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STUDIES ON THERMAL CHARACTERIZATION OF LIGNIN
Substituted phenol formaldehyde resin as wood adhesives

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Thermal properties of control phenol formaldehyde (cpf) adhesive and lignin substituted phenol formaldehyde (lpf) adhesives have been investigated in detail. The effect of varying lignin mass percent of phenol and source of lignin like bagasse, eucalyptus bark, coconut coirpith and coffee bean shell on the thermal stability have been studied using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). 50 mass% of lignin loading in cpf adhesive shows better bond strength, whereas lignin incorporation up to 25 mass% yields a resin of thermal stability comparable to cpf. Loading of lignin in cpf delays the first thermal transition event. The mass loss in this event was found to increase with increasing lignin content. Lignin source has significant effect on the thermal stability of lpf resins. Rate of curing is enhanced by incorporation of lignin into cpf.

Keywords: *curing, degradation, lignin, lignin phenol formaldehyde resin, thermal stability*

Introduction

Phenol formaldehyde resins are used as adhesive for wood composites such as plywood, oriented stand board, waferboard, hardboard, particleboard, etc. Phenol formaldehyde resole resins have been studied extensively in relation to formaldehyde to phenol ratio, catalyst to phenol ratio, reaction temperature, reaction time and pH. A large variety of the above resin with dramatically different properties can be obtained by changing the process variables like the type of phenol used, formaldehyde to phenol ratio, type and amount of catalyst and/or hardener used, reaction time and reaction temperature.

Lignin is a naturally occurring polymer, which is second to the most abundant natural polymer cellulose and constitutes about 20–30% of wood and vascular plants [1]. Lignin is a three dimensional, highly branched polymer, which contains a variety of functional groups, and is capable of undergoing a large number of modification reactions. Both aliphatic and aromatic hydroxyl groups are abundant in it and are potential reactive sites. Because of this multifunctionality, lignin can be considered as a natural polyol. Lignin has structural similarity with PF resin condensates and, hence, has potential for substituting phenol in the Pf resins. Many reports are available which show that the lignin has been successfully substituted in phenol formaldehyde condensate [2–8]. The substituted resins have been characterized in detail [9–12]. Much attention has been paid to the synthesis as well as the characterization of these polymers by gel permeation chromatography [13, 14], nuclear magnetic resonance [15, 16], infrared spectroscopy [17, 18] and dynamic mechanical analysis [19]. Thermal analyses of thermosetting resin have been studied extensively [20, 21]. The availability of reliable instrumental techniques and the realization that the information obtained provides an understanding of the curing properties and thermal stability of these resins are the foremost reason for the popularity of thermal methods. Phenol formaldehyde resins are known to be highly temperature resistant plastics which also give high yield on pyrolysis. Thermal degradation of phenolic resins has been the subject of numerous investigations [22–25]. Conley thoroughly investigated the mechanism of thermochemical degradation. He suggested that a thermoxidative process always takes place during the pyrolysis, regardless of whether this reaction occurs in oxidative or inert atmospheres [22]. The degradation starts by the oxidation at the bridging methylene linkages. The high oxygen content of phenolic resin is the reason for this process. Conley has proposed the degradation mechanism of phenol formaldehyde resin in detail [23–25]. However, the report on thermal stability of substituted phenol formaldehyde resins in literature is scarce [26–28].

In the present work, lignin substituted phenol formaldehyde adhesives were characterized for their thermal stability. The main aim to incorporate lignin into phenol formaldehyde resin was to prepare cost-effective adhesive using lignin and to utilize a sustainable resource derived from agrowastes. We

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have investigated the effect of incorporating lignin from various sources in phenol formaldehyde resin at different mass% ratios on the adhesion and thermal property of lpf resins. Eucalyptus bark, bagasse, coconut coirpith and coffee bean shell have been used as a source of lignin.

Experimental

Materials

Bagasse from Titavi Sugar Mills of Muzaffarnagar, U.P. (India), coconut coir of M/s Bharat Coir Industry, Tamilnadu (India), bark of Eucalyptus from Delhi University Campus, Delhi (India) and coffee beans of Robusta variety from M/s Sri Keshav Impex Pvt. Ltd., Coimbatore (India) were collected for extraction of lignin. Sulphuric acid (98%), ranbaxy (India), sodium hydroxide (98%) and methanol (99%), s.d. fine chemical (India), phenol (99%) and formaldehyde (37%) of Glaxo (India) were used in the present work.

Extraction of lignin

The delignifications of agrowastes were performed in a two-necked round bottom flask of 5 L capacity equipped with condenser and thermometer. 250 g of ground agrowaste and 2.5 kg of 5 mol L^{-1} sodium hydroxide solution were taken in the round bottom flask. The solvent to agrowaste ratio was kept at 10. Delignification was carried out for 7 h at 100±1°C using an oil bath. After completion of the extraction time, the flask was taken out from the oil bath and pulp was transferred into a beaker. The resulting liquor was filtered and neutralized with 50% sulfuric acid solution. Lignin was then precipitated at pH 2.0, filtered and dried.

Preparation of adhesive

Cpf and lpf adhesives were synthesized in a 250 mL capacity, four-neck round-bottom flask equipped with a stirrer, thermometer, condenser and dropping funnel. For preparation of cpf, 23.28 g of phenol (0.246 moles), 37.8 g formaldehyde solution (0.456 moles), 20 g each of distilled water (1.1 moles) and methanol (0.62 moles) were charged in the aforementioned flask. The mixture was heated and the temperature was maintained at 80±1°C. A 50% solution of sodium hydroxide (1.16 g, 0.029 moles) in distilled water was then added and reaction was continued for 4 h.

Lpf resins were synthesized using the methodology described by Khan *et al.* [11]. The first step consists in the preparation of lignin-phenol adduct (lp) and the second step consist of the preparation of lpf adhesive. In the first step, 50 g of lignin cake having 12.5 g of lignin on dry basic was transferred in a beaker and 12.5 g phenol (0.133 moles) was added to it. The mixture was mixed and stirred for an hour at 40°C to obtain a homogenous paste. In the second step, 26 g of lp adduct, 42 g of formaldehyde solution (0.518 moles), 10 g of methanol (0.31 moles) were mixed and heated at 80°C. A 50% solution of 1.16 g of sodium hydroxide (0.029 moles) was then added and reaction was maintained at 80±1°C for 4 h. Reaction yielded LSPF adhesives. By varying the amount of phenol and lignin as required for the lpf adhesives with 10, 25, 35, 50 and 60 mass% incorporation of lignin with respect to phenol were prepared.

Methods

Inherent viscosity (η_i) of the extracted lignin samples were determined using Ubblehode viscometer. The lignin was dissolved in DMSO solvent at ambient temperature. η_i of 0.1 mass% solution was measured at 25°C.

Elemental analysis of lignin was carried out on a CHN rapid elemental analyzer model Heraeus 5002651. 10–20 mg lignin sample was put in oxidative combustion chamber at 950°C using cerium oxide as oxidation catalyst.

Hydroxyl value was determined as per IS 548: Part-I. A known amount of the lignin sample is acetylated under controlled condition and titrated *vs.* alcoholic KOH. Hydroxyl value was calculated using the formula:

$$\text{hydroxyl value} = \frac{56.1Ny}{w}$$

where, N is normality of alcoholic KOH, y is the difference in volume in mL of alcoholic KOH solution used for titrating the samples and the blank, w is mass of the sample taken.

The glass transition temperature (T_g) of lignin and curing of adhesive was determined using model DSC 2910, TA Instruments, USA. The sample (8 mg) was heated at a rate of 10°C min^{-1} from ambient temperature to 150°C under N_2 atmosphere in a sealed aluminum pan. The thermal stability of lignin was investigated using thermogravimetric analyser, SDT-TGA 2960 (TA Instrument, USA) in dynamic mode. The samples (8 mg) were heated at a rate of 10°C min^{-1} from ambient to 350°C in N_2 atmosphere. For thermal degradation studies of resins, the instrument was used in dynamic mode and the sample (8 mg) was heated at a rate of 10°C min^{-1} from ambient temperature to 700°C in N_2 atmosphere. The flow of N_2 gas was maintained at 50 mL min^{-1}.

Table 1 Physical properties of extracted lignin

S. No.	Property	Lignin			
		bgl	ccl	cbl	bkl
1	Hydroxyl value	296	212	207	236
2	Inherent viscosity (η_i) at 25°C/dL g^{-1}	0.75	0.70	0.59	0.67
3	Elemental analysis/%				
	Carbon	44.4	45.2	45.9	50.0
	Hydrogen	5.5	5.7	4.2	4.7
	Oxygen	50.1	49.1	49.9	45.3
4	Glass transition temperature (T_g)/°C	111	105	110	110

Adhesive strength of adhesive samples were tested as per Indian standard. IS 851:1978 describes the method for testing the adhesive strength of a close contact joint of the samples. The teakwood specimens with moisture content of 7 mass% were cut into size of 115×25×3.15 mm. The adhesive was applied on two specimens. Two adherents were joined together by applying the adhesive on 25×125 mm area. The glued samples were then pressed in a clamp under a load of 50 kg. The samples were kept in an oven at 125±2°C for 2 h. The samples were conditioned at ambient temperature (27±2°C) and humidity (60±5%) until constant mass was observed. The specimens were tested for bond strength using tensile testing machine at a crosshead speed of 50 mm min^{-1}. The load taken by the samples were recorded and average bond strength of six test specimens was determined.

The shear strength was measured by tension loading of adhesives as per ASTM D 2339-94 A. 3-Ply laminate of moisture content 7 mass% (on dry basis) was used for specimens preparation of size 300×100×3 mm. The adhesive was applied on the whole surface of one side of the adherents. The two panels were glued and assembled to each other, keeping the grain in parallel. The glued samples were pressed in a compression molding machine at 120°C at a pressure of 40 kg cm^{-2}. The panel was cured for 6 min and then cooled. After conditioning at ambient temperature (27±2°C) and 60±5% humidity until constant mass, the panels were cut into 82.6×25.4 mm specimens. A groove of 3 mm depth was engraved on both sides of adherents and the area between the grooves was kept 25×25 mm. The specimens were tested for shear strength using tensile testing machine at a crosshead speed of 3 mm min^{-1}. The load taken by the samples were recorded and average shear strength of six-test specimens was determined.

Results and discussion

Lignin yield

The delignification process was carried out at agrowastes to alkali solution ratio 1:10 (*w*/*w*), alkali concentration 5 mol L^{-1}, temperature 100°C and time 7 h. The observed lignin yield is 19, 21, 22 and 33 mass% for coffee beans shell (cbs), bagasse (bag), eucalyptus bark (brk) and coconut coirpith (ccp) respectively. The mass% yield shows the highest value for coconut coirpith lignin and the lowest for coffee bean shell lignin.

Characterization of lignin

The physical properties of extracted lignins are given in Table 1. Elemental analysis gives percent content of C, H and O in alkali extracted lignins. We notice that bagasse lignin (bgl) and coconut coirpith lignin (ccl) have same number of C, H and O. The hydroxyl values of four lignins, bgl, ccl, cbl and bkl differs from each other showing the structural difference of these lignins. The highest value of OH in bgl, 296, and the lowest one in ccl, 207 is the case of points. Likewise the inherent viscosity values of these natural materials differ from each other showing the difference in their molar masses, chemical composition and structure. The cbl shows the lowest values of 0.59 dL g^{-1} of η_i as compared with the highest value of 0.75 dL g^{-1} of bgl. Since the values of % C, H and O of bgl and cbl is almost comparable. It can be inferred that the cbl has a more compact structure than the bgl. Thus the η_i values and C, H and O values both bring out clearly the compositional and structural difference of these lignin. The difference in the values of T_g of these lignins further highlights the difference in their structures. The difference in T_g values may be correlated to the difference in the flexibility of the polymeric chains, molecular mass, molecular mass distribution and degree of crosslinking [29].

Mass loss of extracted lignins at different temperature is summarized in Table 2. In the temperature

Table 2 Mass loss of extracted lignins at different temperatures

S. No.	Lignin code	Mass loss/% at temperature/°C					
		100	150	200	250	300	350
1	bgl	8	13	14	22	56	63
2	ccl	7	8	9	18	54	62
3	cbl	12	17	19	26	36	47
4	bkl	8	10	11	17	26	32

range of 100° to 200°C, 2–7 mass% losses is observed on the basis of mass% loss per 50°C. In the temperature range of 200 to 250°C, the mass loss is 6–9 % in all lignin. The major mass loss of 34–37% is recorded in the temperature range of 250 to 300°C for bgl and ccl. In this temperature range, the mass loss of bgl is comparable to ccl, whereas bkl and coffee bean shell lignin (cbl) gives 9–10 mass% losses. It is informative to compare the thermal degradation behavior of the various lignins. Upto 150°C, the mass loss in case of cbl is the highest, 17 mass%, while it is the lowest in ccl, 8 mass%. It can be inferred that cbl which has the highest value of OH group degrades fastest while ccl appears to have comparatively lesser free OH groups which cause its slow degradation upto this temperature. For other lignin the mass loss falls between the above two limits. Beyond 150°C other linkages starts breaking. At 250°C cbl shows the highest mass loss, 26%, but the mass loss in case of ccl and bkl are comparable, 18 and 17 mass% respectively. At 350°C the pattern of mass loss in these lignin change radically which highlight the difference in their chemical composition and structure. At the preceding temperature, bgl shows the highest mass loss, 63%, the mass loss in ccl being comparable, 62 mass%. It can be inferred that aliphatic linkages are fairly high in these lignins. The cbl shows a mass loss of 47% and bkl, 32% at 350°C showing that in these lignin aromatic moieties are comparably higher.

Effect of lignin incorporation

Mechanical property

The properties of lpf adhesives are expected to be influenced by the extent of lignin incorporation in phenol formaldehyde (pf) resin and the source of lignin, hence these factors have been studied in detail. The effect of bark lignin (bkl) incorporation on adhesive and shear strength of Pf has been studied by varying its content from 10 to 60 mass% of phenol. Incorporation of lignin in pf adhesive results in improved bond strength. Figure 1 shows the effect of lignin substitution on adhesive and shear strength. Adhesive and shear strength both increase proportionately with increase in lignin content. A sharp increase in adhesive strength at 10 mass% of lignin substitution in pf adhesive is noticed. On progressive incorporation of bkl up to 50 mass%, adhesive and shear strength increases progressively. It appears that copolymerization of lignin with phenol formaldehyde results into improved adhesive and shear strength than pf. Adhesive strength also depends on cross-link density. The increase in adhesive and shear strength of lpf can be explained by the fact that cross-linking between the polymer chains is enhanced, which provide better reinforcement structurally. It is observed that beyond 50 mass% loading of lignin in pf, adhesive and shear strength decreases. This may be due to the fact that beyond 50 mass% loading of lignin in pf, excess lignin is present in the network which causes loss in adhesive and shear strength [30, 31].

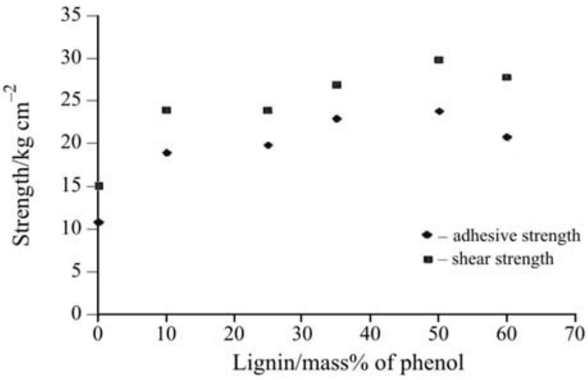

Fig. 1 Effect of lignin substitution on adhesive and shear strength

Thermal property

To assess the thermal stability of lpf, TG and DSC analyses was carried out. Initial decomposition temperature (T_i), temperature at which maximum degradation takes place (T_m) and final decomposition temperature (T_f) in different thermal events was observed. Figure 2 shows the TG-DTG curve of cpf. Two mass loss events are observed in the curve. One in the temperature range of 100 to 250°C and other in the range of 250 to 550°C. It is known that phenolic resin degrades in three steps: postcuring, thermal reforming and ring stripping [26]. In the first thermal event (100–250°C), 15 mass% loss is observed which is at-

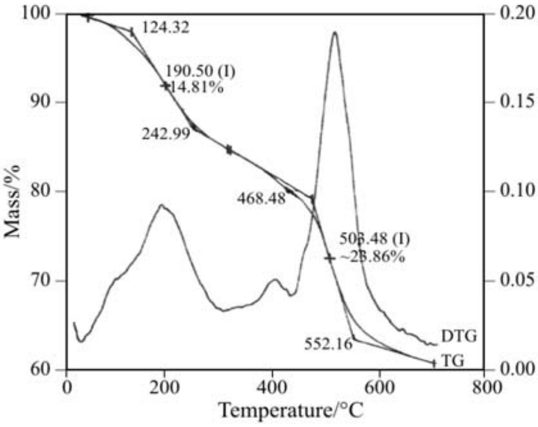

Fig. 2 TG–DTG curves of cpf resin

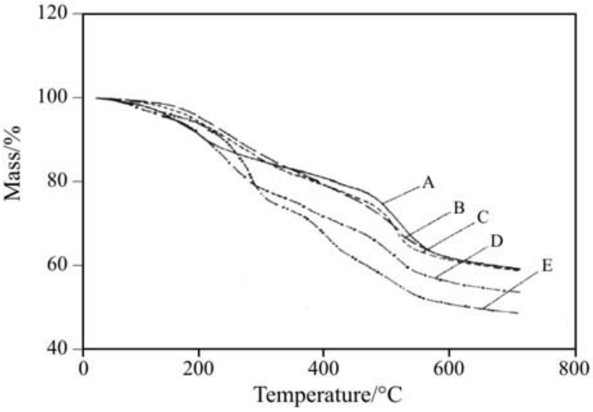

Fig. 3 TG curves of A – cpf, B – 10% bklpf, C – 25% bklpf, D – 35% bklpf and E – 50% bklpf

tributed to the postcuring of phenol formaldehyde resin. DSC curve of cpf (Fig. 7) shows an endotherm in the temperature range of 100 to 250°C. This endothermic transition is due to the postcuring of the resin and it confirms the inference of postcuring in this temperature range from TG curves. Christiansen *et al*. observed an endothermic event in DTA curve in the temperature range of 139–151°C and attributed it to postcuring reactions in pf resin [27]. The mass loss in this event is due to the loss of water and formaldehyde. The formation of water and formaldehyde is a result of the condensation reaction of methylol groups. Methylol groups formed in the curing stage react in the post-curing stage to form methylene bridges and release formaldehyde and water. In the second mass loss event between 468 to 552°C, 24 mass% loss is observed. The mass loss progressively increases on increasing the temperature upto 600°C, beyond this temperature the rate of mass loss slows down. Conley has reported that one of the degradation routes for the phenolic resin system is through oxidation, regardless of the fact that the resin was exposed to elevated temperature in air, oxygen or nitrogen [23].

Figure 3 shows the TG curves of 10, 25, 35 and 50 mass% lignin substituted pf resin (lpf) and the cpf resins. It is observed that cpf shows mass loss of 8 mass% upto 200°C which is due to the liberation of water and formaldehyde. The mass loss at this temperature for bkl substituted pf resins, from 10 to 50 mass%, shows a constant mass loss of 6 mass% which is lower than cpf. The mass loss in 50 mass% bglpf, 50 mass% cblpf, and 50 mass% cclpf is respectively 12, 10 and 9%. These results show that different extent of polycondensation reaction of lignin with formaldehyde occurs depending upon the composition and structure of the former. In the case of lpf resin, two major thermal events are observed. First event is observed in the temperature range of 100 to 350°C and second in the temperature range of 400 to 550°C. Table 3 shows the T_i, T_f, and T_{max} temperature of the thermal events. Thermal stability curve of cpf and lpf show similar pattern of degradation upto 25 mass% lignin substitutions. The difference in mass loss between cpf and lpf resins is substantially high in case of 35 and 50 mass% of bkl substitution. Lpf resin with 10 mass% lignin loading show mass loss in the first event comparable to cpf. At 268°C, 15% mass loss was observed in the temperature range of 194 to 303°C, which is comparable to that of cpf. Beyond

Table 3 Thermal properties of cpf and lpf resins

Resin code	TG analysis								char residue at 700°C/%
	first thermal event				second thermal event				
	T_i/°C	T_{max}/°C	T_f/°C	mass loss/%	T_i/°C	T_{max}/°C	T_f/°C	mass loss/%	
cpf	124	190	242	15	468	503	552	24	61
10% bklpf	174	232	305	16	453	496	535	20	60
25% bklpf	194	268	303	16	484	503	365	21	58
35% bklpf	167	240	275	19	487	513	532	22	54
50% bklpf	214	267	291	25	374	393	484	24	50
50% cblpf	134	263	324	23	405	494	546	16	58
50% cclpf	192	264	341	18	345	378	545	18	54
50% bblpf	155	286	333	20	334	372	565	19	56

25 mass% lignin incorporation higher mass loss is observed in this thermal event. 25% mass loss was observed in the temperature range of 214 to 291°C for 50 mass% of lignin substituted pf resin. However, pf shows faster degradation upto 250°C in comparison to lpf resins. We attribute the initial thermal stability of lpf resins to delayed onset of curing due to steric hindrance. Mass loss in this event is a consequence of post curing of the system. The higher mass loss beyond 25 mass% lignin incorporation is a consequence of degradation of side chains present in the lignin molecules. The is further confirmed by TG analysis of bkl.

Figure 4 depicts the TG-DTG thermogram of bkl. The first thermal event is observed in the temperature range of 56 to 102°C with $T_{\max}$ at 76°C. 9% mass loss is observed in this event due to loss of moisture. Second thermal event starts at 206°C and ends at 254°C with $T_{\max}$ at 241°C resulting in 18% mass loss. The same is attributed to breakdown of side chains present in the lignin. The second thermal event starts at lower temperature for lpf resin but mass loss is comparable to cpf even at 50 mass% lignin loading. 24 mass% loss at 392°C is observed in the temperature range of 374 to 484°C as compared to 23% mass loss at 503°C in the range of 468 to 552°C for cpf. The latter is attributed to the breakdown of methylene linkage present in polymer backbone. Second mass loss event, where the mass loss is the same as in cpf, appears not to be effected by lignin substitution. This shows that mass loss in this event is purely due to breakdown of pf network.

It can be noticed that in the temperature range of 200 to 300°C for all bkl incorporated pf (bklpf) resin compositions, the mass loss is highest, 9–17 mass%. Loading of bkl upto 10–25 mass% produces thermal stability comparable to that of cpf. At 25 mass% loading of bkl mass loss in the resin is 9% while in cpfit is 12 mass%. Beyond, 25% bkl loading in the resin, mass loss increases. A 17% mass loss is observed for 50 mass% loading of bkl in this temperature range. The higher mass loss in this region is due to the degradation of lignin present in the resin. In the temperature range of 300 to 400°C, the mass loss in the bklpf is between 5–10%. In the above temperature region all bklpf resin composition show higher mass loss as compared to cpf, the mass loss being only 4% in the later resin. The foregoing observation is correlated to the breakdown of the side chains present in the lignin molecule. In the temperature range of 400 to 500°C, the mass loss in all bklpf compositions is comparable to that of cpf. This effect is found comparable with 25 mass% bklpff. Beyond 25 mass% loading of bkl, the mass% loss is found to be lower. In the region of 600 to 700°C, the mass loss in bklpf compositions is comparable to cpf up to 25 mass% loading of bkl in the pf resin in the temperature range of 500–600°C. From the study, it is noticed that the mass loss is higher for all bklpf resin compositions between 200–400°C but beyond 400°C, the mass loss is comparable to cpf. The difference in the thermal stability is due to the incorporation of lignin in the system.

The study indicates that thermal degradation of cpf and 25 mass% bklpf resin shows similar pattern. Beyond 25 mass% of bkl substitution, bklpf resin becomes less stable compared to cpf. Similar observations were made by O'Connor *et al.* and compared various alkyl substituted pf resin condensates with pf resin and found later more stable [32].

Effect of lignin source

Mechanical property

The effect of lignin source on the adhesive and shear strength of lpf adhesives have been studied at 50 mass% of lignin loading. Figure 5 shows the adhesive and shear strength of various lpf adhesives. The values of adhesive and shear strength for 50 mass% bglpf and bklpf resins are comparable. The better adhesive and shear strength of these resins results from better copolymerization of bgl and bkl with formaldehyde. On comparing the adhesive and shear strength of lpf adhesives with cpf can be inferred that bglpf and

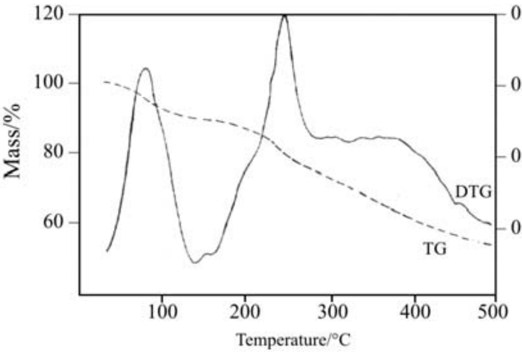

Fig. 4 TG–DTG curves of bark lignin

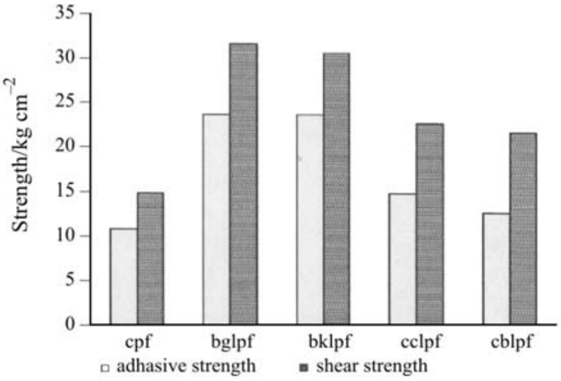

Fig. 5 Effect of lignin source on adhesive and shear strength

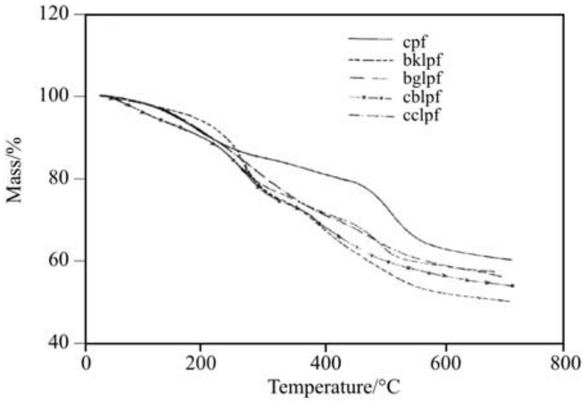

Fig. 6 TG curves of cpf and lpf resin

bklpf form denser three dimensional network structure giving rise to high molecular mass resin. This difference in the adhesive and shear strength with the difference in lignin source is caused by the difference in the structure of the lignins which pronouncely differ in the extent of guaiacyl and syringyl units along with other functional groups. As a result, they have different reactivity towards formaldehyde. A lignin having less steric hindrance will readily react and will produce better adhesive and shear strength.

Thermal property

Thermal stability curves of cpf and 50 mass% loaded bklpf, cclpf, cblpf and bglf resins are shown in Fig. 6. Analyses of the thermal events and char yield are presented in Table 3. In all the lpf resins two distinct decomposition events are observed. Bglpf resin shows mass loss of 23% at 263°C in the temperature range of 134 to 324°C whereas 18 mass% loss is observed at 264°C in the temperature range of 192 to 341°C for cclpf. In comparison to cpf, lpf shows higher mass loss in this event. This is attributed to the postcuring reaction and breakdown of side chains of lignin present in the system. The second mass loss event in case of lpf resins were observed in the temperature range of 350 to 565°C. The rate of mass loss increases on increasing the temperature gradually up to 600°C. 16% mass loss is observed at 494°C in the temperature range of 405 to 546°C for cblpf, whereas bklpf shows 24% mass loss at 393°C in the temperate range of 374 to 484°C. We attribute the stability of bglpf, cblpf and cclpf to greater network formation in the system. Lower mass loss in some of the lpf resins indicates higher cross-linking in these systems. The lower thermal stability of bklpf in this region results from the poor network formation in this case. Bkl is composed of guaiacyl and syringyl–guacacyl lignin unit. It has an additional –OCH_3 group at –C_5 position. Hence, stearic hindrance for network formation is more pronounced in this case and limits the prepolymer reaction with formaldehyde. It is the reason why lignin is chemically enhanced by phenol to improve reaction between lignin and formaldehyde [33]. However, bgl has more free –C_5 position for network formation. The three dimensional network structures in case of bglpf, cclpf and cblpf is more compact as compared to bklpf leading to higher stability in this region. In previous study, Hoareau *et al*. observed that bgl contains high *p*-hydroxyl propane units and does not incorporate methoxy groups in ortho position of the phenolic ring. So the reactivity with formaldehyde would be easier with bgl [34].

It can be noted that in the temperature range of 200 to 300°C for all compositions of different lpf resins, the mass loss is the highest (11–17 mass%) on the basis of mass% loss per 100°C. In case of 50% bglpf resin, the mass loss is only 7 mass%. This may be due to some structural difference in bgl with other lignins. In the temperature range of 300 to 400°C, the mass loss in the different resins with 50% loading of various lignins is between 8–9 mass%. Again, in case of 50% bglpf the mass loss is only 6%, which shows its structural difference from the other resin. In the temperature range of 400 to 500°C, different lpf resin of varying composition shows mass loss of 7–8%, almost similar to each other. In the temperature range of 500–600°C, the % mass loss for 50 mass% substituted lpf resin is less than in the temperature range of 400 to 500°C, maximum mass loss of 6 mass% is noted for 50% bklpf and minimum mass loss of 3 mass% is noted for 50% cblpf. It is noticed that after 500°C, mass% loss in the lpf resin composition decreases. The decomposition reaction is completed and only a mass loss of 2–4 mass% is recorded between 600–700°C.

To observe the curing behavior of cpf and lpf adhesive, DSC analysis was carried out. Figure 7 shows the DSC curves of cpf and lpf adhesives. Thermal transition in the temperature range of 85 to 140°C shows an endotherm, which is a consequence of curing in the system. The peak temperature (T_p), onset temperature (T_0) and ΔT (T_p–T_0) are presented in Table 4. ΔT is a measure of rate of curing. From the table, it is

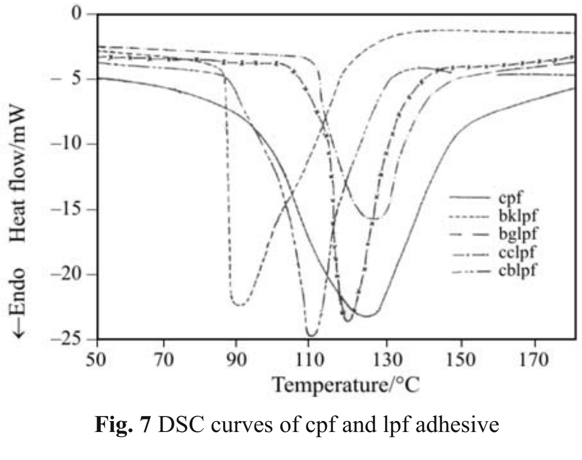

Fig. 7 DSC curves of cpf and lpf adhesive

Table 4 DSC analysis of cpf and lpf adhesives

S. No.	Resin type	T_p/°C	T_0/°C	$\Delta T=T_p-T_0$/°C
1	cpf	125	90	35
2	50% bklpf	92	85	7
3	50% bglpf	119	112	7
4	50% cclpf	123	105	18
5	50% cblpf	110	88	22

observed that in the cpf resin curing starts at a lower temperature but peak temperature is high. In cpf the ΔT value is 35°C in comparison to 7°C for bglpf and bklpf. lpf has low values of free –OH groups. The C, H and O analysis shows low free –OH groups in cclpf and cblpf; ΔT values in these cases are observed to be 18 and 22°C respectively. In bglpf and bklpf, free –OH group are large as observed earlier. Hence, ΔT is small. The higher value of ΔT in cpf shows a lower rate of curing. In all lpf resins, curing start at higher temperature but peak temperature is low. These results show higher rate of curing in lpf as compared to cpf. Higher rate of curing in lpf indicates that incorporation of lignin accelerates the curing in cpf resin. The higher onset temperature in lpf indicates some incubation time required for initiation of the curing. The difference in T_p is due to the diversity in lignin structure depending on source.

Conclusions

- Lpf resins with upto 50 mass% lignin incorporation show improved adhesive and shear strength as compared to cpf resin.
- The loading of lignin in pf resin affects the thermal stability of lpf beyond 25 mass% incorporation.
- Incorporation of lignin delays the start of first mass loss event whereas mass loss in the second event is influenced by the extent of lignin incorporation.
- Thermal stability differs depending on the source of lignin. The bglpf is thermally most stable whereas, bklpf is the least.
- Curing temperature of lpf resin is lower than cpf, whereas rate of curing is higher in lpf.

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