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Novel DCPD-modified polyester containing epoxy groups: thermal, viscoelastic, and mechanical properties of their wood flour filled copolymers

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Abstract In this article, the synthesis of novel DCPD-modified polyesters containing epoxy groups and their possible utilization as polar matrices for wood flour filled copolymers have been studied. The novel DCPD-modified polyester containing epoxy groups was prepared during three-step process. First, the addition reaction of maleic acid to DCPD norbonenyl double bond has been performed. Then, the polyesterification of acidic ester of DCPD, cyclohex-4-ene dicarboxylic anhydride, and ethylene glycol (ethane-1,2-diol, EG) or neopentyl glycol (2,2-dimethyl-1,3-propanediol, NP) in the presence of catalyst was carried out using melt condensation technique. Finally, the oxidation process of prepared DCPD-modified polyesters led to obtain DCPD-modified polyesters containing epoxy groups. The structural characterization of prepared DCPD-modified polyesters containing epoxy functionality has been carried out using FTIR and HNMR spectroscopic methods. The thermal, viscoelastic, and mechanical properties of their unfilled and wood flour filled copolymers have been studied by DSC, DMA, TGA analyses, three-point bending test, and Brinell's hardness. The performed investigations indicated that novel DCPD-modified polyesters containing epoxy groups can be successfully applied as polar matrices for preparation wood flour filled copolymers due to their "compatibility" with hydrophilic wood flour surface which resulted with stronger interactions between wood and polymer surface and thus producing copolymers which were characterized by improved thermo-mechanical properties compared to unfilled copolymers.

Keywords Dicyclopentadiene · Polyesters · Wood flour · Thermal properties · Mechanical properties

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Introduction

The properties of polyesters and their cured products largely depend on the nature of chemical structure of the starting resins. The incorporation of various types of moieties into the polyester backbone allows tailoring and preparation of various resins for different applications [1]. One of the compounds that can be widely applied as a comonomer for polyester synthesis is dicyclopentadiene (DCPD) due to their availability, low cost, and reactivity [2, 3].

DCPD is the Diels–Alder reaction dimmer of cyclopentadiene (CPD), their thermodynamically stable form at room temperature. This reagent is mainly obtained as a by-product in the olefin cracking process or during the synthesis of ethylene [3]. The difference in the reactivity between the norbornene and cyclopentene double bonds in DCPD allows preparing their derivatives which can be successfully used as an intermediate for various syntheses [4]. The addition reaction of various compounds, e.g., alcohols, phenols, glycols, mercaptans, di/carboxylic acids, or water preferentially at the norbornenyl double bond of DCPD without involvement of the markedly less reactive cyclopentene double bonds resulting in production of their ester derivatives and secondary alcohols [5, 6].

The principal methods of DCPD utilization for polyester modification include two methods depending on temperature. In the temperature range of 120–140 °C, the nucleophilic addition of carboxylic or hydroxylic groups from dicarboxylic acids or glycols to more reactive double bond of DCPD at the norbornenyl ring is mainly expected and thus led to obtain ester or ether derivatives of DCPD. However, at temperatures above 150 °C, the de-dimerization of DCPD to CPD and the addition of CPD to unsaturated double bonds in polyester chains results in obtaining cycloalkene structure in their backbone [7]. The ability to incorporate a large amount of bulky and highly aliphatic DCPD moiety into polyester structure allow preparing less expensive polyesters which are characterized by reduced shrinkage during cure [3]. In addition, DCPD and their based products can be easily chemically modified using hydrogen peroxide or peracids and thus forming their epoxy derivatives [8]. The resulting epoxides display high reactivity attributed to the high ring strain present in the epoxycyclopentenyl ring system. The chemically modified DCPD-based polymers possess excellent rigidity, mechanical strength, high thermal stability, electrical properties after curing, high dimensional stability, and highly resistant to ultraviolet light [6]. They are attractive materials for a wide industrial application such as paints, coatings, matrices, packing materials for printed circuit boards, outdoor applications, etc. [9–15].

In this article, the synthesis of novel DCPD-modified polyesters containing epoxy groups and their possible utilization as polar matrices for wood flour filled copolymers have been presented. The structural characterization of prepared DCPD-modified polyesters containing epoxy groups have been carried out using FTIR and HNMR spectroscopic methods. The thermal, viscoelastic, and mechanical properties of their unfilled and wood flour filled copolymers have been studied by DSC, DMA, TGA analyses, three-point bending test, and Brinell's hardness.

Experimental part

Materials

DCPD, maleic acid (MA), ethylene glycol (ethane-1,2-diol, EG), neopentyl glycol (2,2-dimethyl-1,3-propanediol, NP), cyclohex-4-ene-1,2-dicarboxylic anhydride (THPA), hexahydrophthalic anhydride (HHPA) and 40% peracetic acid were obtained from Merck-Schuchardt, Germany. Butylstannoic acid (catalyst) was from Arkema Inc., USA. Benzoyl peroxide (BPO) was supplied by Fluka, Switzerland. Styrene (ST), hydoquinon, and xylene were delivered by POCh, Poland.

Synthesis of DCPD-modified polyesters containing epoxy functionality

DCPD (1.07 mol), MA (1 mol), and hydroquinone (0.035 wt%) were placed into a 500 mL three-necked flask equipped with a mechanical stirrer, thermometer, and condenser. The mixture was heated to 135 °C, and stirred rigorously for a further 2 h maintained at this temperature, under reflux. The drop of an acid value to 226 mgKOH/g was an indicator of the process completion. In this stage, acidic ester of DCPD has been obtained (Step I, Scheme 1).

Then, after cooling, to the acidic ester (Stage I), ethylene glycol or neopentyl glycol (2.15 mol), cyclohex-4-ene-1,2-dicarboxylic anhydride (1.5 mol), and catalyst (0.52 g) were added. The reaction mixture was heated up to 150 °C for 1 h,
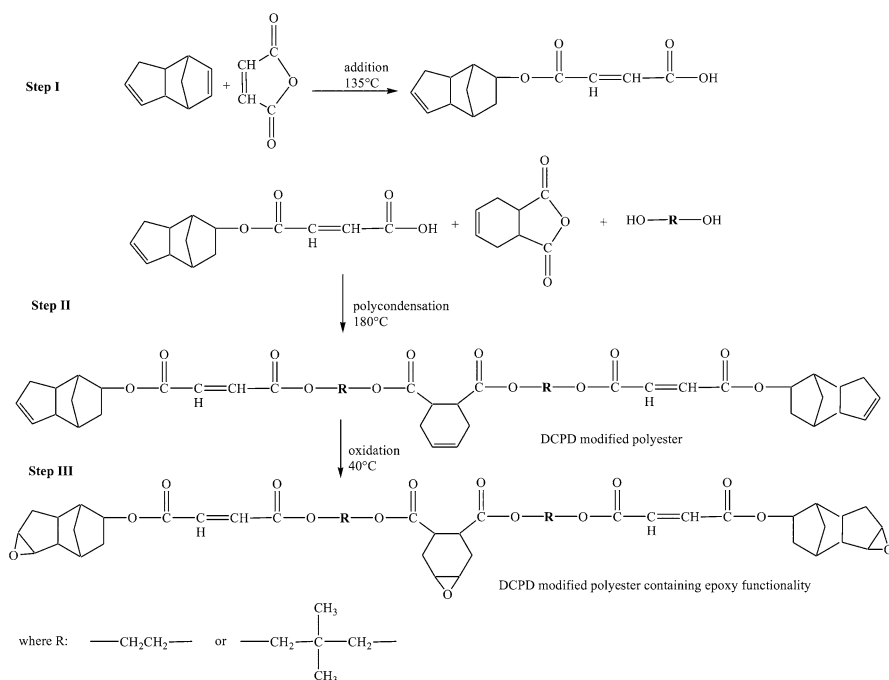
Scheme 1 The scheme of synthesis of novel DCPD-modified polyester containing epoxy groups

and then heated to 180 °C and maintained at this temperature until the drop of an acid value below 3 mgKOH/g. Acid value (mgKOH/g) defined as a number of mg KOH required for titration of 1 g of a sample was determined by titration method. During the reaction, water was removed continuously from the system by azotropic distillation (xylene). After that, xylene was distilled under reduced pressure, and the obtained product was identified, (Step II, Scheme 1).

The preparation of novel DCPD-modified polyesters containing epoxy groups was performed in three-necked flask equipped with a glass stirrer, thermometer, and an addition funnel. The DCPD-modified polyester (100 g) was placed in a three-necked flask dissolved in methylene chloride (200 mL) and heated up to 40 °C. Than, peracetic acid was slowly added dropwise under vigorous stirring over 1 h. The reaction mixture was then stirred rigorously for a further 3 h maintained at the reaction temperature. After cooling, the reactive mixture was washed with an aqueous solution of sodium carbonate to neutralization. Organic phase was thoroughly washed two times with distilled water, dried over anhydrous $MgSO_4$, and distilled under vacuum to remove solvent. Epoxy value (mol/100 g) of prepared novel polyesters determined by dioxane/HCl titration method was 0.35 and 0.33, respectively. The theoretical structure of novel DCPD-modified polyesters containing epoxy groups was presented in Scheme 1, Step III.

Characterization of novel DCPD-modified polyesters containing epoxy functionality

Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer 1725 X FTIR spectrophotometer in the 400–4000 cm^{-1} wavenumber range using KBr pellets.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an NMR Brucker-Avance 300 MSL (Germany) spectrometer at 300 MHz with deuterated chloroform ($CDCl_3$) as the solvent. ^{1}H NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference.

Preparation of copolymers

Wood flour filled copolymers were prepared by mixing novel DCPD-modified polyesters containing epoxy groups, styrene (20 wt%), BPO (1.0 wt%), a stoichiometric ratio of an HHPA, and different amounts of 1, 5, 10, 20, 40, and 60 wt% of unmodified wood flour filler dried in a vacuum oven at 70 °C to remove moisture before making copolymers. To compare the studied properties, samples of unfilled copolymers as well as filled with alkali-treated (10% NaOH for 2 h) wood flour filler (20 wt%) were prepared for the investigations. All components were mixed together, heated to 40 °C, and stirred for about 1 h with the assistance of mechanical stirrer to obtain uniform dispersion. All the compositions (pastes) were placed in a glass mold under vacuum at 50 °C for degassing, cured at 80 °C for 6 h, and then post-cured in an oven over 6 h at 140–150 °C.

Characterization of copolymers

Thermogravimetric analysis (TGA) was carried out on a MOM 3427 derivatograph Paulik and Erdey (Hungary) at a heating rate of 10 °C/min in air in the temperature range of 20–1000 °C with the sample weight of 10 mg. α-Al_2O_3 was used as a reference. The initial decomposition temperature (IDT), the temperature of the maximum rate of weight loss (T_{max}), and the final decomposition temperature (FDT) were determined.

DMA measurements were performed using Dynamic Mechanical Analyzer (DMA) Q 800 TA Instruments (USA). Tests were conducted with a double Cantilever device with a support span of 35 mm, calibrated according to the producer's recommendation. Temperature scanning from room temperature until the sample become too soft to be tested with a constant heating rate of 4 °C/min at an oscillation frequency of 10 Hz was performed. Rectangular samples of 10-mm wide and 4-mm thick were used. Dynamic mechanical properties were estimated from the changes of storage modulus (E'), mechanical loss (E'') as well as from the changes of $\tan\delta$ at constant frequency depending on temperature. Glass transition temperature (α-relaxation) was taken as the maximum of the $\tan\delta$ versus temperature curves.

Flexural properties were measured in a three-point bending test using a Zwick/Roell Strength Machine (model Z010, Germany). The specimen dimensions were 10-mm wide and 4-mm thick. The measurements were carried out at room temperature with a crosshead speed of 2 mm/min using a support span of 64 mm. At least five specimens were tested for each sample to evaluate flexural properties. The flexural modulus at bending (E_{mod}), deflection at maximum force (ε-F_{max}), and flexural stress (σ) were qualified.

Hardness according to Brinell was determined by means of a hardness tester HPK and calculated based on following equation: HK [MPa] $= F_1 * 0.098066$, where F_1 is a strength of pressure under definite load.

Results and discussion

Characterization of novel DCPD-modified polyesters containing epoxy groups

The novel DCPD-modified polyesters containing epoxy groups were characterized by FTIR and ^{1}H NMR. The presence of absorption peaks at 781–835 cm^{-1} characteristic for oxirane ring vibration groups at cycloaliphatic rings are clearly observed. In addition, the presence of absorption signals at 985–990 cm^{-1} (–CH=CH wagging of maleic anhydride) and 1646–1648 cm^{-1} (C=C stretching vibration for carbon–carbon double bonds of maleic anhydride) was indicated, which confirmed the presence of carbon–carbon double bonds (*cis–trans* units) in the structure of DCPD-modified polyesters containing epoxy groups, Fig. 1.

The exemplary ^{1}H NMR spectrum of DCPD-modified polyester containing epoxy groups was shown in Fig. 2. The corresponding proton signals at 6.30–6.35 and 6.90–6.95 ppm were due to carbon–carbon double bonds (*cis–trans* units of
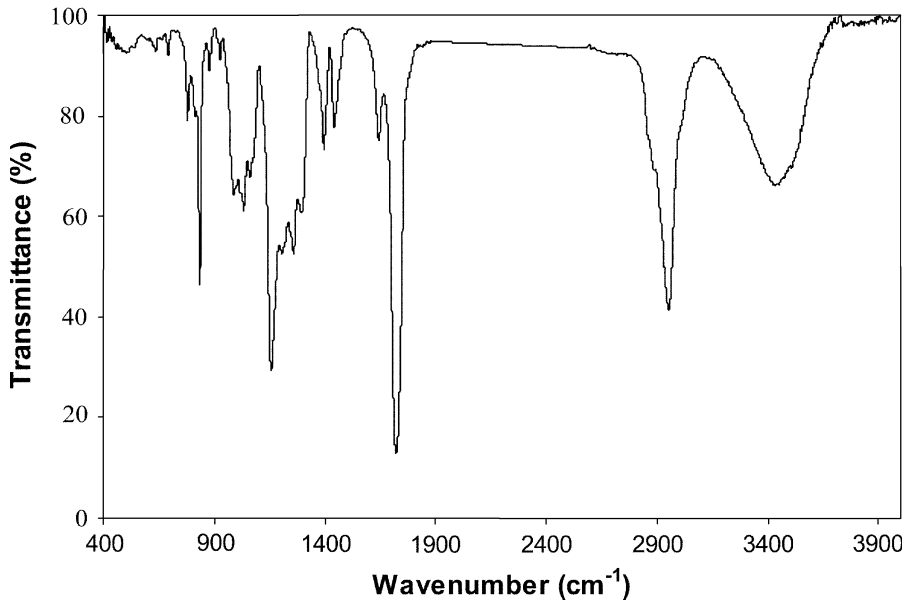
Fig. 1 FTIR spectra of novel DCPD-modified polyester containing epoxy groups

maleic anhydride). The chemical shifts of the protons in surroundings of epoxy groups $\delta = 3.2–3.5$ were clearly observed.

Characterization of copolymers

The data obtained from DMA curves for prepared untreated, alkali-treated wood flour filled copolymers as well as unfilled copolymers are presented in Tables 1 and 2. In addition, the variation of the loss modulus (E'') and the tanδ of unfilled copolymers and different amounts of wood flour filled copolymers (1–60 wt%) and alkali-treated wood flour filled copolymers are shown in Fig. 3. Based on visible results, the values of storage modulus ($E'_{20\ °C}$) increased with the increase of wood flour filler content (1–40 wt%) in copolymers compared to unfilled copolymers, Tables 1 and 2.
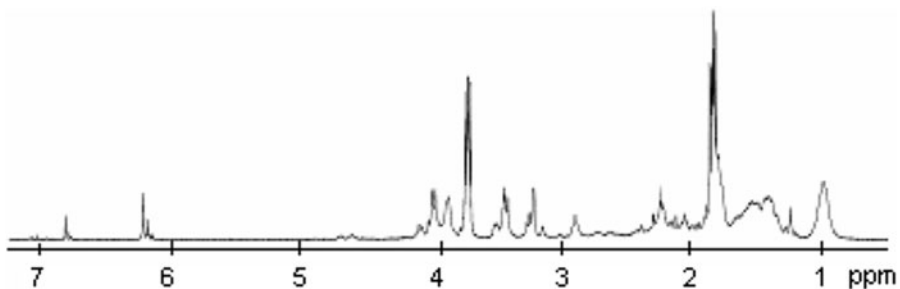

Fig. 2 ^{1}H NMR spectra of novel DCPD-modified polyester containing epoxy groups

Table 1 Data obtained from DMA curves for wood flour filled copolymers (EG)

No	Wood flour content/wt%	$E'_{20\,°C}$/MPa	E''_{max1}/°C	E''_{max1}/MPa	E''_{max2}/°C	E''_{max2}/MPa	$Tan\delta_{max1}$/°C	$Tan\delta_{max1}$/MPa	$Tan\delta_{max2}$/°C	$Tan\delta_{max2}$/MPa
0	0	2700	110.0	222.8	–	–	129.1	0.306	–	–
1	1	2750	110.5	231.2	169.8	21.6	129.5	0.300	190.0	0.043
2	5	2780	110.8	243.3	172.4	23.7	130.3	0.294	189.5	0.051
3	10	2840	111.6	250.6	174.9	31.8	134.6	0.252	192.4	0.062
4	20	2990	111.6	268.9	175.3	40.4	137.6	0.184	193.8	0.076
5	40	3500	115.0	277.2	176.8	57.6	139.8	0.173	187.5	0.077
6	60	1600	111.3	268.9	165.7	85.1	130.2	0.334	180.6	0.096
7	20[a]	3840	115.4	315.4	170.0	106.4	140.3	0.166	190.3	0.076

[a] Alkali-treated wood flour

Table 2 Data obtained from DMA curves for wood flour filled copolymers (NP)

| No	Wood flour content/wt%	$E'_{20\,°C}$/MPa	E''_{max1}/°C	E''_{max1}/MPa	E''_{max2}/°C	E''_{max2}/MPa	$Tan\delta_{max1}$/°C	$Tan\delta_{max1}$/MPa	$Tan\delta_{max2}$/°C	$Tan\delta_{max2}$/MPa
0	0	2820	118.0	220.3	–	–	135.6	0.295	–	–
1	1	2820	118.2	230.0	172.5	21.4	135.4	0.290	190.3	0.041
2	5	2850	118.1	241.8	171.3	24.2	132.6	0.285	190.7	0.050
3	10	2960	120.4	248.5	175.5	32.8	138.9	0.210	193.2	0.061
4	20	3150	121.5	265.2	177.9	39.7	140.3	0.175	193.5	0.074
5	40	3730	129.2	278.1	178.3	57.1	142.5	0.168	188.3	0.075
6	60	1380	121.3	270.5	163.4	89.2	131.9	0.357	181.0	0.096
7	20[a]	3980	132.8	314.8	170.5	103.8	145.8	0.151	191.2	0.074

[a] Alkali-treated wood flour
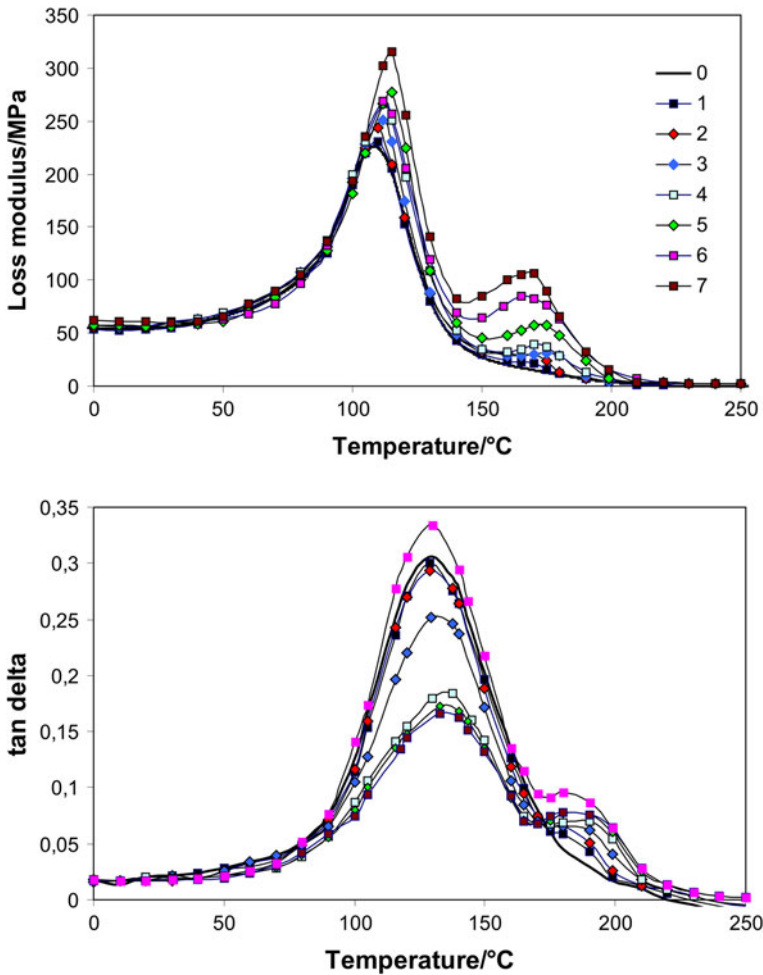
Fig. 3 The variation of the loss modulus (E'') and the tanδ of the (*0*) unfilled resin, (*1*) 1% WF, (*2*) 5% WF, (*3*) 10% WF, (*4*) 20% WF, (*5*) 40% WF, (*6*) 60% WF, and (*7*) 20% alkali-treated WF (*WF* wood flour)

However, for copolymers containing 60 wt% of wood flour filler significant fall of $E'_{20\ °C}$ values were observed. It indicated that the use of wood flour filler at 1–40 wt% content acted as a reinforcement which allowed obtaining stiffer materials probably due to the greater stress transfer at the interface by the wood flour particles. On the contrary, the tendency to agglomeration of wood flour particles used at higher content resulted in dimensional instability and thus poor mechanical properties of the copolymers. Moreover, the $E'_{20\ °C}$ values of alkali-treated wood flour filled copolymers were higher than that of untreated wood flour filled copolymers. It could be connected with the improvement of interfacial adhesion between wood flour particles and novel DCPD-modified polyesters containing epoxy groups (matrices) due to the formation of additional hydrophilic groups (hydroxyl groups) on the

particles surface as well as due to the formation more rough surface of the filler [16]. The increase in hydrophilic nature of wood flour particles makes the filler more compatible with more polar matrices. Also, the rough surface improves the mechanical interlocking of the polyester molecules with the filler as well as the adhesion between filler and matrix. As a result of those, the interfacial interaction between those two components increases due to the formation of hydrogen bonding with hydroxyl groups of the filler and the hydroxyl, carboxyl, ester, or epoxy groups present in the novel DCPD-modified polyesters containing epoxy groups.

The one loss modulus peak (E''_{max1}) as well as $\tan\delta_{max1}$ for unfilled copolymers was indicated, respectively. This peak was attributed to the mobility of the resin molecules [17]. In the wood flour filled copolymers, the position of E''_{max1} and $\tan\delta_{max1}$ was almost independent of the wood flour content. However, $\tan\delta_{max1}$ height was drastically decreased with increasing filler content in copolymers compared to unfilled copolymers. The $\tan\delta_{max1}$ height of the unfilled copolymers was due to the deformation of the resin molecules between the cross links on application of stress. However, the incorporation of the reinforcing filler significantly restricted the mobility of the polyesters molecules in prepared copolymers and thus raised the $E'_{20\ °C}$ values and reduced the $\tan\delta_{max1}$ height, which probably indicated on the effective incorporation of the reinforcing filler into polymer matrix leading to formation of a stronger bond at the interface and thus increasing the relative thickness of the bonded interface [18–20].

In addition, at higher temperature, a small hump only for wood flour filled copolymers was observed, Fig. 3. This hump became more prominent and broader with the increase of wood flour filler content in the copolymers and thus probably connected with cellulose component, their glass transition temperature, which was nearly 200 °C according to literature data [21, 22].

The glass transition temperature (described as $\tan\delta_{max1}$) of the wood flour filled copolymers was found to have imperceptibly shifted to higher temperatures with increase in wood flour loading up to 40 wt%. Also, the increase in $\tan\delta_{max1}$ for alkali-treated wood flour filled copolymers was indicated. It may be attributed to better interfacial interactions in alkali-treated filled copolymers, which significantly decreased the polymer chain mobility, Tables 1 and 2.

Thermal decomposition (IDT) of wood flour filled copolymers started at higher temperatures (about 10–50 °C higher) than that of neat wood flour filler (240 °C), Tables 3 and 4. Also, the results showed that there was a shift to higher temperatures of the peak that correspond to the main degradation process of the wood flour component (T_{max1}). This observation could indicate on stronger interactions between more polar matrices and wood flour component by creating intermolecular bonding between components and thus the presence of polymer matrices protected the filler delaying its degradation [23].

The thermal degradation pattern of unfilled copolymers exhibited two almost separated degradation steps, with two maximum rate peaks (T_{max}) at 375–380 and 575 °C, which were directly associated with the ester/ether and carbon–carbon bonds breakdown formed in copolymers structure during cure [24]. However, wood flour filler as well as wood flour filled copolymers undergoes a complex degradation scheme due to their composition. As it is generally known, wood flour is composed

Table 3 Data obtained from TGA analysis for wood filled copolymers (EG)

Wood flour content/wt%	IDT/°C	T_{max0}/°C	T_{max1}/°C	T_{max2}/°C	FDT/°C
0	280	–	380	575	635
1	280	90	335/385	575	635
5	275	95	335/385	570	630
10	275	90	350/390	560	630
20	270	100	345/385	560	630
40	260	95	345/380	550	635
60	250	100	330/375	550	630
20[a]	255	110	360/390	565	635
Wood flour	240	90	320	510	600

[a] Alkali-treated wood flour

Table 4 Data obtained from TGA analysis for wood filled copolymers (NP)

Wood flour content/wt%	IDT/°C	T_{max0}/°C	T_{max1}/°C	T_{max2}/°C	FDT/°C
0	290	–	375	575	640
1	290	90	330/375	570	640
5	280	90	335/380	570	630
10	275	90	355/380	570	630
20	275	95	345/380	565	635
40	270	95	345/385	560	635
60	250	100	335/385	550	630
20[a]	260	100	350/380	560	630
Wood flour	240	90	320	510	600

[a] Alkali-treated wood flour

Table 5 Mechanical properties of wood flour filled copolymers (EG)

Wood flour content/wt%	E_{mod}/GPa	$\varepsilon\text{-}F_{max}$/%	σ/MPa	HK/MPa
0	2.8	2.40	78.2	127
1	2.8	2.34	75.4	129
5	2.9	2.15	77.2	131
10	3.2	2.03	80.3	136
20	3.5	1.80	85.8	143
40	3.9	1.52	92.6	164
60	1.8	0.60	15.4	90
20[a]	4.0	1.22	102.1	169

[a] Alkali-treated wood flour

mainly by three polymers: cellulose, hemicellulose, and lignin and thus each of those polymers has own characteristic thermal degradation properties [25–27]. Three degradation steps for wood flour filled copolymers were observed, which was directly connected with the presence of the filler, Tables 3 and 4.

Table 6 Mechanical properties of wood flour filled copolymers (NP)

Wood flour content/wt%	E_{mod}/GPa	$\varepsilon\text{-}F_{max}$/%	σ/MPa	HK/MPa
0	2.9	2.20	80.5	135
1	2.8	2.28	82.2	138
5	2.9	2.25	80.5	139
10	3.3	2.00	85.2	145
20	3.4	1.60	90.5	156
40	4.1	1.45	94.8	168
60	1.5	0.35	18.2	86
20[a]	4.1	1.18	106.0	174

[a] Alkali-treated wood flour

Also, the mechanical studies confirmed earlier observations, Tables 5 and 6. Wood flour filled copolymers containing 1–40 wt% of the filler were characterized by higher flexural modulus at bending (E_{mod}), flexural stress (σ) as well as Brinell's hardness (HK) values comparing to unfilled copolymers. The increase in mechanical properties was more distinctive at higher wood flour content copolymers. It confirmed the reinforcement effect of wood flour due to the compatibility between hydrophilic surface components: filler–polyester and thus produced more stiff materials. However, the tendency to agglomeration of wood flour particles used at higher content (60 wt%) probably resulted in dimensional instability and thus decreased E_{mod}, σ, and HK values resulting in poor mechanical properties of prepared copolymers.

Conclusion

The synthesis of novel DCPD-modified polyesters containing epoxy groups and their possible utilization as polar matrices for wood flour filled copolymers have been presented. The performed studies indicated that novel DCPD-modified polyesters containing epoxy groups can be successfully synthesized in three-step process: addition, polyesterification, and oxidation process. The novel materials can be applied as a potential polar matrices for preparation of wood flour filled copolymers due to their "compatibility" with hydrophilic wood flour surface which resulted with stronger interactions between wood and polymer surface and thus producing copolymers which were characterized by improved thermal and mechanical properties compared to unfilled copolymers which was confirmed based on DSC, TGA, DMA analyses, and mechanical test: three-point bending test and Brinell's hardness.

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