

Preparation, Characterization and Properties of Cellulose Diacetate/Poly(caprolactone)diol Graft Copolymer

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Graft copolymer of poly(caprolactone)diol (PCL) and cellulose diacetate (CDA) was successfully synthesized by two-step reactions. The isocyanate-terminated precursor (NCOPCL) was firstly prepared, and then the NCOPCL was grafted onto cellulose diacetate. The graft copolymer was characterized by FT-infrared spectroscopy, ¹H NMR, ¹³C NMR, SEM and DSC. The results showed that PCL was connected to CDA by chemical bonding and the properties of CDA-g-PCL were changed along with the structure. The possible synthetic mechanism for the reaction of PCL graft with CDA was also suggested preliminarily.

Key Words: Cellulose diacetate, Graft copolymerization, Structure characterization, Poly(caprolactone)diol.

INTRODUCTION

Cellulose diacetate (CDA) is one of the most important type of organic cellulose esters¹⁻³. Owing to its strength, toughness and biodegradation⁴, CDA has been widely used in many areas, such as textile, film membrane separation, plastic, paints and so on. Cellulose diacetate can be dissolved in acetone, chloroform, *etc.* which is accessible to homogeneous reaction. But the high flow temperature possessed by CDA results in a constraint on its processing properties. Several techniques have been developed to reduce its flow temperature⁵. The traditional method of adding external plasticizer is not satisfied in application because of the plasticizer's exudation and decomposition problems. So graft modification of CDA becomes an important way to reduce its flow temperature^{6,7}. Poly(caprolactone)diol (PCL) is a type of aliphatic polyester and has ester bonds in molecular structure, which can be easily hydrolyzed^{8,9}. Through graft modification of CDA with PCL, the resulted graft copolymer can reduce significantly the flow temperature of CDA and improve mechanical processing properties while maintaining good biocompatibility and biodegradation of CDA. So far, some work of the modification of CDA has been reported in the literature¹⁰⁻¹², but there is little study of grafting PCL onto CDA through isocyanate group.

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In this work, 4,4'-diphenylene methane diisocyanate (MDI) was used as graft bridge, the PCL was introduced onto CDA to get a graft copolymer (CDA-g-PCL). The structure of the CDA-g-PCL copolymer was analyzed and its properties were investigated.

EXPERIMENTAL

Cellulose diacetate (CDA) with a degree of substitution (DS) of 2.0 was supplied by Ruitai Cellulose Co. Ltd. (Shandong, China) and dried at 50 °C under vacuum before use. Poly (caprolactone) diol with an average molecular mass 2000 was supplied by Acros Organics Co. and was dried under vacuum before use. Dibutyltin dilaurate (DBTDL, Fluka Company, $\geq 90.0\%$), 4,4'-diphenylene methane diisocyanate (MDI, AR, Shanghai Medical Chemical Reagent, China), 1,4-butanediol (BDO, CP Shanghai Medical Chemical Reagent, China and was used after vacuum distillation), acetone (AR, Huadong Pharmaceutical Co., Ltd, HangZhou, China), chloroform (AR, Huadong Pharmaceutical Co., Ltd) and petroleum ether (AR, Huadong Pharmaceutical Co., Ltd, HangZhou, China) were used as received. Other chemical reagents were analytically pure.

Graft copolymerization of cellulose diacetate with poly (caprolactone) diol:

The experimental installation was under water-free and oxygen-free condition, 18 g (0.072 mol) MDI was placed in a four-necked flask with the protection of nitrogen, the temperature was raised to 80 °C, 0.05 mL dibutyltin dilaurate was titrated into this vessel by stirring. Then, 30 mL acetone containing 20 g (0.01 mol) of PCL was added, the reaction was kept 1 h at 80 °C, 3.42 g (0.038 mol) 1,4-butanediol was added and the reaction was continued for 3 h at 90 °C until the colour of solution turned golden yellow. After cooling slowly, the reaction product was precipitated in petroleum ether and then washed three times with petroleum ether for the removal of unreacted reactant. The precursor NCOPCLA (NCO/OH ratio is 1.5) was obtained after petroleum ether was volatilized at 50 °C in vacuum.

Under water-free and oxygen-free condition, 1.5 g of dried CDA and 30 mL of acetone were placed in a reaction flask equipped with an oil bath and a viscous solution was obtained. Then 1.0 g of NCOPCLA was added and the reaction began at 100 °C. The grafting reaction continued for about 7 h, the solvent was removed thoroughly and the crude product was obtained. Then, the crude product was extracted in chloroform and acetone with Soxhlet extractor for 24 h, respectively to remove the residual raw materials and NCOPCLA. The graft copolymer (CDA-g-PCL) was finally obtained after completely drying. The grafting ratio (G %) and graft efficiency ($G_E\%$) were calculated, respectively.

Characterization of graft copolymer with IR and NMR: The Fourier transform infrared (FTIR) spectra was measured with a spectrophotometer (Prestige-21, Shimadzu, Japan), using KBr pellets in the range 4000-500 cm^{-1} .

The ^1H NMR and ^{13}C NMR spectra of CDA and CDA-g-PCL samples were measured by using a Bruker DRX 400 NMR apparatus at 298.16 K. The solvent

used was $(\text{CD}_3)_2\text{CO}$ and the internal standard was tetramethylsilane. The pulse width was $11.0 \mu\text{s}$ for ^{1}H and about 10,000 (^{13}C) scans.

Thermal properties: The thermal behaviours were measured by means of thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC, Sta 409 PC, Netzsch, Germany). The starting and terminating temperature was 25°C and 600°C , respectively. The heating rate was $10^\circ\text{C}\cdot\text{min}^{-1}$ and test was performed under a dried nitrogen stream. The weighed amounts of samples were 8-10 mg.

Morphological characteristics and X-ray diffraction of CDA and CDA-g-PCL: The morphology of the pure CDA and CDA-g-PCL were examined by scanning electron microscope (SEM, SS-550, Shimadzu, Japan), the resolution was 3.5 nm and acceleration voltage set at 30 KV. X-ray diffraction analyses were carried out using a XRD 6000 (Shimadzu, Japan) wide angle X-ray diffraction (WAXD) spectrometer in the range of $2\theta = 4-60^\circ$ with nickel-filtered $\text{CuK}\alpha$ ($\lambda = 1.5405 \times 10^{-10} \text{ m}$) radiation at 40 KV and 30 mA. The scanning rate was 4° min^{-1} .

RESULTS AND DISCUSSION

Graft copolymerization: Fig. 1 shows the chemical structure of cellulose diacetate (CDA).

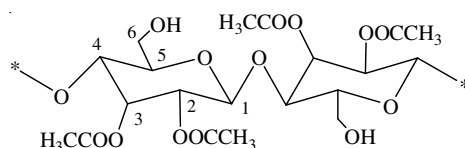


Fig. 1. Chemical structure of cellulose diacetate (CDA)

In general, isocyanates can easily react with poly (caprolactone) diol, the precursor NCOPCLA was produced, as shown in Fig. 2. The end unreacted $-\text{N}=\text{C}=\text{O}$ group can thus be reacted with CDA. The reaction process is also showed as Fig. 2. The grafting ratio (G) and graft efficiency ($G_E\%$) were calculated by the following equations:

$$G \% = \frac{(W_2 - W_1)}{W_0} \times 100 \quad (1)$$

$$G \% = \frac{(W_2 - W_0)}{(W_1 - W_0)} \times 100 \quad (2)$$

where W_0 , W_1 and W_2 are the weights of CDA, crude and pure graft polymer, respectively. The grafting ratio (G) and graft efficiency ($G_E\%$) were 37.4 % and 29.4 %, respectively.

Fourier transform infrared spectroscopy: FT-infrared is of importance to the study of the molecular structure. The width and intensity of spectral bands as well as position of the peaks are all sensitive to environmental changes and to conformations of macromolecules on the molecular level. Fig. 3 shows the infrared spectra for the reactants and product. The FTIR spectrum of PCL shows a strong hydroxyl peak at 3338 cm^{-1} and a sharp peak at 1720 cm^{-1} for the internal ester groups. The band in the region of 1413 cm^{-1} is attributed to the $-\text{CH}_2-$ group. For

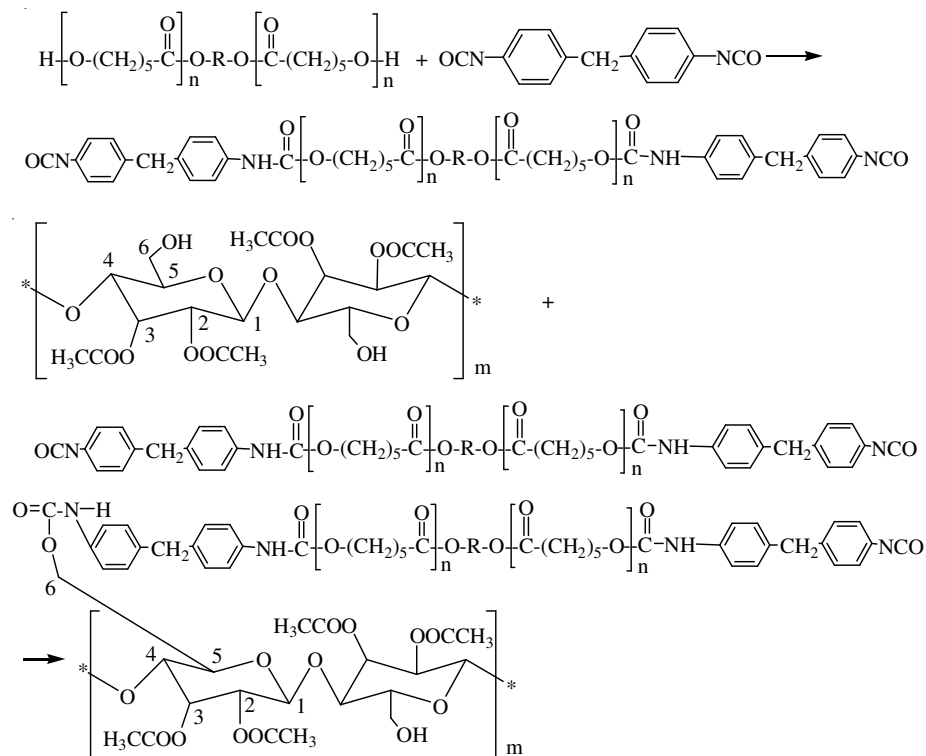


Fig. 2. Synthesis reaction scheme of CDA-g-PCL

CDA, the band around 1725 cm^{-1} is attributed to $-\text{C}=\text{O}$, 1341 cm^{-1} is due to methyl group and 1060 cm^{-1} represents the cyclic ether of cellulose. By grafting PCL onto CDA, the FTIR spectrum of CDA-g-PCL shows new peaks at 1726 cm^{-1} for the internal ester linkage, at 1533 cm^{-1} for the amide NH group (bond II) and at 1598 cm^{-1} for the aromatic ring from MDI.

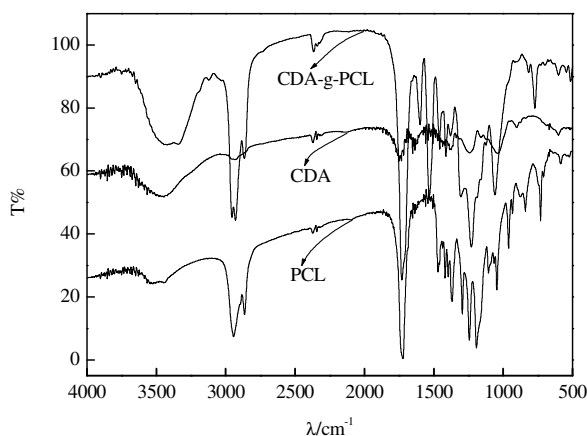


Fig. 3. FTIR spectra of CDA-g-PCL

It can be also found that the small shift of characteristic peaks for product has been observed comparing with that of the reactant, which suggests that the bond formation takes place between PCL and CDA and the functional group has been influenced by its chemical surroundings^{13,14}.

¹H NMR spectroscopy: Proton NMR spectroscopy is one of the most powerful tools for the quantitative analysis on the polymer microstructure. ¹H NMR analyses were carried out with a Bruker DMX 400 Hz spectrometer in (CD₃)₂CO. As shown in Fig. 4, the proton nuclear magnetic resonance spectroscopy (¹H NMR) spectrum of CDA shows methyl hydrogen of ester from cellulose diacetate at around 1.87-1.92 ppm and the -OH group hydrogen at around 2.48 ppm. Signals at 1.97-2.04 ppm are due to residual H for (CD₃)₂CO molecule and the peak around 2.78 ppm due to H₂O signal in dissolvent (CD₃)₂CO¹⁵. One broad signal at 3.41-3.58 ppm is due to C₄ and C₅ protons of cellulose ring, the presence of 3.70-3.89 ppm are attributed to C₆ protons, the peak of 4.11-4.38 ppm represents C₂ and C₃ protons and the peak at 4.67-5.01 ppm is due to C₁ protons, respectively¹².

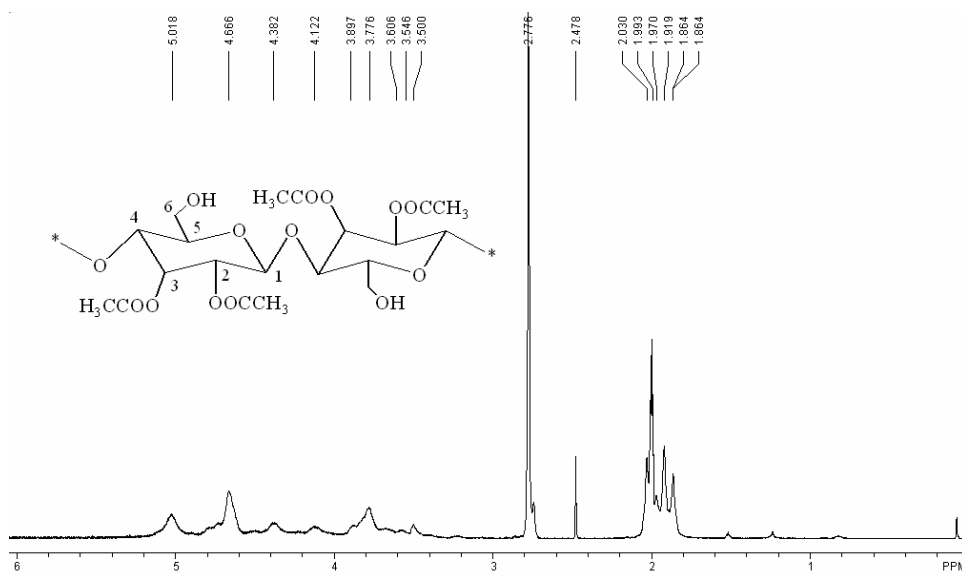


Fig. 4. ¹H NMR spectra of CDA

The ¹H NMR spectrum of CDA-g-PCLA was recorded in Fig. 5. The multiple peaks at 1.27-1.60 ppm were originated from methylene of PCL. Signals at 1.99-2.04 ppm are due to residual H for (CD₃)₂CO molecule and the peak around 2.79 ppm for H₂O signal in dissolvent (CD₃)₂CO. The triple peaks at 2.26 ppm are attributed to methylene linked carbonyl (α -position), around 2.48 ppm for end -OH group (one-end closed product between PCL and MDI) and the resonance at 3.82 ppm for the methylene of MDI. As shown in Fig. 5, the ¹H NMR spectrum of CDA-g-PCL also shows 1.86-1.92 ppm for the methyl hydrogen of ester from cellulose diacetate,

3.45-3.65 ppm (multiple peaks) for C₄, C₅ protons of cellulose ring and the end methylene of PCL (ϵ -position), 3.92-4.15 ppm (multiple peaks) for C₂, C₃ and C₆ protons of cellulose ring, resonance at 4.66 ppm for the C₁ protons of cellulose ring. CDA-g-PCL shows signals at 7.06-7.41 ppm which are attributed to the proton of benzene ring, signals at 8.47 ppm for -N-H, signals at 1.35 ppm for γ -position methylene proton (multiple peaks) and overlapping signals at 1.60 ppm for β -, δ -position methylene protons (multiple peaks)^{16,17}. The ¹H NMR spectrum confirms the grafting of PCL onto CDA.

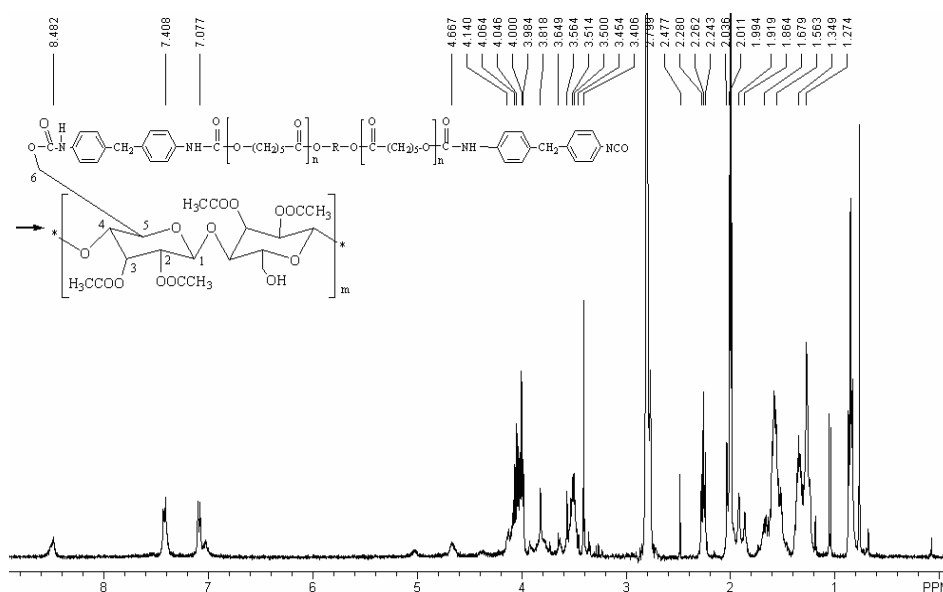
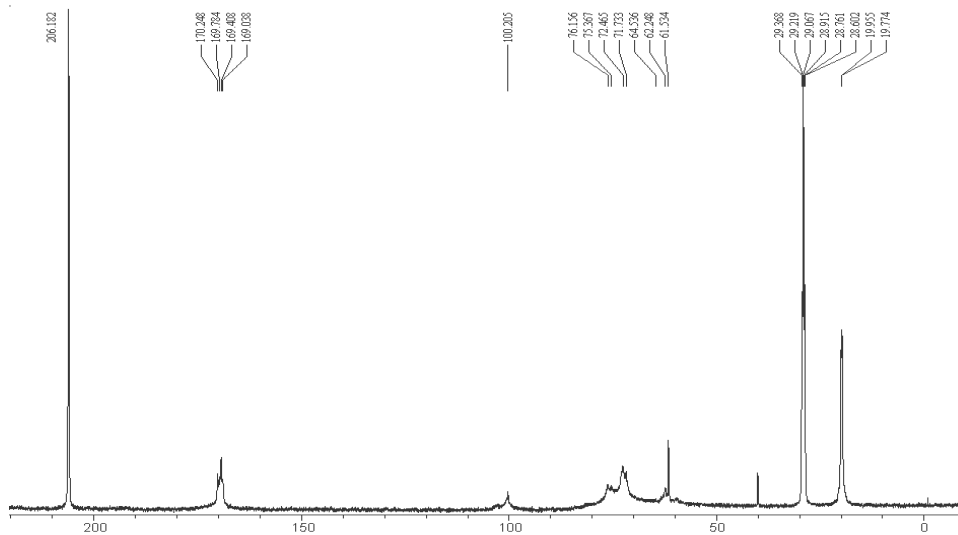
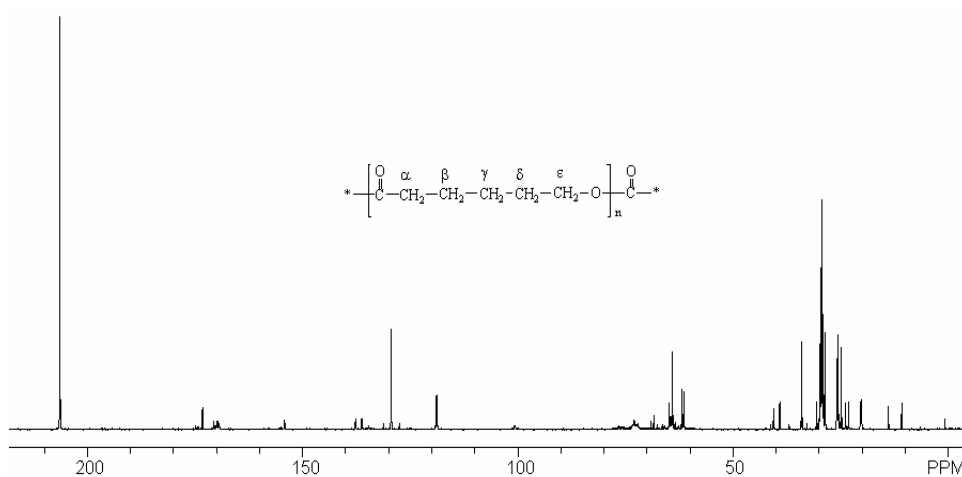


Fig. 5. ¹H NMR spectra of CDA-g-PCL

¹³C NMR spectroscopy: The ¹³C NMR spectrum of CDA is shown in Fig. 6. ¹³C NMR analyses were also carried out with a Bruker DMX 400-Hz spectrometer in (CD₃)₂CO and subtle molecular characteristics could be observed by comparing with ¹H NMR^{18,19}. The methyl carbon signal of cellulose diacetate are at 28.6-29.4 ppm, the C₆ carbon signals of cellulose ring can be observed at 61.5-64.5 ppm, carbon signal at 71.7 ppm for C₂ of cellulose ring, carbon signal at 72.5 ppm for C₃ of cellulose ring, carbon signal at 75.4 ppm for C₅ of cellulose ring, carbon signal at 76.1 ppm for C₄ of cellulose ring, carbon signal at 100.2 ppm for C₁ of cellulose ring, respectively. The carbonyl carbon signals of the acetyl for CDA are at 169.0-169.8 ppm and 170.2 ppm. At the same time, the signals in the position 19.8 ppm, 20.0 ppm and 206.2 ppm are well assigned to solvent peaks (CD₃)₂CO.

The ¹³C NMR spectrum of CDA-g-PCL is shown in Fig. 7. The more detailed signals appear except from CDA and the methylene carbon signals in the PCL structure (α , β , γ , δ and ϵ) can be observed. The γ -position carbon signals of grafting

Fig. 6. ^{13}C NMR spectra of CDAFig. 7. ^{13}C NMR spectra of CDA-g-PCL

poly (caprolactone) diol onto CDA can be observed at 30.5 ppm (a new peak), the carbon signal in the α -position of grafting PCL appears at 34.0 ppm, the carbon signal in the ϵ -position of grafting PCL appears at 64.0 ppm. It is also noted that the methylene proton signals in the β -position and δ -position of PCL overlap (multiplets), but the methylene carbon signals in the same position are well separated and can be observed two distinguishable peaks at 24.8 ppm (δ -position) and 25.7 ppm (β -position), respectively. The ^{13}C NMR spectrum of CDA-g-PCL also shows resonance at 118.9 ppm for the carbon signal of benzene ring, the chemical shifts at 129.4 ppm can be easily assigned to carbonyl carbon of the end $-\text{NCO}$ group and resonance at 154.2-154.9 ppm for the carbonyl carbon of carbamate group. In addition,

the chemical shifts at 169.4-174.8 ppm for carbonyl carbon were appeared clearly, suggesting that the grafting reaction occurred between NCOPCL (the isocyanate-terminated intermediate, by introducing NCO groups onto the PCL terminal) and CDA and new bond generated and linked to CDA backbone chain. The ^{13}C NMR spectrum further confirms the grafting of PCL onto CDA by carbamate group^{12,20,21}.

Thermal properties

Thermogravimetric analysis (TGA) is an important method for thermal characteristics of polymer at the present time and it is of momentous significance to processing and forming and thermal stability of polymer materials. The test of thermogravimetry of cellulose diacetate (CDA) and its grafting product were, respectively preceded in the N_2 atmosphere. Fig. 8 shows the thermogravimetric curve and measured data were listed in the Table-1. According to the differential thermogravimetry (DTG) curve, its initial weight-losing temperature (T_{di}) was 252.5 °C, maximal weight-losing temperature (T_{dm}) was 365.1 °C and its final weight-losing temperature (T_{df}) was 391.8 °C. The rate of weight-losing of sample was 80.92 % during the whole test. The initial weight-losing temperature and maximal weight-losing temperature of grafting polymer CDA-g-PCL were lower than the CDA's for 83.9 and 108.8 °C, respectively. However the final weight-losing temperature rose 77.9 °C than CDA's, the rate of weight-losing of sample descended to 66.74 %, 14.18 % lower than the CDA's. It proved that after CDA took place grafting reaction with PCL through MDI grafting bridge, its flowing temperature descended at a certain degree, so that the compactness of polymer configuration changed more or less. It was simultaneously measured that the initial weight-losing temperature, maximal weight-losing temperature and final weight-losing temperature of CDA/prepolymer blend took place inconspicuous change compared with raw material CDA. It further attested that there was a difference between grafting copolymer and blends' configuration after some carbamate groups were introduced to the grafting copolymer and the thermal stability of grafting copolymer was changed.

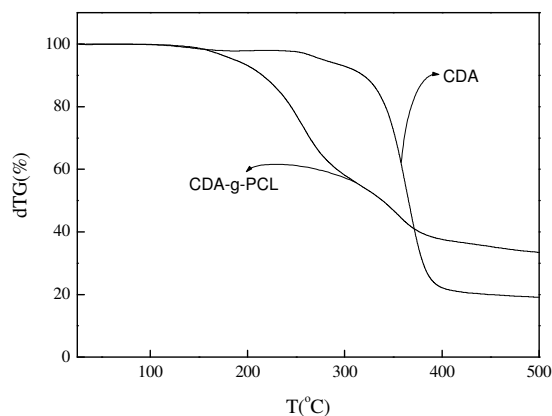


Fig. 8. Thermogravimetric curve of CDA and CDA-g-PCL

TABLE-1
THERMAL PROPERTIES OF CDA AND GRAFT COPOLYMERS CDA-g-PCL

Sample	T_{dm} (°C)	T_{di} (°C)	T_{df} (°C)	Char yields at 500 °C (Wt %)
CDA	365.1	252.5	391.8	80.92%
CDA-g-PCL	256.3	168.6	469.7	66.74%

Analysis of differential scanning calorimetry: Differential scanning calorimetry (DSC) is an analytical method that measures the difference of power between sample and reference compound and temperature relations keeping sample the same temperature to reference compound at the condition of programming temperature-controlled²². Poly(caprolactone)diol belonged to semi-crystalline polymer (its melting point is 55.2 °C), meanwhile CDA was amorphous polymer, their thermal capability was changed accordingly after they polymerized. The DSC curve of thermal absorption of the raw material CDA and grafting polymer CDA-g-PCL was shown in Fig. 9.

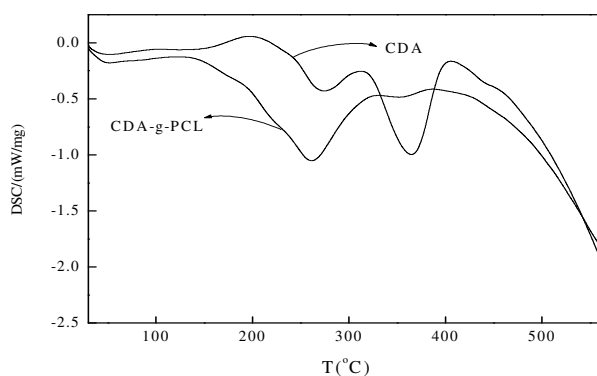


Fig. 9. Differential scanning calorimetry curve of CDA and CDA-g-PCL

According to Fig. 9, the initial weight-lose temperature (T_i), the final weight-lose temperature (T_f), the width of thermal absorption peak ($\Delta T = T_f - T_i$), the temperature of thermal absorption peak amplitude (T_p) and caloric power (ΔH) of sample's characteristic thermal absorption peak were listed in the Table-2. It could be learned from Table-2 that the ΔT of grafting polymer CDA-g-PCL was wider, stated that CDA-g-PCL could slow down the thermal absorption reaction, urged to form a homogeneous construction in the course of temperature-rising and charring, enhanced its mechanical property finally.

TABLE-2
DIFFERENTIAL SCANNING CALORIMETRY (DSC) DATA
OF CDA AND CDA-g-PCL

Sample	T_i (°C)		T_f (°C)		ΔT (°C)		T_p (°C)		ΔH J/g
	peak I	peak II	peak I	peak II	peak I	peak II	peak I	peak II	
CDA	209.8	310.8	310.8	401.5	101	90.7	274.3	364.5	208.2 (peak II)
CDA-g-PCL	140.3	328.6	328.6	388.2	188.3	59.6	260.9	252.1	266.9 (peak I)

Analysis of surface topography: Magnification was one of the most significant parameters to observe surface topography by using scanning electron microscope (SEM). Different magnification would be chosen by different material and different requirement. In this test, CDA could be observed the whole topography when the magnification was 250, while the surface topography of CDA-g-PCL would be clearly seen at the magnification of 800.

It was observed through SEM that the surface topography of CDA changed a lot that surface of original CDA was relative harsh and some corrugation existed, apparent lacertus could be observed (as Fig. 10). However, after CDA grafting onto PCL, the surface of product CDA-g-PCL could be observed to be smoothing and its construction was loosen (Fig. 11).

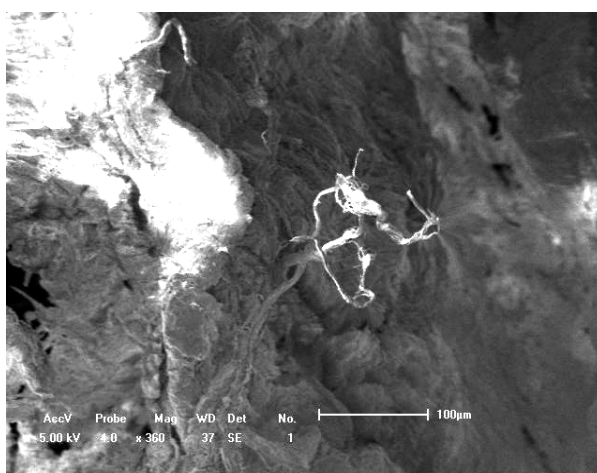


Fig. 10. CDA, $\times 250$, 5 KV, $\delta = 100 \mu\text{m}$

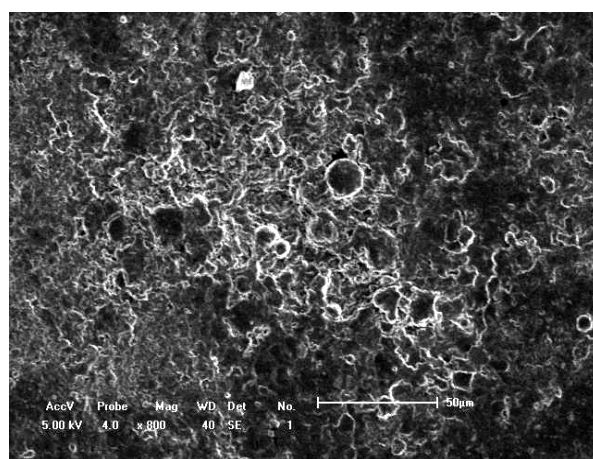


Fig. 11. CDA-g-PCL, $\times 800$, 5 KV, $\delta = 50 \mu\text{m}$

Fig. 12 shows the WAXD curves of solid cellulose diacetate (CDA), cellulose diacetate/poly (caprolactone) diol graft copolymer (CDA-g-PCL) and poly-(caprolactone) diol (PCL). The degree of crystallinity (X_c) was calculated according to the usual formula.

$$X_c (\%) = A_c / (A_c + K A_a) \times 100 \quad (3)$$

where, A_c is the area of diffraction crystalline peak, A_a is the area of diffraction amorphous peak and K is correction factor.

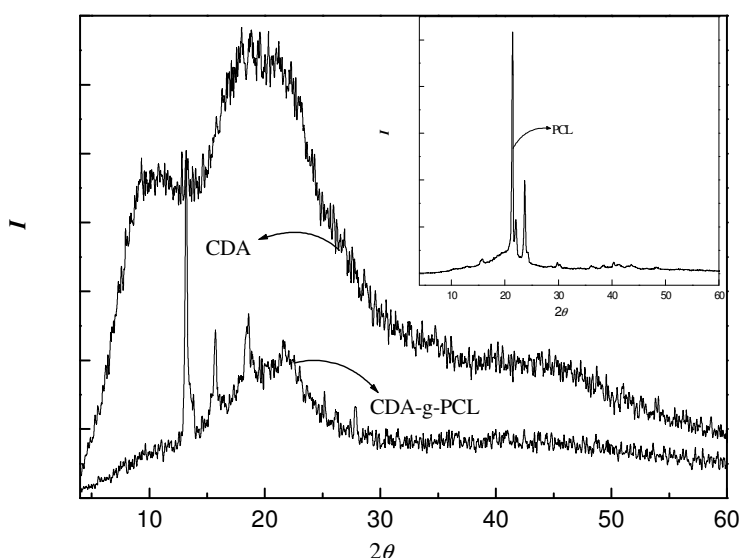


Fig. 12. WAXD of CDA, PCL and CDA-g-PCL

The crystallinity of the reactant CDA, PCL and the copolymers CDA-g-PCL are 44.93, 63.33 and 50.01 % ($K = 0.1$) by eqn. 3, respectively. This result implies that PCL chains will promote the crystallization of the CDA chains when the PCL chains are grafted on the CDA backbone.

Analysis of polyreaction mechanism: Poly(caprolactone)diol (PCL) was grafted to the backbone of cellulose diacetate (CDA) for that there were hydroxyl groups at both ends of PCL and they could be grafted to CDA through reacting with 4,4'-diphenylene methane diisocyanate (MDI). Quadrivalence Sn was contained in the catalyst dibutyltindilaurate (DBTDL) which could accelerate the reaction between hydroxyl and isocyanate with high activity. The catalytic mechanism of quadrivalence Sn maybe as follow²³⁻²⁵: when isocyanate reacted with hydroxyl, the compound contained quadrivalence Sn and the compound which contained hydroxyl group formed complex compound firstly, so that the dipole moment of complex compound was enlarged and the bond length of $-OH$ was extended, it finally urge to form an activated complex compound of four-member rings. After the activated complex compound of four-member rings appeared, the electron of N atom which belong to

isocyanate was transferred to the proton of alcohol, simultaneously the electron of oxygen atom of alcohol was transferred to the carbon atom of isocyanate, carbamate now generated and then the carbamate grafted CDA to form the ultimate product CDA-PCL.

Conclusions

In conclusion, considering MDI as grafting bridge, graft copolymers of CDA and PCL were synthesized successfully by the two-step grafting method. FT-IR was used to observe characteristic absorption band such as 1533 cm^{-1} peak of carbamate group of the product, which initially confirmed the reaction had happened. The comparison analysis of CDA and CDA-g-PCL by utilizing ^1H NMR and ^{13}C NMR techniques, further proved that CDA-g-PCL was obtained through the formation of carbamate group which was bridged by MDI. Wang *et al.*²⁶ describes basically technique to this kind of reaction although the poly (caprolactone) derivative differences from ours. It can also test the designed reaction route. The synthesis mechanism of grafting polymerization was suggested, the likely mechanism was that Sn^{4+} and hydroxyl compounds formed an activated four member ring complex that prompted isocyanate group reacted with the hydroxyl compounds to form carbamate bond which then reacted with CDA to form CDA-g-PCL. The result of DTG indicated that the flow temperature and the weight loss rate of graft copolymers were both reduced after grafting of PCL onto CDA. It showed that the molecular chain of CDA grafted PCL prompted some changes of the density of material. The result of DSC showed that the thermodynamic characteristics of obtained CDA-g-PCL had new changes, CDA-g-PCL could slow down endothermic reaction, which prompted the formation of uniform structure in the carbonization process and enhanced its mechanical properties ultimately. A great change of the surface morphology of CDA was observed by using SEM. The surface of CDA was rough, however, the graft copolymers CDA-g-PCL was relatively smooth after grafting reaction.

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