



# Cavitation-crazing transition in rubber toughening of poly(lactic acid)-cellulose nanocrystal composites

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## ABSTRACT

In this work, the mechanism behind rubber toughening of poly(lactic acid)/cellulose nanocrystal-g-rubber-g-poly(D-lactide) (CNC-rDx-PDLA) composites was elucidated through systematic study of the effects of rubber segment content (length) in CNC-rDx-PDLA nanofillers and the nanofiller concentrations on the deformation behavior of the nanocomposites. It was shown that with an increase of rubber segment length and rubber filler concentration, the elongation at break of the resulting composites increased. Moreover, a dramatic increase in elongation at break (from 20% to 200%) was observed when the rubber segment content (length) in the CNC-rDx-PDLA nanofillers was increased from 52 to 68%. Cavitation mechanism was found dominant when the rubber segment content in the nanofillers was 52% and below, whereas, stable crazes were formed and followed by fibrillation when the rubber segment content in the nanofillers was increased to 68%, which was evident by small angle X-ray scattering (SAXS) study and scanning electron microscopy (SEM) analysis. The existence of a transition from cavitation to crazing in the composite systems could be attributed to a more mobile rubber phase because of longer rubber chain length. Our study suggests that the effective toughening mechanism for thermoplastics such as PLA is crazing induced plastic deformation.

## 1. Introduction

Poly(lactic acid) (PLA) is regarded as the most promising bio-based biodegradable polymer, with respect to its overall properties [1]. Additionally, PLA is among the bio-based polymers that are generally recognized as safe (GRAS) by America's Food and Drugs Administration (FDA), to humans and the environment. This has led to intense research on PLA applications in biodegradable and environmentally benign products, as substitutes to petrochemical-based products [2,3]. Nevertheless, PLA does not meet stringent marketplace requirements for high performance applications, especially due to its brittleness [4]. However, toughness limitations of PLA can be altered elegantly through many strategies, such as blending with other flexible polymers/copolymers or rubbers, copolymerization, plasticization, filler addition, and stereocomplexation and so on [1,5–8].

Rubber toughening for brittle polymers, such as PLA, is a widely

accepted technique in the polymer world [8,9]. In this technique, rubber particles delocalizes the strain in brittle polymers, thereby enhancing the impact energy absorption [10,11]. However, improvement in toughness or ductility is often achieved with some sacrifice in stiffness and strength. Nonetheless, enhanced material performance can be achieved by designing 'core-shell' rubber tougheners with stereocomplexed interface [6,7]. Stereocomplexation between stereospecific PLLA and PDLA – an important discovery in 1987 – opened a new fabrication technique of materials with enhanced thermal and mechanical properties [12,13].

Recently, many studies have reported the inclusion of rubber-like flexible copolymers/elastomers, capable of forming stereocomplex for PLA toughening. For instance, Sun et al. [14] fabricated biodegradable PLLA/lignin-rubber-PDLA composites with enhanced elongation at break of about 180%. This improvement was attributed to the presence of rubber and good interface adhesion through stereocomplex

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formation. In another study, Purnama et al. [15] reported enhanced melt stability of PLA by the inclusion of poly(D-lactide-co-ε-caprolactone) (PDLCL) with small CL content (~2.5%). The enhancement was ascribed to the increased chain mobility induced by neighboring participation of antiparallel structures. In a similar study, Odent et al. [16] incorporated 10% P(CL-co-LA) copolyester in PLA, and obtained over 400% increase in impact energy (~11.4 kJ/m<sup>2</sup>) compared to neat PLLA (~2.7 kJ/m<sup>2</sup>).

In a previous work [6], highly biodegradable and flexible CNC-rD-PDLA nanofillers with CNCs as core, P(CL-LA) or rubber as middle layer, and PDLA chains were reported. The CL/D-LA molar ratio was 2:1, and the rubber segment content of about 68%. These nanofillers were incredibly effective in enhancing the tensile toughness of PLA; for instance, PLLA/2.5% CNC-rD-PDLA had over 180% strain at break. Such enormous mechanical properties' improvements were attributed to the rubber segment content in the nanofillers and the interface control through stereocomplexation.

In this present work, slight reduction in the rubber segment content (length) to 52 wt% from 68 wt% in the nanofillers resulted in dramatic decrease in the elongation at break to ~20% from 187%. Such a drastic change in elongation at break alludes to the fact that the length of the rubber segment rather than the concentration of the nanofiller has a profound effect on the deformation mechanism. Polymers deform in three distinct ways: shear banding i.e. deformation through bulk flow of polymer chains without changing the volume; crazing which is described as a tension-induced deformation through formation of load-bearing fibrils; and cavitation which involves the formation of microvoids to dissipate local stress [17,18].

It has been widely reported in literature that cavitation and crazing in polymers are in competition, and many questions regarding this competition remain unsolved to date [19–21]. The present work investigates the effect of the addition of nanofillers on the toughening and deformation behavior of PLLA/CNC-rDx-PDLA nanocomposites, with a focus on the effect of rubber segment length in the nanofillers. To the best of our knowledge, such a systematic study has not been reported so far. The results presented in this study bring new insight that could help in predicting the macroscopic mechanical behavior of semi-crystalline polymers.

## 2. Experimental

CNC-rDx-PDLA nanofillers with varying rubber segment length (rDx) were prepared by sequential ring opening polymerization (ROP), where x refers to rubber segment contents in the nanofillers (wt% in feed). The detailed synthesis, characterization procedures and feed compositions of CNC-rDx-PDLA nanofillers and PLLA/CNC-rDx-PDLA nanocomposites are presented in the [supporting information](#).

## 3. Results and discussion

### 3.1. Characterization of CNC-rDx-PDLA nanofillers

The chemical structures of the graft copolymers were confirmed using <sup>1</sup>H NMR. Fig. 1 shows the overlay patterns of <sup>1</sup>H NMR spectra of CNC-rDx-PDLA nanofillers. CNC-rD0-PDLA has chemical shift peaks assigned only to PLA at δ = 5.2 and 1.6 ppm, for –CH and –CH<sub>3</sub>, respectively. All other CNC-rDx-PDLA nanofillers exhibit additional peaks at chemical shifts of 1.3, 1.6, 2.3 and 4.06–4.16 ppm assigned to methylene (–CH<sub>2</sub>) protons from PCL, indicating successful grafting of the rubber segments and PDLA blocks onto the CNC surface [6,22]. It is worth noting that the intensities of the peaks assigned to PCL decrease with decreasing the rubber segment contents in the nanofillers.

WAXD was used to determine the structures of the nanofillers and elucidate the effect of the rubber segment content on the structures as seen in Fig. S2. CNC diffraction peaks (β and α) are not clearly displayed in nanofillers, probably due to low CNC content or overlapping

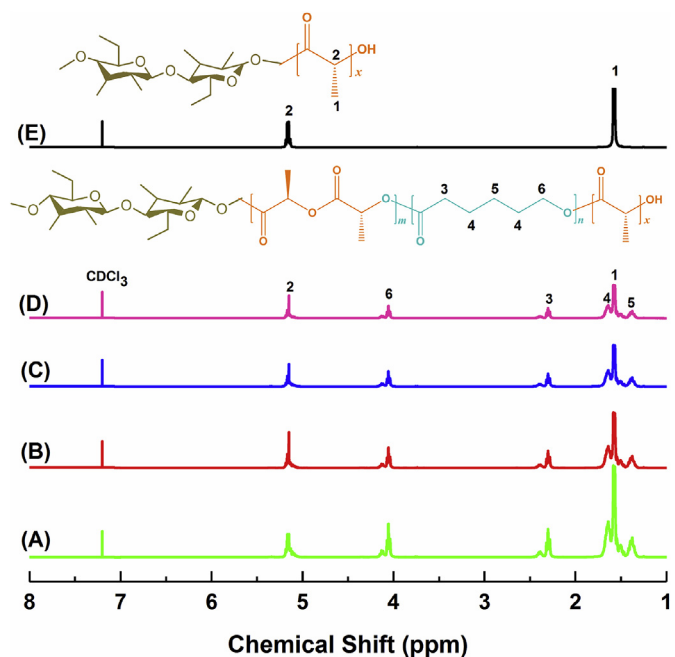


Fig. 1. <sup>1</sup>H NMR spectra of (A) CNC-rD68-PDLA, (B) CNC-rD52-PDLA, (C) CNC-rD35-PDLA, (D) CNC-rD21-PDLA, and (E) CNC-rD0-PDLA nanofillers in CDCl<sub>3</sub>.

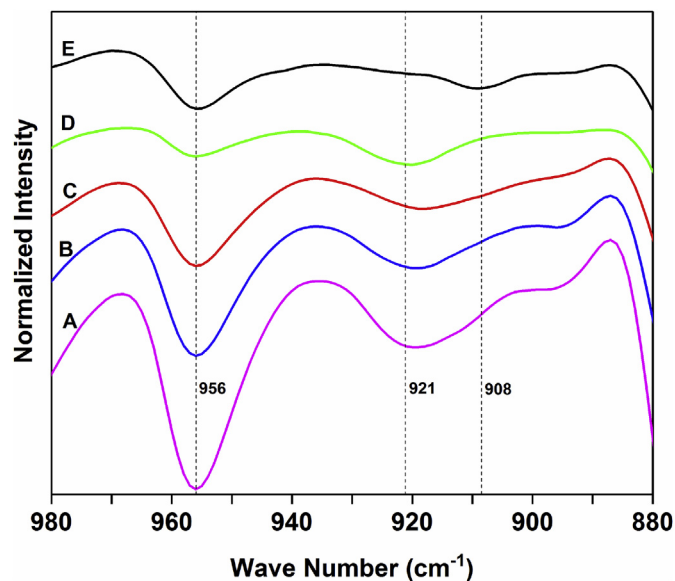


Fig. 2. IR spectra for PLLA/10% CNC-rDx-PDLA nanocomposites with (A) rD68, (B) rD52, (C) rD35, (D) rD21 and (E) rD0.

with PLA and PCL peaks or [6]. CNC-rD68-PDLA displays a broad ‘diffraction halo’ with low peak intensities. This observation agrees with the presence of high rubber segment content in the nanofiller and low crystallinity. The amorphous part becomes smaller when the rubber segment content in the nanofillers reduces, resulting in sharper diffraction peaks due to enhanced crystallinity.

DSC characterization reveals that all the nanofillers have a glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ) and melting temperature ( $T_m$ ) as seen in Fig. S3. The  $T_g$  increases with decreasing the rubber segment contents, shifting from –38 °C for CNC-rD68-PDLA to about 70 °C for CNC-rD0-PDLA. Moreover, all the nanofillers exhibit a cold crystallization ( $T_{cc}$ ) in the range of 50–100 °C and a melting ( $T_m$ ) peak between 130 and 170 °C (Fig. S3). Clearly, the increase in rubber segment contents in the nanofillers affects the cold

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