365.75	403.67	3.88
80/20	373.06	413.56	6.05
75/25	405.70	433.07	7.92

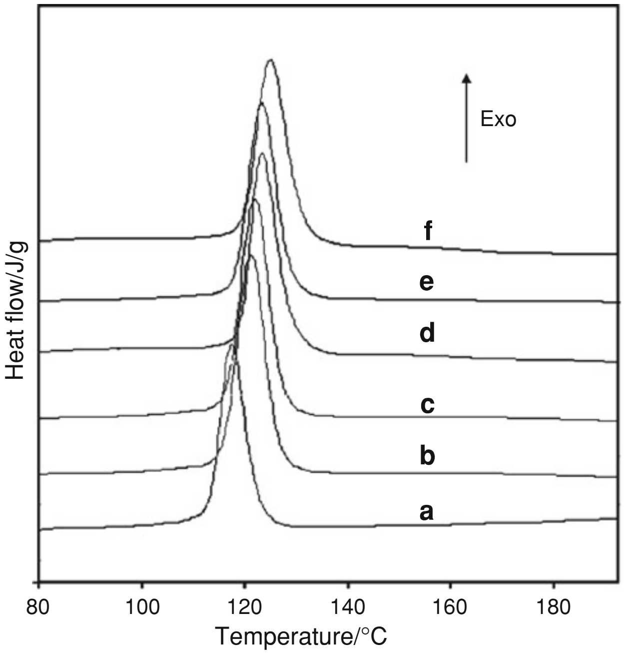

Fig. 4 Non-isothermal crystallization curves of *a* PP and PP/ML blends *b* 95/5, *c* 90/10, *d* 85/15, *e* 80/20, *f* 75/25

In general, the thermal degradation temperature and percentage residue increases with an increase in the amount of ML in blend.

Differential scanning calorimetry analysis

The DSC cooling scan for pure PP and PPML blends is shown in the Fig. 4. The non-isothermal crystallization parameters of DSC curves are summarized in Table 2. PPML blends show slight increase in crystallization peak temperature (T_c); this may be due to nucleating effect of ML on PP matrix resulting in reduced need of supercooling for crystallization and thus the crystallization occurs at higher temperature [34].

The heat of crystallization is related to composition of blends which is tabulated in Table 2 and it decreases continuously with increase in ML proportion. The changes in crystallization peak width and heat of crystallization indicate that in case of PPML blends, particularly at higher concentrations, crystallization is little slower process.

The subsequent reheating curves of PP and PPML blends, non-isothermally crystallized at a heating rate of 10 °C/min are shown in Fig. 5. The melting temperature (T_m) and enthalpies of fusion (ΔH_m) are also listed in Table 3. DSC is one of the tools to investigate miscibility in polymer blends. A single compositional-dependant glass transition temperature (T_g) is an indication of miscibility of blend components at dimensional scale between 5 and 15 nm. If there are two T_g then it shows that both the components in blend are in their own phase and not mixed homogeneously [35]. Kadla [36] reported from DSC analysis that, when Kraft lignin blended with PP did not show miscible blend behaviors it remains immiscible in the PP matrix, the DSC curves reported by Kadla shows two T_g values. However, from DSC curves of PP/ML blends shown in Fig. 5, we can conclude that ML shows some

Table 2 Crystallization parameter of PP and PPML blends

PP/ML	T_{onset}/°C	T_c/°C	ΔH_m/J/g
100/0	122.76	117.45	89.97
95/5	126.22	122.85	85.58
90/10	127.95	123.9	84.95
85/15	127.14	124.35	63.83
80/20	129.45	124.02	47.32
75/25	128.46	125.22	40.18

Table 3 Melting parameter of pure PP and PPML blends

PP/ML	T_{onset}/°C	T_m/°C	ΔH_m/J/g	X_c/%	K_β/%
100/0	156.82	161.80	89.52	42.83	00.00
95/5	154.05	158.25	84.84	42.73	16.31
90/10	153.99	158.83	84.73	45.10	9.25
85/15	153.59	158.45	59.78	33.65	10.11
80/20	152.85	157.67	44.73	26.75	14.23
75/25	150.32	155.38	36.59	23.34	11.03

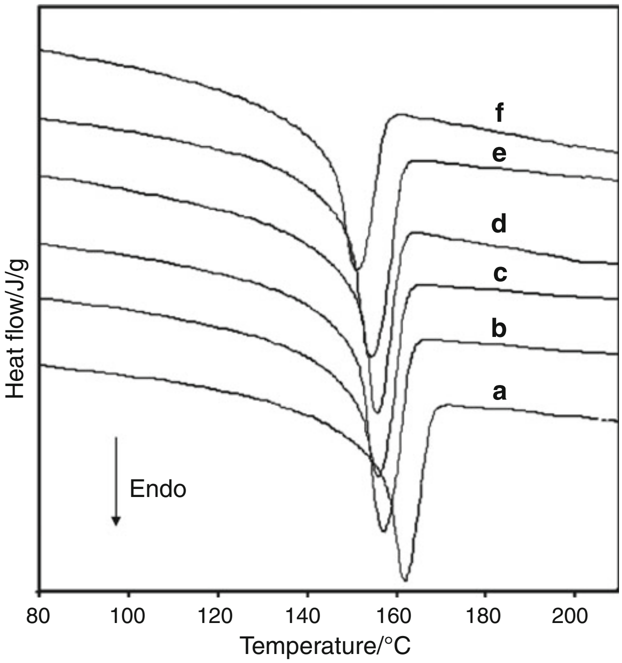

Fig. 5 Melting curves of *a* PP and PPML blends *b* 95/5, *c* 90/10, *d* 85/15, *e* 80/20, *f* 75/25

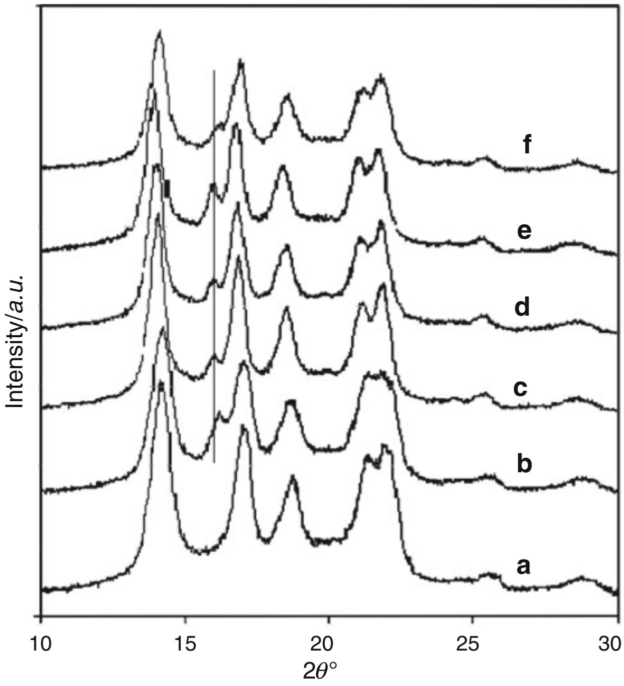

Fig. 6 XRD patterns of *a* PP and PP/ML blends *b* 95/5, *c* 90/10, *d* 85/15, *e* 80/20, *f* 75/25

miscibility or interaction with PP matrix as all blends exhibit only one T_g value. Further evidence supporting a partially miscible blend between PP and ML can be seen from melting temperature peaks. The melting temperatures of the PPML blends decrease linearly with increasing ML proportion in blends. The increased miscibility of ML in PP matrix may be due to increased aliphatic content in modified lignin that may impart positive effect on mechanical properties.

The enthalpy of fusion ΔH_m decreases with increase in ML proportion in PPML blends. This may be due to some kind of reduced or weaker interactions between ML and PP even typically oriented CH_3 group may alter the kind of van der Waals type of interactions within the matrix of PP.

In melt crystallized PP the predominant crystal structure is α-form, which is eventually accompanied by the presence of the β-form. The relative amount of α- and β- forms in the melt-crystallized PP is determined by the crystallization temperature and the cooling rate because of different nucleation and growth rate of two crystalline forms. The formation of β-form crystal structure can be promoted by the addition of foreign seed material to PP matrix [20]. The percentage crystallinity (X_c) of PP and PPML blends was calculated according to the following Eq. 1, and the data is listed in Table 3.

$$X_c\% = \left(\frac{\Delta H_m}{w \Delta H_m^0}\right) \times 100 \tag{1}$$

Where, w is mass fraction of the PP in PPML blends, ΔH_m is enthalpy of fusion of the PP or PPML blends, ΔH_m^0 (209 J/g) denotes the melting enthalpy of perfect PP crystals [37]. Data on X_c (%) given in Table 3, shows that the crystallinity decreases continuously in the blends with increasing ML proportion. This also supports some kind of interactions between ML and PP matrix.

XRD analysis

It is well known that the PP may exhibit three crystalline forms viz; monoclinic α, trigonal β, and triclinic γ. The ratio among these depends on crystallization conditions [38]. Figure 6 shows the WAXD pattern of PPML blends which indicated that the neat PP in blends crystallizes primarily in monoclinic α-form via reflections at 2θ of 14.1, 16.8, 18.5, 21.1, and 22.0 corresponding to 110, 040, 130, 111, and 041 planes and exhibits the β monoclinic structure via reflection

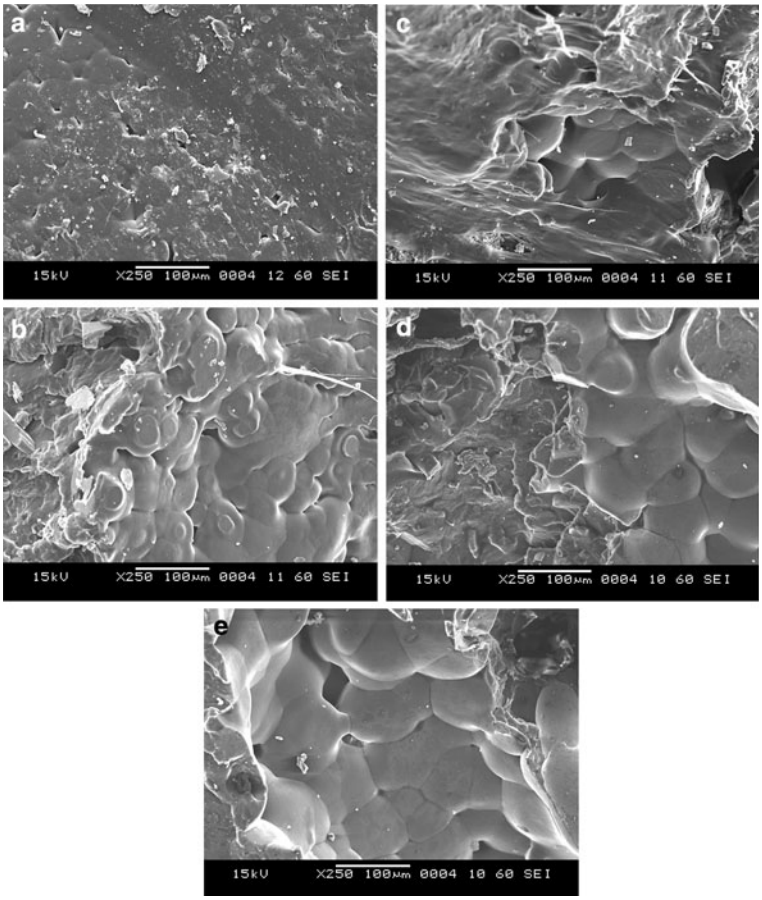

Fig. 7 SEM micrographs of **a** Pure PP and PP-modified lignin blends **b** 95/5 **c** 90/10 **d** 85/15 **e** 80/20

at 2θ at 16.0 corresponding to 300 crystal plane [39]. Peak corresponding to dominant β crystal becomes visible in PPML blends at 5% ML content which is totally absent in PP and remains as is it with increasing ML content in blend. Incorporation of ML affects the crystalline structure of PP. ML may act as β nucleating agent but the intensity of 300 peak does not change linearly with the increasing ML proportion further.

The relative proportion of the β-form (K_β) % was determined by the following Eq. 2 [39],

$$K_\beta\% = \frac{I_\beta}{I_\beta + I_{\alpha1} + I_{\alpha2} + I_{\alpha3}} \times 100 \tag{2}$$

Where, I_β is the intensity of 300 peak and $I_{\alpha1}$, $I_{\alpha2}$, and $I_{\alpha3}$ are intensities of 110, 040, and 130 peak's of α-form, respectively. Data in Table 3 does not indicate any relationship between the ML content on value of K_β. It can be speculated that the formation of β crystalline form is mainly due to the partial dissolution of ML particles in the matrix of PP.

Morphological analysis

In order to further investigate the interaction between ML and the polypropylene in the blend we have performed morphological investigations by scanning electron microscopy (SEM) on neat polymer (Fig. 7a) and on blends (Fig. 7b–e). In all cases, ML is distributed homogeneously within a polymer matrix itself. Better homogeneity may be due to availability of considerable proportion of aliphatic side chain structure made available by esterification of lignin, which utilizes aliphatic alcoholic group on lignin and one of the carboxylic acid groups of maleic acid. It is also supported by the fact that holes are not created by ML in a polymer matrix (Fig. 7b–e). This may lead to no change in mechanical properties of polymer by the addition of modified lignin. In the presence of ML, PP may be crystallized in α- and β-form. The formation of β-form during crystallization promotes increase in crystallization rate [40] and hence addition of ML in PP may predictably retain its strength. However, it needs actual conformation.

Conclusions

Application of microwaves in the chemical modification of pure lignin to maleated lignin was useful on account of time reduction. Successful modification leads to change in polarity of the ML which is responsible for increasing its solubility and compatibility in polypropylene matrix. All polyblends exhibit improved thermal stability, partly due to antioxidants property of ML which may resist to oxidative degradation process of PP. Present modification of lignin shows benefit on account of improved miscibility in polymer blends, which is confirmed by slight depression in glass transition temperature as well as melting temperatures of all blends.

Crystallization peak temperature was found to be increased slightly due to the presence of ML in PP matrix, which signifies modification in the nucleation process of PP in the presence of ML. The peak width of crystallization also increases with ML which suggests relatively slower rate of crystallization process. This change in the rate of crystallization process may be useful in actual processability in typical circumstances.

The WAXD data demonstrated that the different crystalline polymorphs of PP α and β were obtained in PPML blends, whereas PP only crystallized in α-form in the absence of ML, thus ML can act as β nucleating agent. Morphological analysis shows good dispersion and good adhesion between the ML particle and PP matrix in the blends.

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