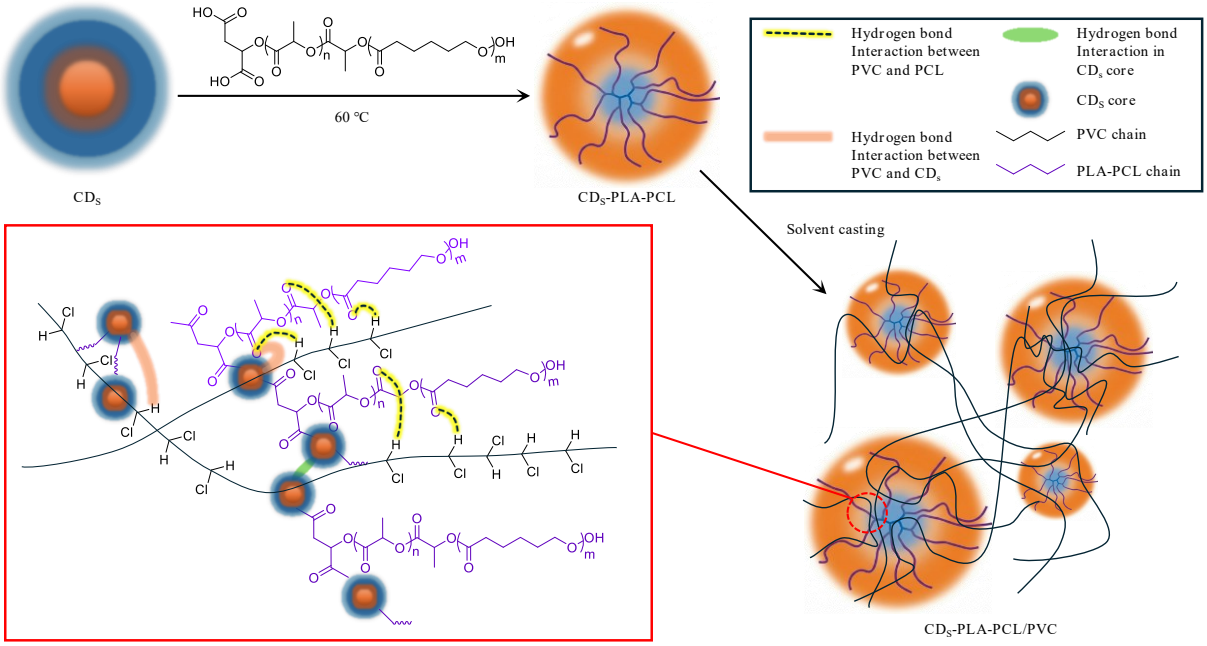
Preparation of Green CDs-PLA-PCL Composite Plasticizer and Its Application in Flexible PVC

Yunhan Wu,[a,b,c] Xiaohui Li,[d] Tianyu Liu,[a,b,c] Tong Shen,[a,b,c] Yun Jie,[a,b,c] Fengying Wang,[a,b,c,*] Zezhong Lin ,[a,b,c,*] and Rongchao Xue [a,b,c,*]

**Corresponding authors: Fengying Wang 843334858@qq.com, Zezhong Lin 1020210013@tju.edu.cn, Rongchao Xue xrc15922275952@tju.edu.cn*

DOI: 10.15376/biores.21.3.6825-6845

GRAPHICAL ABSTRACT



Preparation of Green CDs-PLA-PCL Composite Plasticizer and Its Application in Flexible PVC

Yunhan Wu,[a,b,c] Xiaohui Li,[d] Tianyu Liu,[a,b,c] Tong Shen,[a,b,c] Yun Jie,[a,b,c] Fengying Wang,[a,b,c,*] Zezhong Lin ,[a,b,c,*] and Rongchao Xue [a,b,c,*]

Polyvinyl chloride (PVC) is widely used in construction, medical devices, wire and cable insulation, and consumer products because of its low cost, flame retardancy, and resistance to degradation. However, its inherent rigidity and brittleness limit its use in flexible materials, making plasticization necessary in various applications. In this study, polylactic acid-block-polycaprolactone (PLA-PCL) was synthesized by ring-opening polymerization, and multi-amino carbon dots (CDs) were prepared by a hydrothermal method and incorporated into PLA-PCL through acid-base interactions. The PLA/PCL ratio was optimized to improve the mechanical performance of flexible PVC. Results showed that CDs-PLA-PCL had good compatibility with PVC. Under the optimal PVC/CDs-PLA-PCL1:30 formulation, the film exhibited a tensile strength of 56.0 MPa and a toughness of 173 MJ/m³, representing 2.31- and 2.09-fold increases over DOP-plasticized PVC, respectively. The PVC/CDs-PLA-PCL1:30 blend also showed the best comprehensive properties based on the mechanical, thermal, morphological, fluorescence, and migration-resistance characterizations, indicating that CDs-PLA-PCL is a promising plasticizer for high-performance flexible PVC materials.

DOI: 10.15376/biores.21.3.6825-6845

Keywords: Polyvinyl chloride; Plasticizer; Carbon dots; Polylactic acid; Polycaprolactone

*Contact information: a: College of Chemistry and Materials Science, Qinghai Minzu University, 81000, Xining, China; b: Qinghai Provincial Key Laboratory of Nanomaterials and Technology Qinghai Minzu University, 810007, Xining, China; c: Key Laboratory of Resource Chemistry and Eco-Environmental Protection on Tibetan Plateau, State Ethnic Affairs Commission; d: Shanxi Traditional Chinese Medical Hospital, 030024, Taiyuan, China; *Corresponding authors: Fengying Wang 843334858@qq.com, Zezhong Lin 1020210013@tju.edu.cn, Rongchao Xue xrc15922275952@tju.edu.cn*

INTRODUCTION

Polyvinyl chloride (PVC), a polymeric material produced *via* free-radical polymerization of vinyl chloride monomers, has attracted extensive attention in industry because of its excellent film-forming ability, good processability, and favorable mechanical strength (Fariha *et al.* 2023). Owing to its high rigidity, ultraviolet resistance, inherent flame retardancy, and good compatibility with various plasticizers, PVC occupies an important position in construction, medical, packaging, and electronic applications (Quoc Pham *et al.* 2021). In PVC-based materials, the incorporation of plasticizers is currently the most common strategy to impart flexibility. Although plasticization effectively overcomes the intrinsic hardness and brittleness of PVC, increasing evidence indicates that most conventional plasticizers exhibit a certain degree of toxicity (Jamarani *et al.* 2018). Moreover, these plasticizers are prone to migration during service, thereby posing potential risks to both the environment and human health (Schettler 2006). Among

traditional plasticizers, phthalate-based compounds have been widely used because of their low cost (Camacho *et al.* 2020). However, their cytotoxicity and extensive migration during use, which can result in environmental contamination, have become increasingly prominent concerns (Wang and Qian 2021). Therefore, the development of novel plasticizers that are nontoxic and exhibit excellent migration resistance is urgently needed. Previous studies have shown that bio-based polymeric plasticizers derived from renewable resources, such as vegetable oils (Liu *et al.* 2020), glycerol (Howell and Lazar 2019), cardanol (Ali *et al.* 2020) and caprolactone (Sun *et al.* 2019) can effectively mitigate plasticizer migration and related issues (Han *et al.* 2024).

In recent years, with the continuous development of green polymer materials, hyperbranched polymeric plasticizers have been recognized as a class of plasticizers with excellent plasticization performance (Zhang *et al.* 2019). Compared with conventional linear polymeric plasticizers, hyperbranched plasticizers generally possess higher molecular weights, higher degrees of branching, and abundant terminal functional groups available for further modification. These structural characteristics not only strengthen their entanglement interactions with the PVC matrix (Duarah *et al.* 2016), but also greatly increase the free volume of PVC, thereby significantly improving their compatibility with the PVC matrix (Li *et al.* 2019). Such a multipoint synergistic effect not only overcomes the migration and exudation problems commonly associated with small-molecule plasticizers, but also enables the resulting materials to retain good mechanical properties over prolonged use (Wei *et al.* 2020). At present, most reported hyperbranched plasticizers are prepared by copolymerization of core monomers such as glycerol with monomers such as polycaprolactone (PCL) (Zhang *et al.* 2018).

Lee *et al.* (2018) prepared a hyperbranched biobased plasticizer based on PCL/glycidyl triglyceride *via* one-pot solvent-free polymerization. Howell and Lazar (2019) first synthesized hydroxyl-terminated hyperbranched molecules and subsequently carried out end-capping modification with different organic acids to obtain a series of glycerol/adipic acid-type hyperbranched polyesters, which were found to exhibit good plasticization performance. Lin *et al.* (2023) prepared a three-armed star polymer (S3-PLA-PCL) with a rigid polylactic acid (PLA) core and a soft polycaprolactone (PCL) shell, and employed it as a plasticizer for flexible PVC. The results showed that the PVC materials plasticized with S3-PLA-PCL exhibited higher modulus, strength, and toughness than those plasticized with the corresponding linear PLA-PCL. Li *et al.* (2020) polymerized triethyl citrate with triglyceride and then end-capped the resulting hyperbranched molecules with acetic anhydride to obtain an acetate product (BHE). Further investigation demonstrated that, compared with DOP-plasticized PVC, BHE-plasticized PVC exhibited superior thermal stability and plasticizer migration resistance. Shi *et al.* (2011) synthesized a series of plasticizers with different topological structures based on PCL terminated with caprylate and benzoate groups. They found that, compared with DEHP-plasticized PVC, PCL-caprylate-plasticized PVC exhibited a much higher T_g, with an increase of 20 °C, and therefore showed an approximately twofold increase in yield stress. Chen *et al.* (2021) used a degradable and sustainable polylactide/N,N-bis(2-hydroxyethyl)glycine (PLA/BHEG) branched polymer as the precursor and prepared star-shaped PCL polymers (RN-SPCLs) through ring-opening polymerization. This type of plasticizer can significantly increase the elongation at break of PVC to as high as 450%, while maintaining high tensile strength and exhibiting excellent migration resistance. Wang *et al.* (2024) designed and synthesized a series of star-shaped polymers (PEI-PCL) with hyperbranched polyethyleneimine (PEI) as the core and PCL as the shell. The experimental results showed that, while maintaining an

elongation at break greater than 400%, the maximum modulus of the resulting PVC material reached approximately 392 MPa, making it one of the stiffest systems reported to date. These studies collectively demonstrate that hyperbranched-structure plasticizers exhibit excellent performance in PVC plasticization. Therefore, research on hyperbranched polymeric plasticizers is of great importance.

In recent years, researchers have found that plasticizers with only a single functional role can no longer satisfy the practical application requirements of PVC materials. Therefore, broadening the application scope of plasticizers is of considerable importance. At present, carbon dots (CDs) and PLA have attracted substantial attention owing to their favorable biocompatibility, particularly because CDs possess a small size, facile functionalization, abundant modifiable functional groups such as amino, hydroxyl, and carboxyl groups, and unique optical properties (Kong *et al.* 2024), which have enabled their widespread application (Zhou *et al.* 2017). Despite these advantages, CDs and PLA are difficult to employ directly as PVC plasticizers because CDs are highly polar nanoscale carbonaceous particles that can aggregate in hydrophobic polymer matrices and mainly function as optical or interfacial fillers, whereas PLA has relatively rigid polyester chains and limited chain mobility, which weakens its ability to soften PVC when used alone (Wei *et al.* 2020). By contrast, PCL exhibits excellent biodegradability, high miscibility with PVC, good flexibility, and the potential for synthesis from bio-based sources; accordingly, it is especially attractive as a green plasticizer for PVC (Ferruti *et al.* 2003). Therefore, the organic combination of PCL, CDs, and PLA can exploit the plasticizing effect of PCL segments, the rigid and biodegradable features of PLA, and the fluorescence and interfacial functions of CDs, thereby enabling multifunctional PVC materials.

The objective of this study was to construct a green composite plasticizer by integrating a CDs- and PLA-rich hard core with a PCL-rich flexible shell, and to evaluate its application in flexible PVC blend films. The innovation of this study lies in the fact that, compared to traditional low-molecular-weight plasticizers, this plasticizer exhibits superior anti-migration and ductility, while also enhancing the mechanical properties of PVC without compromising environmental friendliness. Furthermore, both PLA and PCL are non-toxic, biocompatible, and industrially compostable; thus, CDs-PLA-PCL can be regarded as a high-performance, eco-friendly macromolecular plasticizer suitable for polyvinyl chloride plastics.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF, 99.0%) was purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. The ε-Caprolactone (ε-CL, 99.9%) was purchased from Shandong Keyuan Biochemical Co., Ltd. Stannous octoate ($Sn(Oct)_2$, 99.0%), poly(vinyl chloride) (PVC), and DL-malic acid (MA, 99.8%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Citric acid (CA, 99.0%), dioctyl phthalate (DOP, 99.8%), polyethyleneimine (PEI, 99.0%), and DL-lactide (DL-LA, 99.9%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Synthesis of CDs-PLA-PCL

Synthesis of carbon dots (CDs)

Carbon dots (CDs) were synthesized according to a previously reported method (Wang *et al.* 2022). Briefly, polyethyleneimine (PEI, 1.8 K, 4.5 g) was added to a Teflon-lined stainless-steel autoclave, followed by 30 mL of deionized water. The mixture was stirred until the PEI was completely dissolved. Citric acid (CA, 1.5 g) was then added, and the solution was further stirred until complete dissolution. The hydrothermal reaction was carried out at 180 °C for 6 h. After the reaction, water was removed by rotary evaporation to obtain a yellow viscous liquid, which was stored in a refrigerator for subsequent use.

Synthesis of PLA-PCL

Malic acid (1.5 g, 11.2 mmol), DL-lactide (10.8 g, 112.0 mmol), and $Sn(Oct)_2$ (0.1 mL, 10% solution in toluene) were sequentially added into a 25 mL single-neck round-bottom flask. After three vacuum-nitrogen purge cycles to remove air, the reaction system was heated to 130 °C and stirred continuously for 16 h. Upon completion, the reaction mixture was cooled to room temperature and diluted with a small amount of THF. The crude product was then precipitated three times in 300 mL of cold methanol/water (v/v = 1:1). A white solid was finally obtained and dried under vacuum overnight to give PLA-PCL. Subsequently, together with 2.0 g of polylactic acid (PLA) and 6.0 g of ε-caprolactone (ε-CL), was added into a 25 mL single-neck round-bottom flask. Under a nitrogen atmosphere, the reaction system was heated to 135 °C and maintained for 16 h. After the reaction, the mixture was cooled to room temperature and diluted with a small amount of THF. The crude product was precipitated three times in 300 mL of cold methanol, filtered, and vacuum-dried to afford PLA-PCL with a PLA/PCL ratio of 1:30 (PLA-PCL1:30). Other polymers with different compositions were synthesized from PLA-PCL as the starting material by varying the feed ratio of ε-CL using a similar procedure.

Table 1. Feed Ratios Used to Synthesize PLA-PCL Copolymers with Different PLA/PCL Ratios

Plasticizer ID	PLA/g	CL/g	$Sn(OCT)_2$/g
PLA-PCL $_{1:10}$	0.2	2	0.07
PLA-PCL $_{1:20}$	0.2	4	0.14
PLA-PCL $_{1:30}$	0.2	6	0.21
PLA-PCL $_{1:40}$	0.2	8	0.28

Synthesis of the composite plasticizer (CDs-PLA-PCL)

PLA-PCL (1 g), CDs (0.1 g), and methanol (10 mL) were sequentially added into a 25 mL single-neck round-bottom flask. After three vacuum-nitrogen purge cycles to remove air, the reaction system was heated to 60 °C and stirred continuously for 10 h. After the reaction, the mixture was cooled to room temperature and allowed to stand until the precipitate had completely formed. The precipitate was collected by Büchner filtration and washed twice with 10 mL of methanol. A yellow solid was obtained and dried under vacuum overnight to yield the final product, CDs-PLA-PCL.

Preparation of Flexible PVC Blend Films

The PVC blends were prepared using the solvent evaporation method. Briefly, a specific quantity of PVC and the prepared copolymer were dissolved in a certain amount of THF. The mixture was then vigorously stirred at room temperature overnight. After that,

the solution was poured onto a cleaned glass substrate, and the THF was slowly allowed to evaporate at room temperature for 12 h. Subsequently, the films were dried under a vacuum to obtain the PVC blends. The blends prepared with copolymers having PLA/PCL ratios of 1:10, 1:20, 1:30, and 1:40 were named PVC/CDs-PLA-PCL1:10, PVC/CDs-PLA-PCL1:20, PVC/CDs-PLA-PCL1:30, and PVC/CDs-PLA-PCL1:40, respectively. The overall synthetic route and film-preparation process are summarized in Fig. 1.

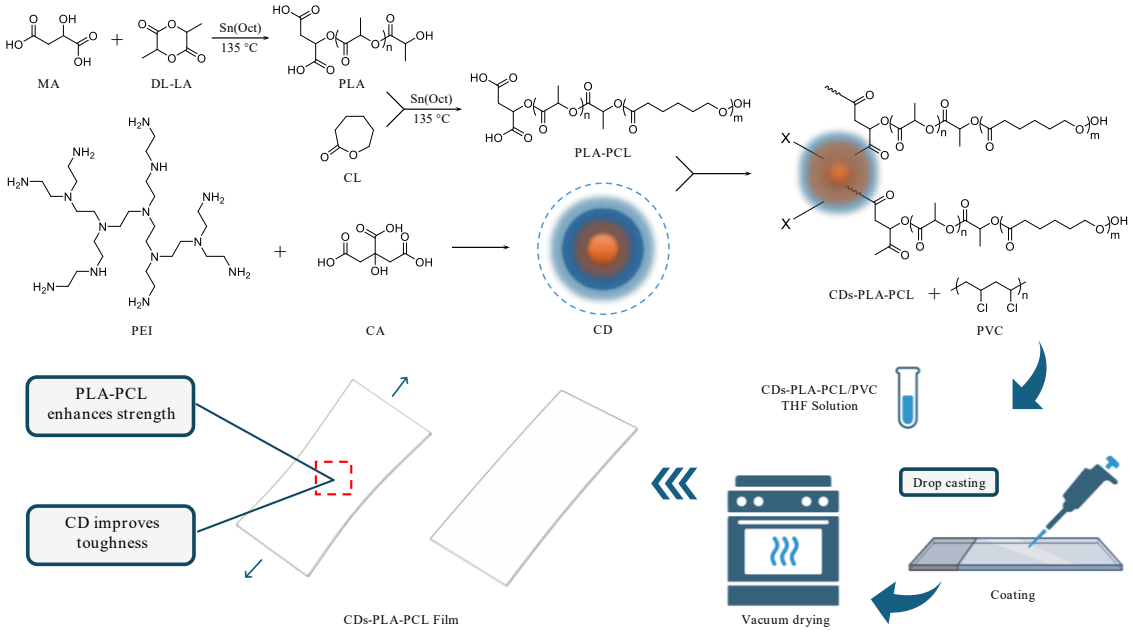


Fig. 1. CDs and PLA-PCL synthesis as well as PVC film preparation

Characterization

The structures of the synthesized CDs, PLA-PCL samples with different ratios, and the composite plasticizer CDs-PLA-PCL were characterized using a PerkinElmer Spectrum Two Fourier transform infrared (FTIR) spectrometer over the range of 4000 to 500 cm^{-1}. ^{1}H NMR spectra were recorded on a 400 MHz instrument using CDCl3 as the solvent and tetramethylsilane (TMS) as the internal standard. Thermogravimetric analysis (TGA) was carried out from -30 to 600 °C at a heating rate of 10 K/min. Differential scanning calorimetry (DSC) measurements were conducted as follows: the first heating scan was performed from 30 to 150 °C at 20 K/min, followed by an isothermal hold for 5 min to eliminate thermal history; the first cooling scan was conducted from 150 to -30°C at 10 K/min, followed by an isothermal hold for 3 min; the second heating scan was then performed from -30 to 110 °C at 10 K/min. All DSC measurements were carried out under a nitrogen atmosphere with a purge gas flow rate of 40 mL/min and a protective gas flow rate of 60 mL/min. Tensile testing was standardized according to GB/T 1040.1-(2006) and performed at 25°C using a universal testing machine. Before testing, all films were conditioned at 23 ± 2 °C and 50 ± 5% relative humidity for 24 h, and specimens were cut from defect-free central regions of the cast films using the same cutting procedure and the same specimen geometry specified by GB/T1040.1-(2006). For each formulation, five independent specimens (n=5) were tested at a tensile rate of 0.4 mm/min, and the mechanical properties were reported as the mean ± standard deviation. Specimens showing visible bubbles, edge defects, non-uniform thickness, or premature slippage were excluded

to reduce experimental variability. Fluorescence spectra were recorded using a Gangdong F-320 fluorescence spectrophotometer. UV-Vis spectra were measured using a Puxi General T6 UV-Vis spectrophotometer. The fracture cross-sections and surface morphologies of the samples were observed by scanning electron microscopy (SEM, ZEISS Sigma 300, Germany) at an accelerating voltage of 0.02 to 30 kV. Prior to SEM observation, the sample surfaces were sputter-coated with gold.

RESULTS AND DISCUSSION

Synthesis and Formulation Overview

Citric acid (CA) and polyethyleneimine (PEI) were selected as the carbon sources and the nitrogen source, and CDs with abundant amino groups on their surfaces were synthesized *via* a hydrothermal method. Malic acid initiated the ring-opening polymerization of DL-lactide through its hydroxyl groups to afford hydroxyl-terminated PLA-OH, which subsequently initiated *ε*-CL polymerization to obtain PLA-PCL. After adjustment of the *ε*-CL feed ratio, a series of PLA-PCL copolymers designated as PLA-PCL1:n (w/w) was obtained and compounded with CDs through acid-base interactions to form CDs-PLA-PCL. The synthetic route and the feed ratios are summarized in Fig. 1 and Table 1 in the Methodology section.

^{1}H NMR Analysis

The systematic characterizations of the intermediate product (PLA-PCL) and the final product (CDs-PLA-PCL) are shown in Fig. 2, which presents their ^{1}H NMR spectra. From the NMR spectra, all signal peaks of PLA and PCL can be clearly observed. Among them, the proton signal at approximately 5.08 to 5.20 ppm is assigned to the chemical shift of the methylene protons in the PLA segment. This characteristic peak appeared in all NMR spectra with relatively consistent intensity, indicating the successful incorporation of PLA. The proton signal at 4.06 ppm is attributed to the methylene protons adjacent to the ester group in the PCL segment. In the NMR spectra of all intermediate PLA-PCL products, the integral area of this peak increased significantly, indicating the successful introduction of PCL and further confirming the successful preparation of PLA-PCL. After the introduction of CDs, no obvious chemical shift signal was observed in the NMR spectra, which may be due to the extremely low content of CDs (10%).

GPC Analysis

The GPC curves showed that, as the PCL feed ratio was increased from 1:20 to 1:40, the molecular-weight distribution peaks of the PLA-PCL copolymers gradually shifted toward the higher-molecular-weight region in Fig. 3 This result indicates that the growth of *ε*-caprolactone segments effectively increased the apparent molecular weight of the copolymers. The PLA-PCL$_{1:20}$ sample exhibited a relatively broad peak with a shoulder, suggesting a broader molecular-weight distribution, which may be associated with the presence of low-molecular-weight chains or nonuniform chain growth. In contrast, the peak positions of PLA-PCL$_{1:30}$ and PLA-PCL$_{1:40}$ shifted markedly to higher molecular weights and showed more concentrated distributions. These results indicate that different PCL feed ratios increased the relative proportion of PCL segments in the PLA-PCL chains, thereby increasing the content of flexible segments in the composite plasticizer.

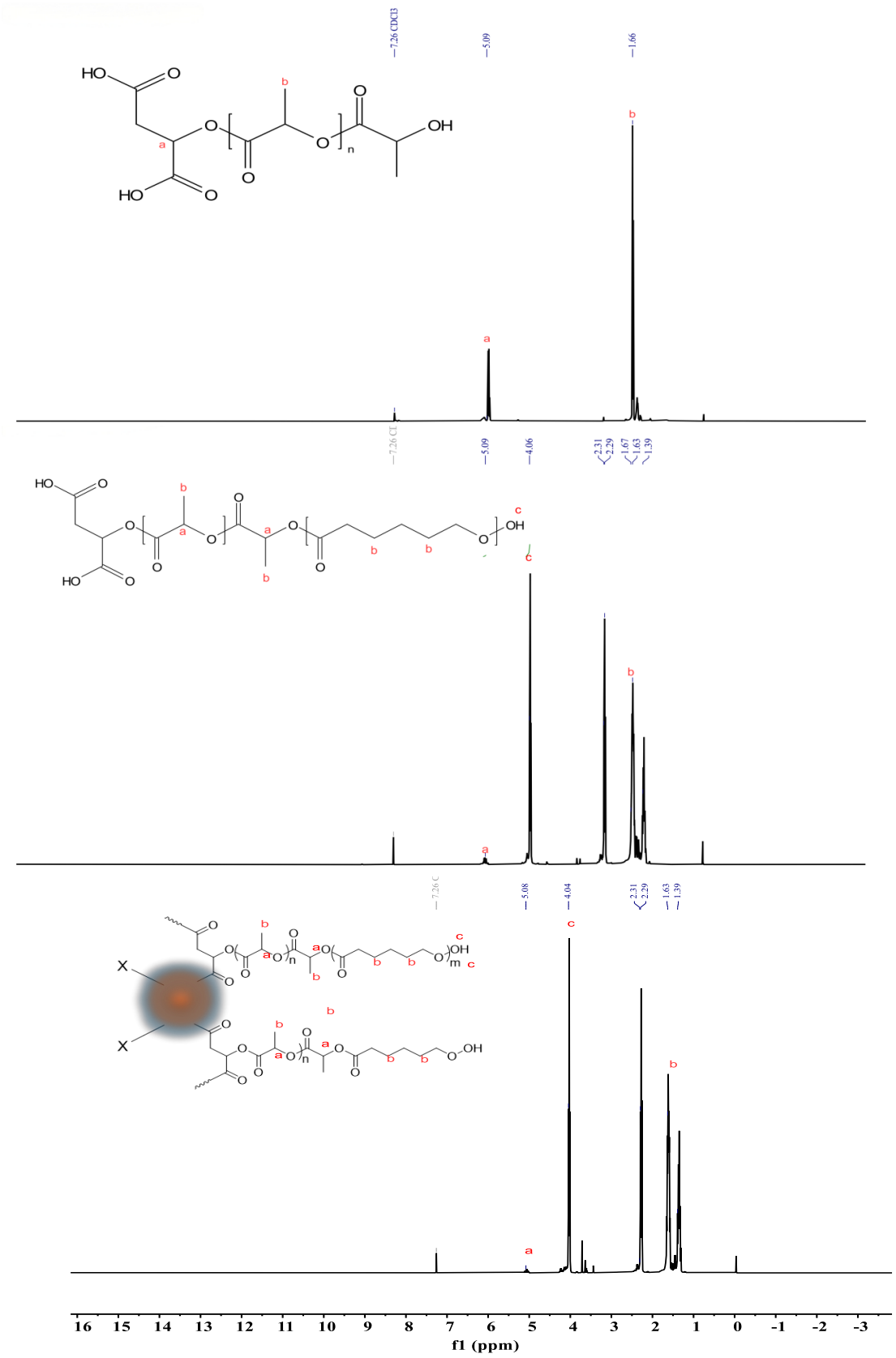


Fig. 2. [1]H NMR spectra of PLA, PLA-PCL and CDs-PLA-PCL

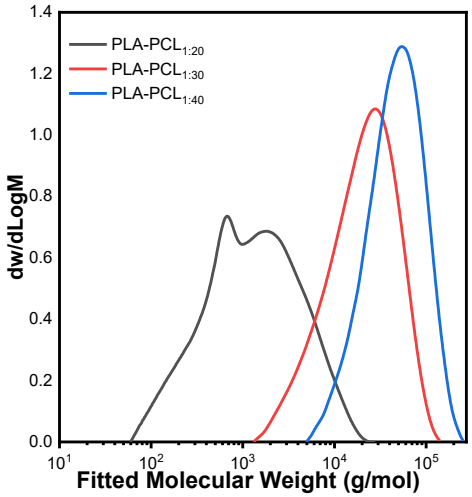


Fig. 3. GPC molecular-weight distribution curves of PLA-PCL copolymers with different PLA/PCL feed ratios

XPS Analysis

To further identify the surface chemical states and possible interfacial interaction sites of CDs-PLA-PCL, XPS analysis was carried out in Fig. 4. The C 1s spectrum was fitted with C-C, C-N, C-O-C, and N-C=O peaks, indicating the presence of carbon frameworks, nitrogen-containing groups, polyester chains, and amide-related structures. The N 1s spectrum contained C-N-C, C-N, and $-NH^{3+}$ peaks, confirming that PEI-derived amino groups and protonated nitrogen species were present on the surface of CDs. The O 1s spectrum showed C=O, C-O, and -OH peaks, which were assigned to ester carbonyl groups, ester oxygen atoms, hydroxyl groups, and carboxyl-related oxygen species.

These results show that CDs interacted with PLA-PCL through acid-base association rather than simple physical mixing. In addition, CDs-PLA-PCL contains abundant nitrogen- and oxygen-containing functional groups, which can act as interfacial interaction sites. Therefore, the improved compatibility and mechanical properties are mainly attributed to hydrogen bonding, acid-base association, and polar interactions among CDs, PLA-PCL, and polyvinyl chloride.

FTIR Analysis

The structures of PLA-PCL and CDs-PLA-PCL polymers were characterized by FT-IR spectroscopy. As shown in Fig. 5, the FT-IR spectra of PLA-PCL$_{1:10}$, PLA-PCL$_{1:20}$, PLA-PCL$_{1:30}$, and PLA-PCL$_{1:40}$ all exhibited the stretching vibration of C=O at 1730 cm^{-1} and the absorbance band of C–O–C at 1183 cm^{-1}, while the weak broad peak in the range of 3200 to 3600 cm^{-1} was associated with the stretching vibration of terminal hydroxyl groups. After the combination of PLA-PCL with CDs, the weak broad peak at 3200 to 3600 cm^{-1} became more pronounced and more undulating in all CDs-PLA-PCL samples. This may be attributed to the presence of amino groups on the surface of CDs, often giving rise to broader hydrogen-bond-related absorption features. No obvious changes were observed in the positions of the other characteristic peaks, which further confirmed the successful preparation of PLA-PCL and CDs-PLA-PCL.

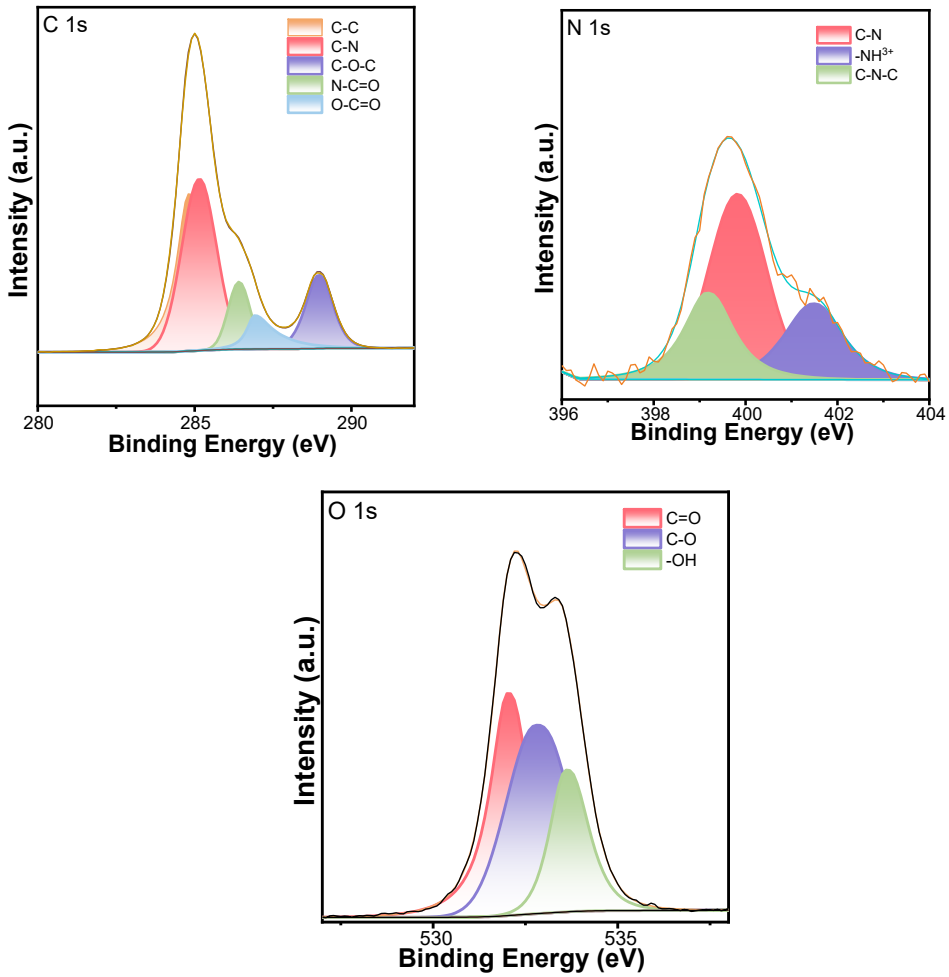


Fig. 4. XPS spectra of CDs-PLA-PCL$_{1:30}$

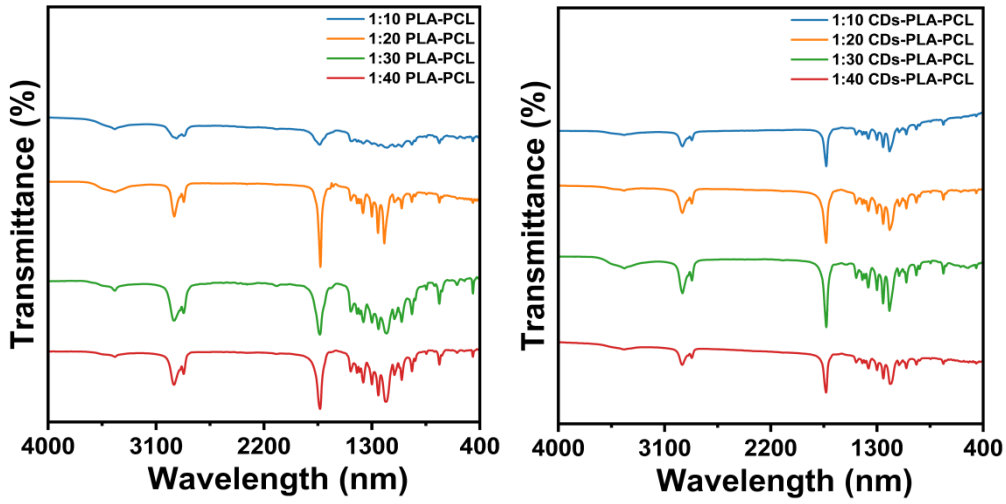


Fig. 5. FT-IR spectra of PLA-PCL and CDs-PLA-PCL

The structures of the PVC/PLA-PCL and PVC/CDs-PLA-PCL blend films were characterized by FT-IR spectroscopy. As shown in Fig. 6, the FT-IR spectra of both PVC/CDs-PLA-PCL and PVC/PLA-PCL blend films exhibited the bending vibration of

C–H at 2940 cm^{-1}, the bending vibration of C=O at 1730 cm^{-1}, and the absorption band of C-Cl at 625 cm^{-1}. In the PVC/CDs-PLA-PCL blend films, an enhanced weak absorbance appeared at approximately 3300 to 3400 cm^{-1}, corresponding to the stretching vibration of -NH, while the peak near 1700 cm^{-1} became broader. This was attributed to the formation of hydrogen bonding between the surface groups of CDs and the polyester C=O and C-O groups, resulting in enhanced interfacial interactions. No obvious shifts were observed for the other characteristic peaks, which further confirmed that the incorporation of the CDs-PLA-PCL plasticizer improved the mechanical properties of the PVC blend films.

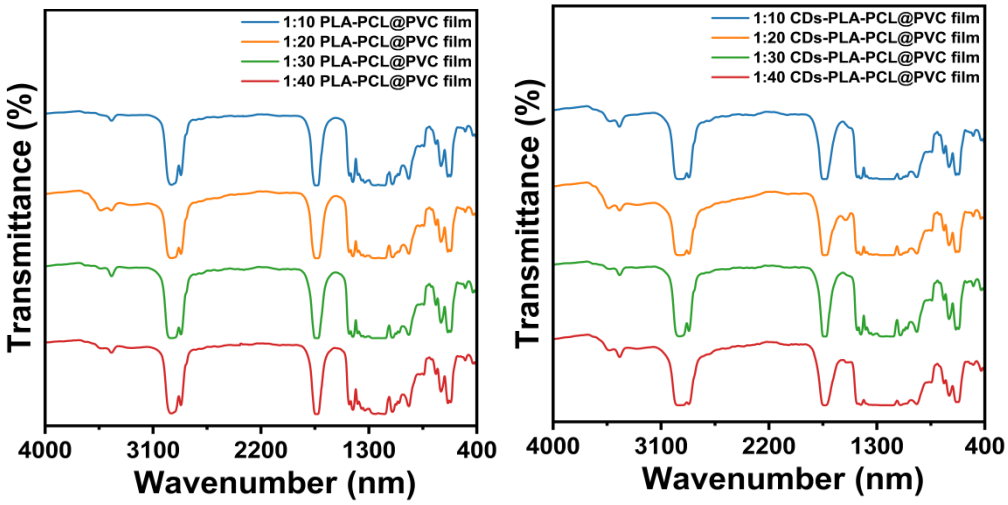


Fig. 6. FT-IR spectra of PLA-PCL/PVC and CDs-PLA-PCL/PVC

UV-Vis Analysis

In many flexible PVC products, transparency is of considerable importance for practical applications. Therefore, in this study, the transparency of all films was investigated by UV-Vis spectroscopy. As shown in Fig. 7, the transmittance of both PVC/CDs-PLA-PCL and PVC/PLA-PCL blend films was within the range of 80% to 95% in the visible region. These results indicate that the incorporation of the plasticizer did not affect the transparency of the films. The results further demonstrate the good compatibility between the plasticizer and the PVC matrix.

Because CDs possess excellent fluorescence properties as well as UV absorption and energy-harvesting capabilities, the UV absorbance and fluorescence properties of the blend films were further investigated by UV-Vis spectroscopy and fluorescence spectroscopy. As shown in Fig. 8, both the CDs-containing and CDs-free blend films exhibited the same general trend in UV absorption, namely, a gradual decrease in absorbance with increasing wavelength, with the absorbance bands mainly concentrated in the short-wavelength region. Interestingly, the absorbance spectrum of the PVC film without CDs was dominated by a primary absorbance band in the short-wavelength UV region, and the absorbance decayed rapidly as the wavelength increased. In addition to the primary absorbance band, the absorbance spectrum of the CDs-containing PVC film exhibited an obvious broad peak in the mid-UV to near-visible region, indicating that the blend films containing CDs possessed a broader spectral absorbance capability. Although the CDs-containing blend film samples significantly improved UV resistance, they might also introduce absorbance in the visible region, resulting in a decrease in transparency.

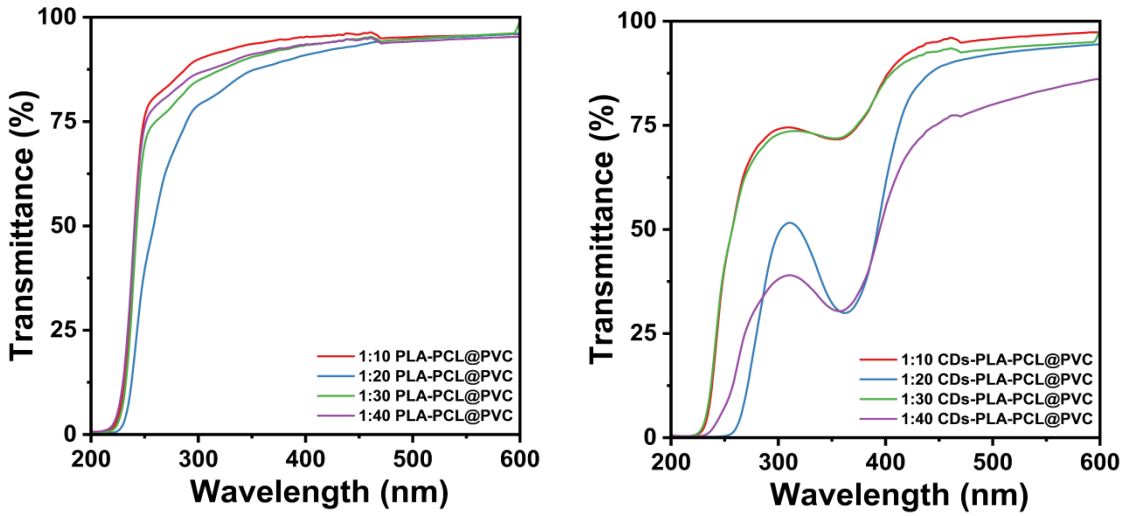


Fig. 7. UV transmission spectrum of PLA-PCL/PVC and CDs-PLA-PCL/PVC

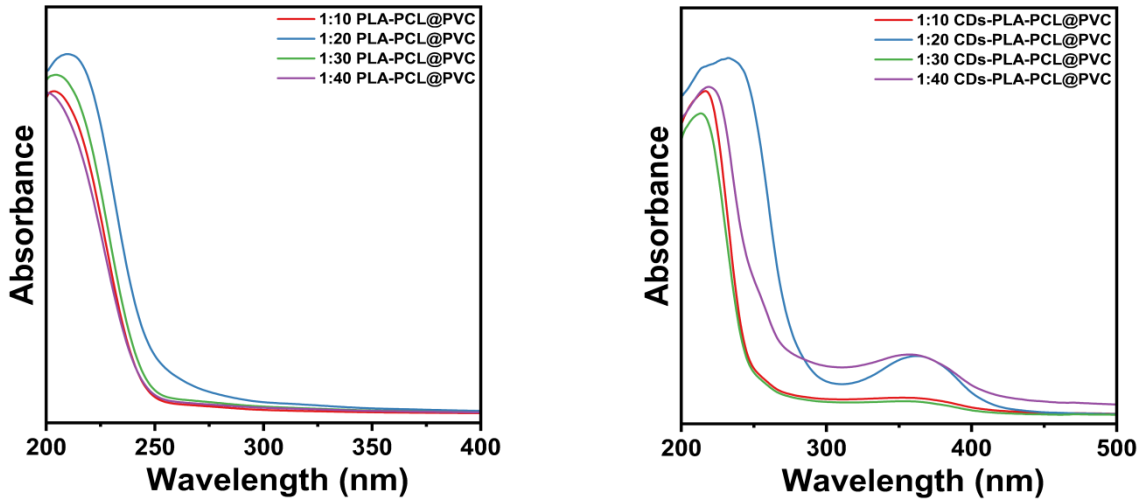


Fig. 8. UV absorbance spectrum of PLA-PCL/PVC and CDs-PLA-PCL/PVC

Fluorescence Analysis

As shown in Fig. 9, PVC blend films containing different ratios of CDs-PLA-PCL emitted bright blue fluorescence under 365 nm UV irradiation, indicating good compatibility between CDs-PLA-PCL and PVC. Upon excitation at 365 nm, a fluorescence emission peak appeared near 454 nm. After plasticization of PVC with CDs-PLA-PCL, the UV absorption and fluorescence emission properties were retained without alteration. The fluorescence properties of CDs-PLA-PCL$_{1:30}$ were further investigated by emission scanning under excitation at 365 nm. The fluorescence quantum yield was determined to be 30.03% in Fig. 10.

Fluorescence emission spectrum of CDs-PLA-PCL/PVC

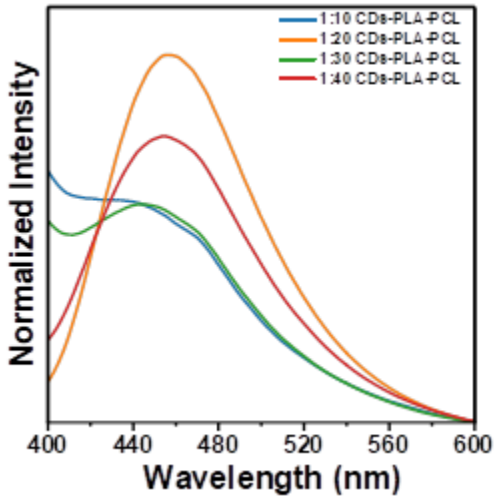


Fig. 9. Fluorescence emission spectrum of CDs-PLA-PCL/PVC

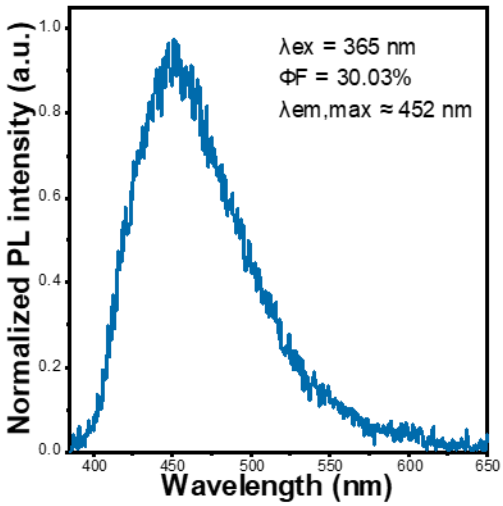


Fig. 10. CDs-PLA-PCL$_{1:30}$ fluorescence emission spectrum under 365 nm excitation

TGA Analysis

Excellent thermal stability and mechanical performance are of critical importance for the practical application of PVC plastics. The elongation at break, tensile strength, and glass transition temperature of all blend films were measured to evaluate their thermodynamic and mechanical properties.

As shown in Fig. 11, the TGA and DTG curves of all blend films exhibited thermal decomposition behaviors similar to that of the control film, all undergoing a typical two-stage thermal decomposition process. All samples remained stable under a nitrogen atmosphere below 225 °C. The first degradation stage in the range of 250 to 360 °C corresponded to the elimination of a large amount of HCl from the PVC matrix, whereas the second stage at approximately 360 to 480 °C was attributed to the further thermal degradation of crosslinked polyene structures containing C=C bonds, a process involving cyclization and chain scission (Jia *et al.* 2015). The thermal stability of the blend films decreased slightly with increasing CDs content, which may be due to the large number of amide bonds in the CDs that reduced the thermal stability of the PVC films. Overall, the initial weight-loss temperature of the plasticized PVC films was around 250 °C, which was

significantly higher than the conventional extrusion processing temperature range of PVC (180 to 200 °C), thereby providing good thermal processability for the heated extrusion of PVC products based on CDs-PLA-PCL/PVC blends. This finding is of great significance for optimizing material formulations and improving material performance under high-temperature conditions.

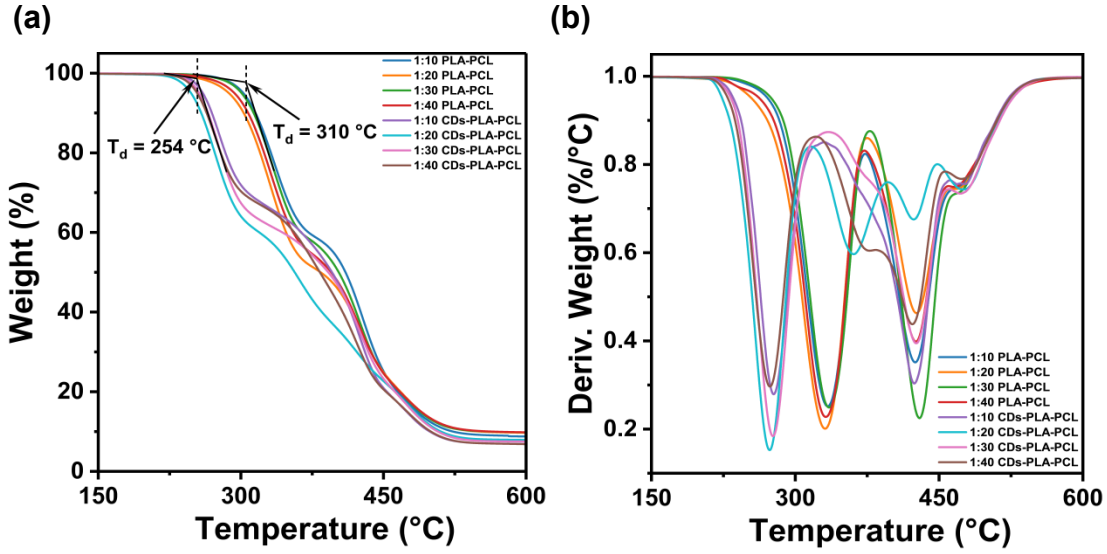


Fig. 11. (a) Thermal gravimetric analysis (TGA) curves of PLA-PCL/PVC and CDs-PLA-PCL/PVC and (b) derivative thermogravimetric analysis (DTG) curve

DSC Analysis

The DSC curves in Fig. 12 showed that all CDs-PLA-PCL samples exhibited distinct melting peaks, indicating that the PLA-PCL polyester segments retained their typical thermal response after composite formation.

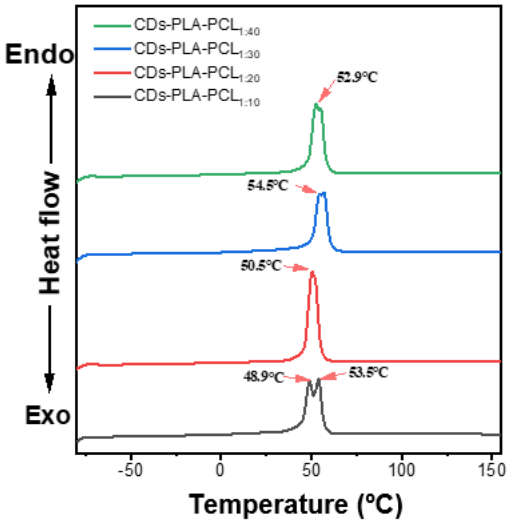


Fig. 12. DSC curves of CDs-PLA-PCL at different ratios

As the PCL content increased, the melting peaks gradually became sharper, suggesting that longer PCL segments favored more regular chain packing and the

formation of more ordered crystalline structures. The broader peak shape observed for samples with lower PCL content may be associated with a less uniform chain-length distribution and a lower degree of crystal perfection. The introduction of CDs may promote hydrogen bonding and acid-base association between the amino, hydroxyl, and carboxyl groups on the CD surface and the ester carbonyl groups or terminal groups of PLA-PCL, thereby restricting partial segmental motion and regulating the crystallization behavior.

To investigate the thermodynamic properties of the blend films, differential scanning calorimetry (DSC) was employed to characterize their glass transition temperature (T_g). As shown in Fig. 13, pure PVC showed a T_g of 71.8 °C, whereas PLA-PCL-plasticized PVC exhibited markedly lower T_g values of -29.5, -30.4, -15.4, and -15.0 °C for the 1:10, 1:20, 1:30, and 1:40 PLA/PCL ratios, respectively. After CD incorporation, the T_g values of the corresponding PVC/CDs-PLA-PCL blends were -1.72, -16.55, -7.59, and -7.99 °C, respectively, indicating that CDs restricted the cooperative motion of PVC chains and plasticizing segments to different extents. The most pronounced T_g increase occurred in the 1:10 formulation, which can be attributed to the reduced relative content of flexible PLA-PCL segments and the enhanced interactions between the functional groups on CDs and PVC molecular chains. These DSC results demonstrate good compatibility between CDs-PLA-PCL and PVC, while the flexible PCL segments and polar ester bonds contributed to the plasticization behavior of the composite films.

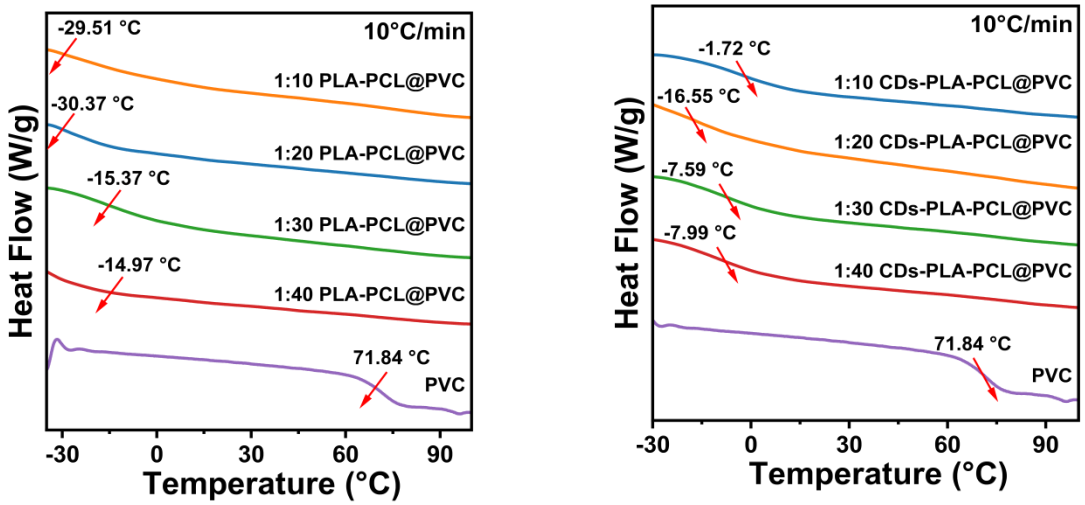


Fig. 13. DSC curve of PLA-PCL/PVC and CDs-PLA-PCL/PVC

SEM Analysis

During the practical use of PVC materials, mechanical damage such as friction and stretching is unavoidable. Therefore, in this study, the morphological changes of the fracture-plane surfaces of all blend films under tensile fracture were further simulated. As shown in Fig. 14, unlike the smooth PVC surface reported in the literature, the plasticized PVC exhibited a fibrous surface morphology after mechanical damage. This may be because the plasticizer can effectively suppress the strong polar interactions of the C-Cl bonds and disperse PVC into fiber bundles (Chen *et al.* 2021). The results indicated that the plasticized PVC possessed higher extensibility and toughness.

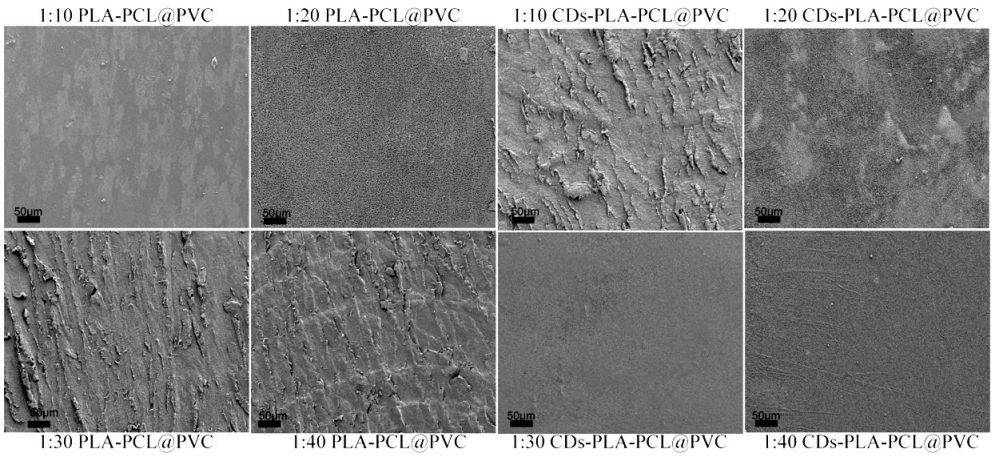


Fig. 14. SEM of PLA-PCL/PVC and CDs-PLA-PCL/PVC film plane

Mechanical Tests

Excellent mechanical properties are of great importance for the practical application of PVC materials. Therefore, the mechanical properties of all blend films were investigated in detail in this study. Polymers with and without CDs and with different PLA/PCL ratios were blended with the PVC matrix to obtain eight blend films, namely PVC/PLA-PCL1:10, PVC/PLA-PCL1:20, PVC/PLA-PCL1:30, PVC/PLA-PCL1:40, PVC/CDs-PLA-PCL1:10, PVC/CDs-PLA-PCL1:20, PVC/CDs-PLA-PCL1:30, and PVC/CDs-PLA-PCL1:40, with PVC and PVC/DOP films used as control groups.

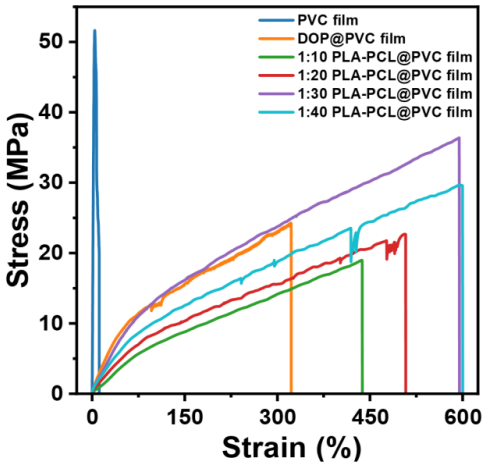


Fig. 15. Stress-strain diagram of different proportions PLA-PCL/PVC

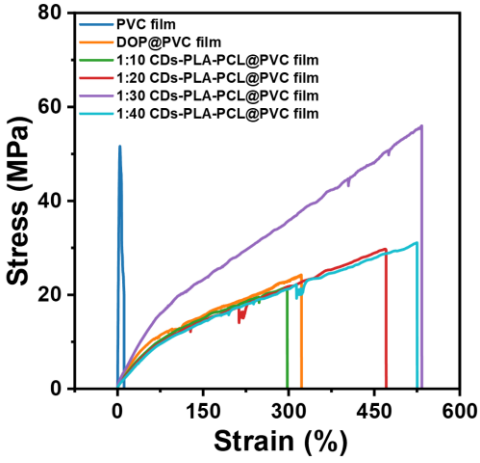


Fig. 16. Stress-strain diagram of different proportions CDs-PLA-PCL/PVC

The mechanical properties of all films were further measured using a universal testing machine. The reported mechanical values were calculated from five parallel specimens for each formulation, and error bars in the bar charts represent standard deviations. This replicate-based analysis, together with controlled conditioning (23 ± 2 °C and 50 ± 5% relative humidity for 24 h), identical specimen cutting, and exclusion of defective specimens, was used to improve the reliability of the mechanical data and reduce variability. As shown in Figs. 15 and 16, the unplasticized PVC film exhibited hard and brittle characteristics, whereas the incorporation of DOP, PLA-PCL, or CDs-PLA-PCL

substantially improved flexibility. Among all formulations, PVC/CDs-PLA-PCL1:30 showed the best comprehensive mechanical performance, with a tensile strength of 56.01 MPa, a toughness of 173 MJ/m³, and an elongation at break of 534%.

The bar charts in Figs. 17 and 18 present the mean mechanical values with standard deviations from five replicate specimens (n=5), allowing comparison of the effects of plasticizers with and without CDs on the mechanical properties of PVC films. The modulus, toughness, and tensile strength of PVC/DOP, PVC/PLA-PCL1:10, PVC/PLA-PCL1:20, PVC/CDs-PLA-PCL1:10, and PVC/CDs-PLA-PCL1:20 were lower than those of PVC/PLA-PCL1:30, PVC/PLA-PCL1:40, PVC/CDs-PLA-PCL1:30, and PVC/CDs-PLA-PCL1:40. The strength and toughness of the CDs-containing blend films were improved to a certain extent, which may be attributed to the abundant polar ester groups in PCL, which can form hydrogen bonds with the hydrogen atoms of PVC molecular units, thereby suppressing the strong interactions between polar C-Cl bonds.

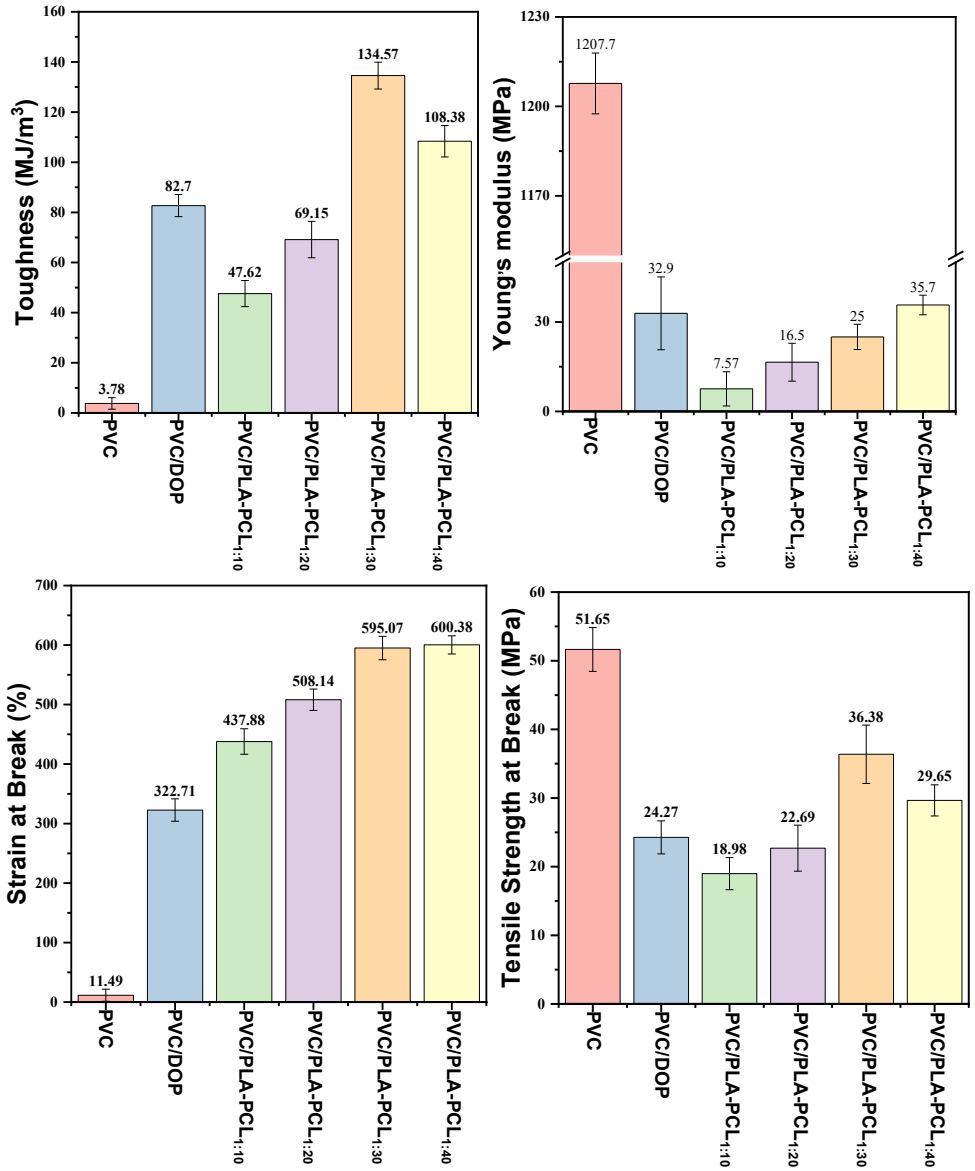


Fig. 17. Bar chart of mechanical data for PLA-PCL/PVC with different proportions (mean ± standard deviation, n=5)

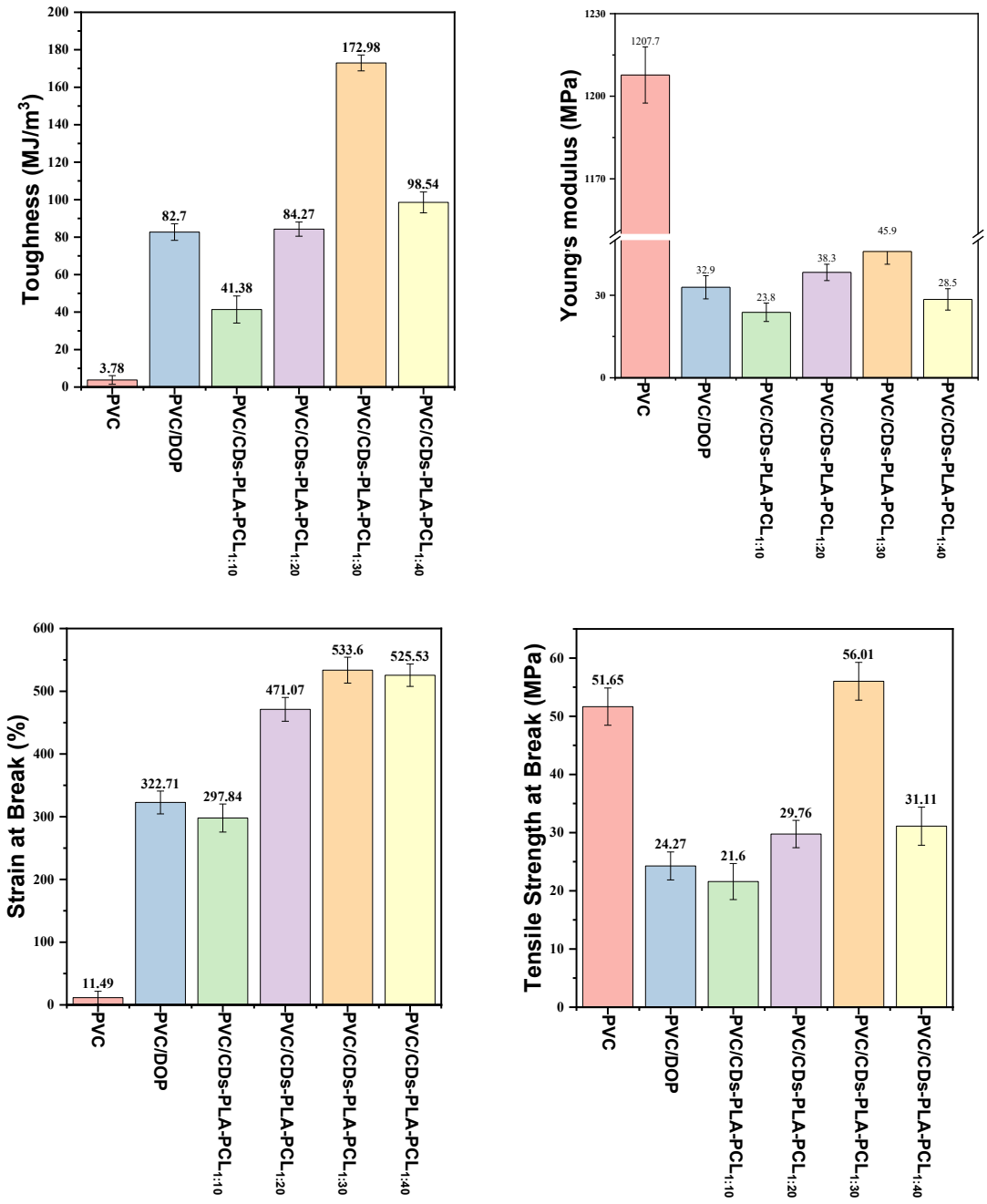


Fig. 18. Bar chart of mechanical data for CDs-PLA-PCL/PVC with different proportions (mean ± standard deviation, n=5)

Under the action of the ester groups, the long flexible alkyl segments of PCL were also inserted between the PVC chains, providing greater free volume for PVC chain mobility and thereby forming a material that was more easily deformable. The presence of PLA provided a rigid chain segment for the flexible PCL chains. Due to the presence of CDs, when stress was applied, PLA-PCL extended in one direction together with the PVC chain segments. To fracture the film, it was necessary to overcome the resistance generated at the PVC/CDs interface; therefore, CDs provided a rigid center for PLA-PCL.

Migration Resistance

As shown in Fig. 19, the migration rate could be observed. The migration resistance of plasticizers is a key parameter for plastic materials used as packaging materials, particularly in the food industry. When the films were immersed in n-hexane at 50 °C for 2 h, the weight loss should not exceed 5.5% for food-packaging applications. As shown in the figure, compared with DOP, after immersion in petroleum ether and n-hexane at 50 °C for 2 h, as well as in water at room temperature, the CDs-PLA-PCL plasticizer exhibited satisfactory migration resistance. The remarkably improved migration stability of CDs-PLA-PCL can be attributed to its high molecular weight and the large number of ester groups in its molecular structure, which can form strong interactions with PVC. Evidently, the prepared CDs-PLA-PCL can be regarded as a non-migrating plasticizer for PVC.

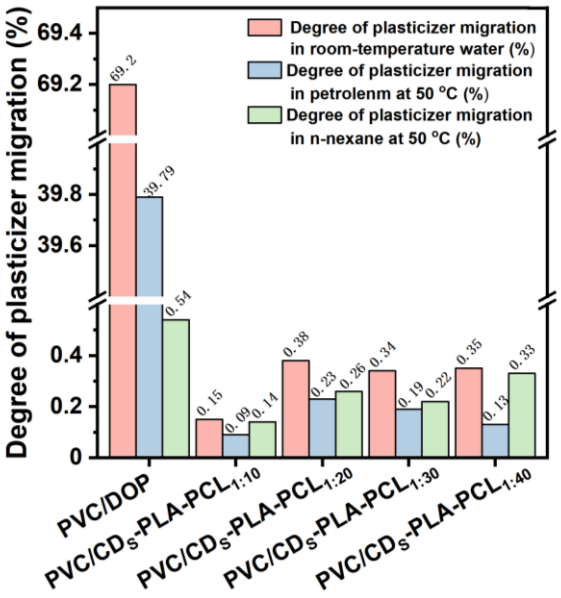


Fig. 19. Migration rates of films prepared from CDs-PLA-PCL with different ratios

CONCLUSIONS

1. Multifunctional carbon dots – poly(lactic acid) – poly(caprolactone) (CDs-PLA-PCL) copolymers composed of luminescent multi-amino carbon dots, rigid polylactic acid segments, and flexible polycaprolactone segments were successfully prepared and applied as green composite plasticizers for poly(vinyl chloride) (PVC). 1H nuclear magnetic resonance (NMR) confirmed the incorporation of PLA and PCL segments, while Fourier transform infrared (FTIR) spectroscopy verified the characteristic ester absorptions and the intensified -OH/-NH hydrogen-bond-related bands after CD incorporation. UV-Vis analysis showed that the plasticized films maintained high visible-light transmittance of approximately 80% to 95%, and fluorescence spectroscopy confirmed that the CDs-containing films retained strong blue emission near 454 nm. Thermogravimetric analysis (TGA) showed that all plasticized PVC films remained stable below approximately 225 °C and underwent the typical two-stage PVC degradation process, confirming suitability for conventional PVC thermal processing.

2. Differential scanning calorimetry (DSC) analysis indicated that CD incorporation adjusted the T_g values of the PVC blends by restricting chain-segment motion, with the T_g data incorporated into the DSC discussion. SEM analysis revealed fibrous fracture morphologies after plasticization, indicating improved ductility and toughness. Mechanical testing identified PVC/CDs-PLA-PCL1:30 as the optimal formulation, with a tensile strength of 56.01 MPa, toughness of 173 MJ/m³, and elongation at break of 534%, while migration testing demonstrated superior resistance to n-hexane water and petroleum ether extraction compared with DOP-plasticized PVC. These findings indicate that the 1:30 CDs-PLA-PCL/PVC blend combined plasticization, reinforcement, fluorescence, thermal processability, and migration resistance, making it a promising multifunctional flexible PVC material for packaging and functional-film applications.

ACKNOWLEDGMENTS

The authors are grateful for support from the following sources: Research on Chlorovinyl Resin and Polycaprolactone Composite as Solid- State Lithium Battery Electrolyte (2025-ZJ-755), Study on Preparation and Properties of Vinylidene Chloride and Acrylate Copolymer Emulsion for PVC Based on Comprehensive Utilization of Salt Lake Resources (2024XJMD02).

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Use of Generative AI

No generative artificial intelligence tools were used in the preparation of this manuscript.

REFERENCES CITED

Ali, M., Lu, Y., Ahmed, S., Khanal, S., and Xu, S. (2020). "Effect of modified cardanol as secondary plasticizer on thermal and mechanical properties of soft polyvinylchloride," *ACS Omega* 5(28), 17111-17117. https://doi.org/10.1021/acsomega.0c00826

Camacho, L., Latendresse, J. R., Muskhelishvili, L., Law, C. D., and Delclos, K. B. (2020). "Effects of intravenous and oral di(2-ethylhexyl) phthalate (DEHP) and 20% Intralipid vehicle on neonatal rat testis, lung, liver, and kidney," *Food and Chemical Toxicology* 144, article 111497. https://doi.org/10.1016/j.fct.2020.111497

Chen, W.-G., Wei, H.-J., Luo, J., Chen, Y., and Cao, P.-F. (2021). "Highly stretchable, ultratough, and multifunctional poly(vinyl chloride)-based plastics *via* a green, star-shaped macromolecular additive," *Macromolecules* 54(7), 3169-3180. https://doi.org/10.1021/acs.macromol.1c00029

Duarah, R., Singh, Y. P., Mandal, B. B., and Karak, N. (2016). "Sustainable starch modified polyol based tough, biocompatible, hyperbranched polyurethane with a shape memory attribute," *New Journal of Chemistry* 40(6), 5152-5163. https://doi.org/10.1039/c5nj03294f

Fariha, S., Islam, M. S., Rockshat, Md., Umme Hani, S., Islam, J., Zabed, H. M., Khandaker, M. U., Rahman, I. M. M., and Chowdhury, F. I. (2023). "Review—Advances in PVC-based blend nanocomposites," *ECS Journal of Solid State Science and Technology* 12(12), article 121005. https://doi.org/10.1149/2162-8777/ad145a

Ferruti, P., Mancin, I., Ranucci, E., and Latini, G. (2003). "Polycaprolactone-poly(ethylene glycol)multiblock copolymers as potential substitutes for di(ethylhexyl) phthalate in flexible poly(vinyl chloride) formulations," *Biomacromolecules* 4(1), 181-188. https://doi.org/10.1021/bm020115q

Han, Y., Weng, Y., and Zhang, C. (2024). "Development of biobased plasticizers with synergistic effects of plasticization, thermal stabilization, and migration resistance: A review," *Journal of Vinyl and Additive Technology* 30(1), 26-43. https://doi.org/10.1002/vnl.22048

Howell, B. A., and Lazar, S. T. (2019). "Biobased plasticizers from glycerol/adipic acid hyperbranched poly(ester)s," *Industrial & Engineering Chemistry Research* 58(37), 17227-17234. https://doi.org/10.1021/acs.iecr.9b03869

Jamarani, R., Erythropel, H. C., Nicell, J. A., Leask, R. L., and Marić, M. (2018). "How green is your plasticizer?," *Polymers* 10(8), article 834. https://doi.org/10.3390/polym10080834

Jia, P., Zhang, M., Hu, L., Feng, G., Bo, C., and Zhou, Y. (2015). "Synthesis and application of environmental castor oil based polyol ester plasticizers for poly(vinyl chloride)," *ACS Sustainable Chemistry & Engineering* 3(9), 2187-2193. https://doi.org/10.1021/acssuschemeng.5b00449

Kong, J., Wei, Y., Zhou, F., Shi, L., Zhao, S., Wan, M., and Zhang, X. (2024). "Carbon quantum dots: Properties, preparation, and applications," *Molecules* 29(9), article 2002. https://doi.org/10.3390/molecules29092002

Lee, K. W., Chung, J. W., and Kwak, S.-Y. (2018). "Highly branched polycaprolactone/glycidol copolymeric green plasticizer by one-pot solvent-free polymerization," *ACS Sustainable Chemistry & Engineering* 6(7), 9006-9017. https://doi.org/10.1021/acssuschemeng.8b01356

Li, Q., Shu, X., Jia, P., and Zhou, Y. (2020). "Preparation of biomass-based ester end-capped hyperbranched poly(ether)s via facile one-pot reaction and their performance as non-toxic plasticizers," *Polymers* 12(4), article 913. https://doi.org/10.3390/polym12040913

Li, Y., Yu, E., Yang, X., and Wei, Z. (2019). "Multiarm hyperbranched polyester-b-Poly(ε-caprolactone): Plasticization effect and migration resistance for PVC," *Journal of Vinyl and Additive Technology* 26(1), 35-42. https://doi.org/10.1002/vnl.21713

Lin, Z.-Z., Wang, Y., Yang, X.-B., Yan, S.-R., Chen, Y., Li, H.-C., and Wang, G. (2023). "Strengthening soft poly(vinyl chloride) plastics *via* three-arm star copolymeric plasticizers," *Materials Today Communications* 35, article 105847. https://doi.org/10.1016/j.mtcomm.2023.105847

Liu, D., Jiang, P., Nie, Z., Wang, H., Dai, Z., Deng, J., and Cao, Z. (2020). "Synthesis of an efficient bio-based plasticizer derived from waste cooking oil and its performance testing in PVC," *Polymer Testing* 90, article 106625. https://doi.org/10.1016/j.polymertesting.2020.106625

Quoc Pham, L., Uspenskaya, M. V., Olekhnovich, R. O., and Olvera Bernal, R. A. (2021). "A review on electrospun PVC nanofibers: Fabrication, properties, and application," *Fibers* 9(2), article 12. https://doi.org/10.3390/fib9020012

Schettler, T. (2006). "Human exposure to phthalates *via* consumer products," *International Journal of Andrology* 29(1), 134-139. https://doi.org/10.1111/j.1365-2605.2005.00567.x

Shi, G., Cooper, D. G., and Maric, M. (2011). "Poly(ε-caprolactone)-based 'green' plasticizers for poly(vinyl choride)," *Polymer Degradation and Stability* 96(9), 1639-1647. https://doi.org/10.1016/j.polymdegradstab.2011.06.007

Sun, Z., Choi, B., Feng, A., Moad, G., and Thang, S. H. (2019). "Nonmigratory poly(vinyl chloride)-block-polycaprolactone plasticizers and compatibilizers prepared by sequential RAFT and ring-opening polymerization (RAFT-T-ROP)," *Macromolecules* 52(4), 1746-1756. https://doi.org/10.1021/acs.macromol.8b02146

Wang, C., Liu, P.-Y., Lin, Z.-Z., Chen, Y., and Li, H.-C. (2024). "Functional highly-stretchable semi-rigid poly(vinyl chloride) plastics via the addition of core-shell type star polyethylenimine-block-poly(ε-caprolactone)," *Reactive and Functional Polymers* 197, article 105855. https://doi.org/10.1016/j.reactfunctpolym.2024.105855

Wang, W.-R., Chen, P.-Y., Deng, J., Chen, Y., and Liu, H.-J. (2022). "Carbon-dot hydrogels as superior carbonaceous adsorbents for removing perfluorooctane sulfonate from water," *Chemical Engineering Journal* 435, article 135021. https://doi.org/10.1016/j.cej.2022.135021

Wang, Y., and Qian, H. (2021). "Phthalates and their impacts on human health," *Healthcare* 9(5), article 603. https://doi.org/10.3390/healthcare9050603

Wei, G., Jiang, P.-P., Gu, Q., Zhang, H. (2020). "Synthesis and properties of a bio-based PVC plasticizer derived from lactic acid," *New Journal of Chemistry* 45, 123-130. https://doi.org/10.1039/d0nj00870b

Zhang, G., Li, J., Sun, S., and Luo, Y. (2019). "Azido-terminated hyperbranched multi-arm copolymer as energetic macromolecular plasticizer," *Propellants Explosives Pyrotechnics* 44(3), 345-354. https://doi.org/10.1002/prep.201800270

Zhang, K., Zhang, K., Cheng, F., Lin, Y., Zhou, M., and Zhu, P. (2018). "Aging properties and hydrophilicity of maize starch plasticized by hyperbranched poly(citrate glyceride)," *Journal of Applied Polymer Science* 136(1), article 46899. https://doi.org/10.1002/app.46899

Zhou, Y., Sharma, S., and Peng, Z. (2017). "Polymers in carbon dots: A review," *Polymers* 9(2), article 67. https://doi.org/10.3390/polym9020067

Article submitted: March 31, 2026; Peer review completed: April 23, 2026; Revised version received: May 13, 2026; Accepted: May 28, 2026; Published: June 9, 2026.
DOI: 10.15376/biores.21.3.6825-6845