

Preparation of A Dynamically Vulcanized Nanocomposite Thermoplastic Based on PLA/NR and Cellulose Nanocrystal (CNC)

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Submitted: 12 Dec 2022; Accepted: 24 Dec 2022; Published: 03 Jan 2023

Citation: Naeini, N. H., Katbab, A., Tabashi, S., Kiani, A. (2023). Preparation of A Dynamically Vulcanized Nanocomposite Thermoplastic Based on PLA/NR And Cellulose Nanocrystal (CNC). *World J Clin Med Img*, 2(1), 01-06.

Abstract

Dynamically vulcanized nanocomposite thermoplastic based on poly (lactic acid) (PLA)/natural rubber (NR) is prepared through a dynamic curing process. The cross-linked NR phase exhibits a continuous network structure embedded in the PLA phase, which differs from the conventional plastic/rubber system with an "island-sea" morphology in which vulcanized rubber particles are dispersed in the plastic matrix. Its favorable internal interfacial compatibility was confirmed by SEM analysis.

Also, CNC has been used as a sustainable additive to improve the mechanical properties of PLA/NR thermoplastic vulcanizate (TPV). To achieve homogeneous dispersion of CNC, the melt mixing method was used. The mechanical properties were considerably enhanced by CNC addition, which increased from 14% of the unfilled TPV to 70% of the sample with CNC (1.5 phr relative to PLA).

The "green" raw materials and high mechanical properties of PLA/NR/CNC prepared from the dynamic curing process are expected to open up a wide range of potential applications in the fields of smart medicine.

Keywords: Poly (lactic acid), Nanocomposite, Natural Rubber, Cellulose Nanocrystal, Biodegradable Polymers.

Introduction

In recent years, due to increasing environmental awareness, crude oil prices and the challenges associated with global warming, attention to biopolymers has increased. As biopolymers are obtained from renewable sources and are biodegradable, their use has minimal negative environmental effects compared to polymers based on petroleum compounds. Today, these compounds are used in various fields such as physiotherapy, pharmacy, medicine, coating, food products and packaging materials [1, 2].

The most important and commonly used biodegradable polymers are aliphatic polyesters, such as polylactic acid (PLA), poly(3-hydroxybutyrate) (PHB), polycaprolactone (PCL), polyglycolic acid (PGA) and polyethylene oxide (PEO) [3]. Although these biodegradable polymers have wide range of mechanical and physical properties and degradation rate [4].

Inappropriate stiffness or degradation rate still restrict their usages, therefore, it is best to blend with other polymers, copolymerize or add plasticizer to enhance their properties according to application needed [5].

Poly(lactic acid) (PLA), is one of the most promising biopolymers due to the fact that the monomers may be produced from non-toxic renewable feedstock as well as its naturally occurring organic acid [6]. Lactic acid can be made by fermentation of sugars obtained from renewable resources such as sugarcane. Therefore, PLA is an eco-friendly product with better features for use in the human body (nontoxicity) [7, 8].

PLA has good mechanical properties, thermal plasticity, and biocompatibility. However, PLA is a comparatively brittle and stiff polymer with low deformation at break. Therefore, modification of PLA is needed in order to compete with other flexible poly-

mers such as polypropylene or polyethylene [9]. There are many techniques to modify PLA such as copolymerization [10, 11] blending with other polymers [12-14] the addition of plasticizers [15] the addition of nucleating agents [16, 17] and forming composites with fiber or nanoparticles [18, 19].

Increasing the impact strength of PLA and improving its flexibility is mostly done by mixing it with a curing agent. Elastomers have also been used to reduce the brittle behavior and increase toughness. There are reports of using Natural Rubber (NR) to improve toughness [8]. In fact, this elastomer is used as a suitable shrinking agent due to its low glass transition temperature, high strength,

high elasticity and high strain to failure [20]. On the other hand, most polymer materials, including PLA and NR, are immiscible with each other. Therefore, in order to achieve the desired properties, it is necessary to create compatibility between the components of the mixture [1, 21].

Recently, there has been an increase in interest in using natural fibers to replace synthetic fibers in polymer composites due to their compatibility with the environment and renewability. These composites reinforced with natural fibers have acceptable mechanical properties and a number of well-known advantages such as light weight, low density, low cost, availability, biodegradability, high mechanical strength, low hardness, renewability and the ability to be recycled. Cellulose mainly exists naturally in plants and is also synthesized by algae, tunicates and certain types of bacteria [22].

Cellulose NanoCrystals (CNCs) are ideal candidates as nanomaterials for nanotechnology due to their nanofibrous structure [23] abundance, biodegradability, renewability, and multipurpose capability, and they can replace expensive and non-degradable synthetic fibers. CNCs can be synthesized from native cellulosic source materials by different means [22, 24]. It has been determined that CNCs are good reinforcing fillers in a wide range of polymeric matrices due to their high specific modulus, hardness, nanoscale dimensions and high phase ratio [22, 25, 26].

The objective of this paper is to investigate the effect of addition of cellulose nanocrystal on the mechanical properties of PLA/NR blend. Various characterization techniques such as Scanning Electron Microscopy (SEM) and mechanical test such as tensile properties were used to study the effect of addition of CNC on the properties of PLA/NR blend.

Experimental Materials

In this study poly(lactic acid) with a density of 1.24 g/cm³ was purchased from Nature Work (PLA 2003D) as the matrix and was used as received. The natural rubber used in this paper was brought from Malaysia (SMR-GP) with a density of 0.9125 g/cm³. And finally, the cellulose nanocrystal was supplied from Nanografi Products (Nanocrystalline Cellulose,CNC) with a density of 1/49 g/cm³.

EPDM-g-MAH and Dicumyl Peroxide (DCP) were also used along the way which were obtained from China.

Preparation of PLA/NR/CNC Nanocomposites

In this polymeric system, in order to mix homogeneously and at the same time to form droplet-matrix morphology, it is very important to find an optimal mixing condition in terms of time, phase ratios of ingredients, mixing rotor speed and etc. In order to optimize this, the changes in the melting torque during the mixing process (which itself indicates changes in the morphology of the system and the degree of phase interaction) should be investigated. Finally, to stabilize the morphology, a curing system is needed in the system. In this research, simple blends and cured samples were prepared by melt mixing method and by internal mixer in under 10 minutes in 150 °C with rotor speed of 60 rpm fed into Brabender Plastograph EC. At first, we started by adding PLA, then after about 1-2 minutes EPDM-g-MAH and CNC was added. Followed by the addition of NR after about 4-5 minutes, and 2 minutes before reaching 10 the curing agent was added (2 phr relative to NR). The samples were then removed from the internal mixer and were cooled down to room temperature.

In order to prepare sheets for further testing, the blends were first preheated by an electrically heated hydraulic press without any pressure under 170 °C for 2 minutes, then they were compression molded under a pressure of 85 kg/cm² at 170 °C for another 4 minutes and cold-pressed at room for about 5 min to avoid shrinkage. Finally, samples with thickness of 1 mm were obtained for measurements and testing [27].

The sample codes and compositions of different TPVs are shown in Table 1. It should be noted that the content of DCP was fixed as 2 phr of NR, and EPDM-g-MAH was fixed as 1 phr of the total content of (PLA+ENR) and at last CNC was used relative to PLA. For example, for DV-1.5, the mass of PLA, NR, CNC, DCP and EPDM-g-MAH were 70 g, 30 g, 1.05 g, 0.6 g and 1 g, respectively.

Table 1: Sample codes of different TPVs

Sample Codes	Description
P100	Pure PLA
BPxNy	Simple blend of x percentages of PLA and y percentages of NR
DPxNy	Cured blend of x percentages of PLA and y percentages of NR
DPxNyECz	Cured blend of x percentages of PLA, y percentages of NR, z phr of CNC relative to PLA and EPDM-g-MAH

Tensile Properties

The tensile test was performed by Galdabini Machine model Sun 2500 made in Italy. The samples were prepared and stamped according to ASTM D638 standard dumbbell parameters. The test was conducted with a load of 50 N at a constant tension rate of 5 mm/min.

Scanning Electron Microscopy (SEM)

As we know, the properties of polymers (both mechanical and shape memory) are highly dependent on the microstructure of the sample. For this purpose, the surface morphology of fracture surfaces of tensile test samples was analyzed with Scanning Electron Microscope (SEM) Strautum es sais-2100 via voltage of 0.5 to 30 volt and the magnification of 5 to 50 μm. Before viewing, the specimens were broken in nitrogen liquid and were

then coated with a thin layer of gold.

Results and Discussions

Tensile Properties

The typical stress-strain curves of the simple blends with different phase ratios are shown in figure 1, and the corresponding detailed mechanical properties are summarized in Table 2. As can be clearly seen, tensile strength (TS), yield strength (YS), Young's modulus (YM) and also elongation at break (EB) of the simple blends were all improved in the phase ratio of P70/N30. Therefore, in this project, this phase ratio has been used for further characterization.

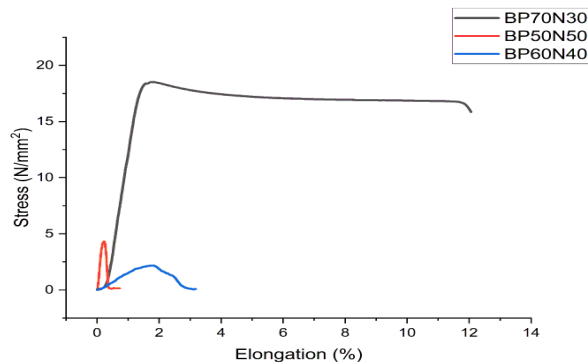


Figure 1: The typical stress-strain curves of the simple blends with different phase ratios of 50/50, 60/40 and 70/30.

Table 2: Mechanical properties of simple blends with different phase ratios of 50/50, 60/40 and 70/30.

Sample codes	Young Modulus (N/mm ²)	Elongation at break (%)	Stress at break (N/mm ²)	Stress at Maximum Load (N/mm ²)	Elongation at Yield (%)	Stress at Yield (N/mm ²)
BP70N30	1765.16	12.06	15.85	18.39	1.59	18.39
BP60N40	164.31	3.18	0.08	2.17	1.82	2.17
BP50N50	229.90	0.73	0.14	4.31	0.24	4.31

TPVs with different CNC content were also tested and their mechanical properties are presented in figure 2, and their mechanical properties are summarized in Table 3. As can be clearly seen, tensile strength (TS), yield strength (YS) and Young's modulus (YM) of the TPVs were all improved with increasing the content of CNC to 1.5 phr.

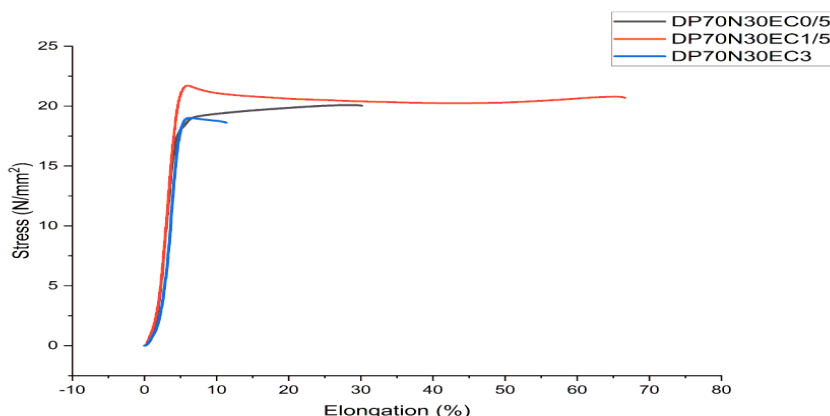


Figure 2: The typical stress-strain curves of the TPVs with different CNC content of 0.5, 1.5 and 3 phr relative to PLA for P70/N30.

Table 3: Mechanical properties of the TPVs with different CNC content of 0.5, 1.5 and 3 phr relative to PLA for P70/N30.

Sample codes	Young Modulus (N/mm ²)	Elongation at break (%)	Stress at break (N/mm ²)	Stress at Maximum Load (N/mm ²)	Elongation at Yield (%)	Stress at Yield (N/mm ²)
DP70N30EC0/5	621.19	30.11	20.04	20.04	4.41	17.08
DP70N30EC1/5	652.14	70.01	20.69	21.71	5.95	21.71
DP70N30EC3	626.04	11.33	18.62	19.01	6.33	19.01

As it can be concluded in this section, the presence of 1.5 phr CNC can significantly raises the elongation rate at break and also the area under the curve. However, by increasing the CNC content to 3 phr a decrease in mechanical properties is seen due to overpassing the percolation threshold. So, in the rest of this paper only blends with 1.5 phr CNC will be discussed.

Scanning Electron Microscopy (SEM) test results

By comparing with the figure 3, it is possible to see the droplet structure of NR in PLA, which represents the droplet-matrix morphology of the system. In fact, in general, in immiscible binary polymer mixtures, the phase with a lower concentration, such as a droplet, is dispersed within the phase with a higher concentration (matrix). As the percentage of the component increases, the size of the dispersed phase decreases due to the phenomenon of dispersion. The viscosity increases by 20. Also, at higher percentages of rubber, the dispersed phase will become co-continuous which is the case with the phase ratio of 50/50.

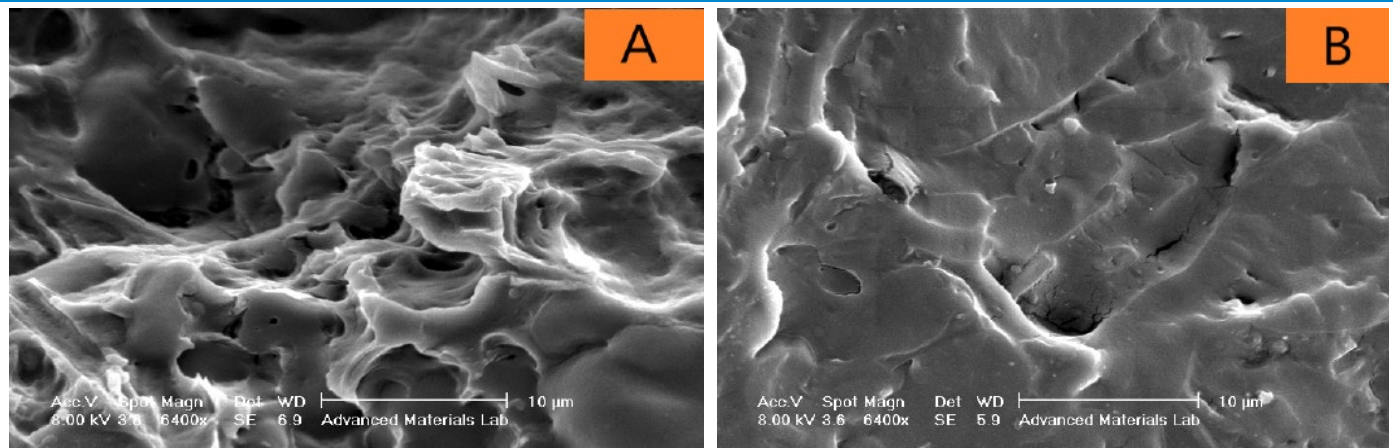


Figure 3: The SEM images of cold fracture surface (in liquid nitrogen) of final samples of P70N30 and P50N50 in the scale of 10 micron: A) DP70N30EC1/5 B) DP50N50EC1/5.

The effect of CNC on the morphology in the SEM images from the cold fracture surface of samples is brought in figure 4. By comparing these images, it can be concluded that by adding CNC to P70/N30 sample, a decrease in the size of the rubber droplet is seen. This change can be observed with the addition of CNC, that is, the thickness of rubber “wall” increased gradually with increasing the content of CNC. This is due to that CNC is an excellent reinforcing filler for NR, both strength and modulus of rubber phase can be improved with the addition of CNC [28, 29]. In fact, two main factors can be a cause of that: 1- the presence of CNC resulted in the increase of matrix phase’s viscosity and with the increased applied force the rubber droplet decreased and 2- the compatibility role that CNC plays is another reason of it.

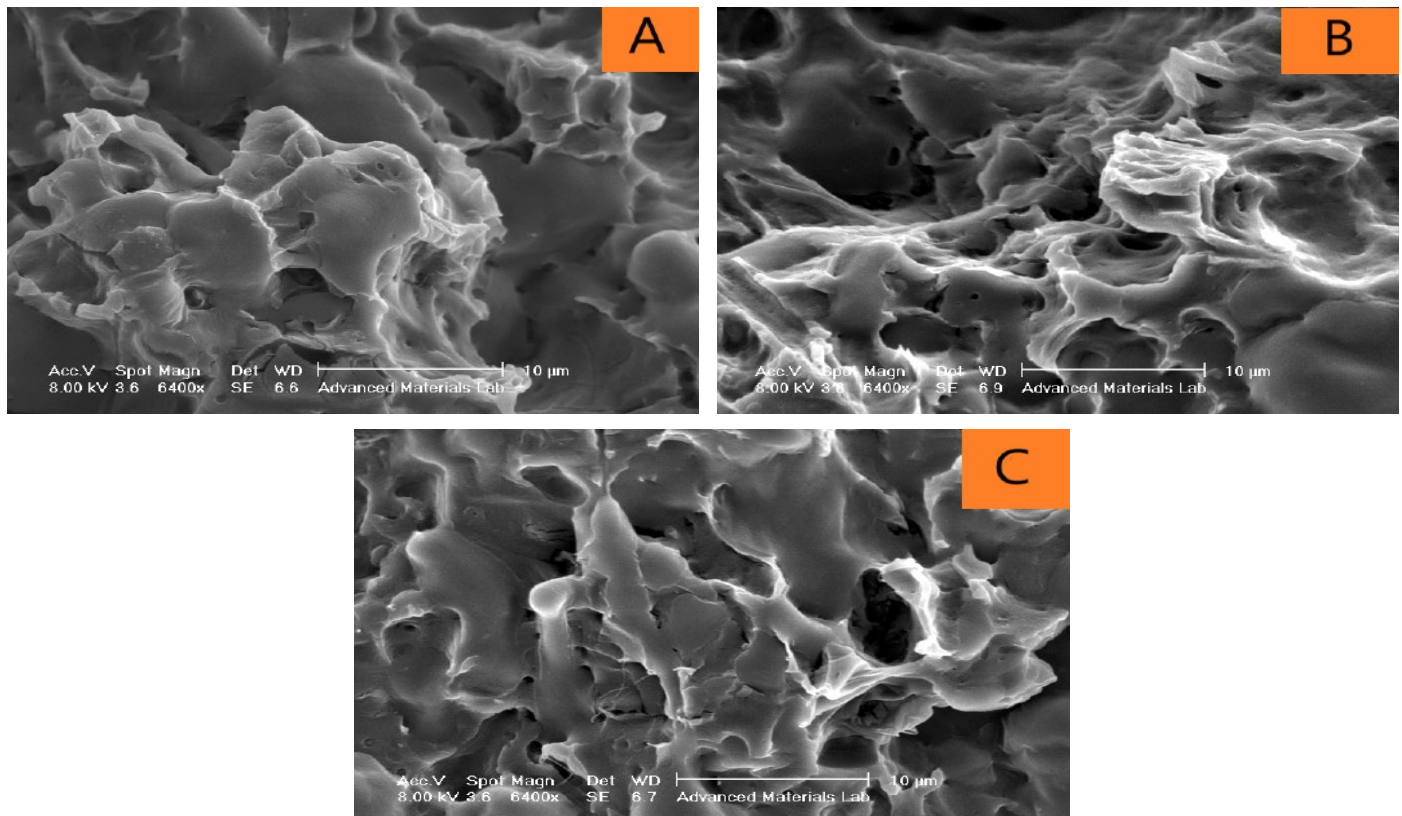


Figure 4: The SEM images of cold fracture surface (in liquid nitrogen) of P70/N30 samples with different CNC content in the scale of 10 micron.

As can be seen in figure 5, a decrease in rubber’s droplets size has been observed by increasing the CNC content from 0.5 phr to 1.5 phr (6.65 µm to 4.55 µm). The size distribution has improved as well. Yet, by increasing the CNC content from 1.5 to 3 phr and surpassing the percolation threshold, a decrease in size and has been seen.

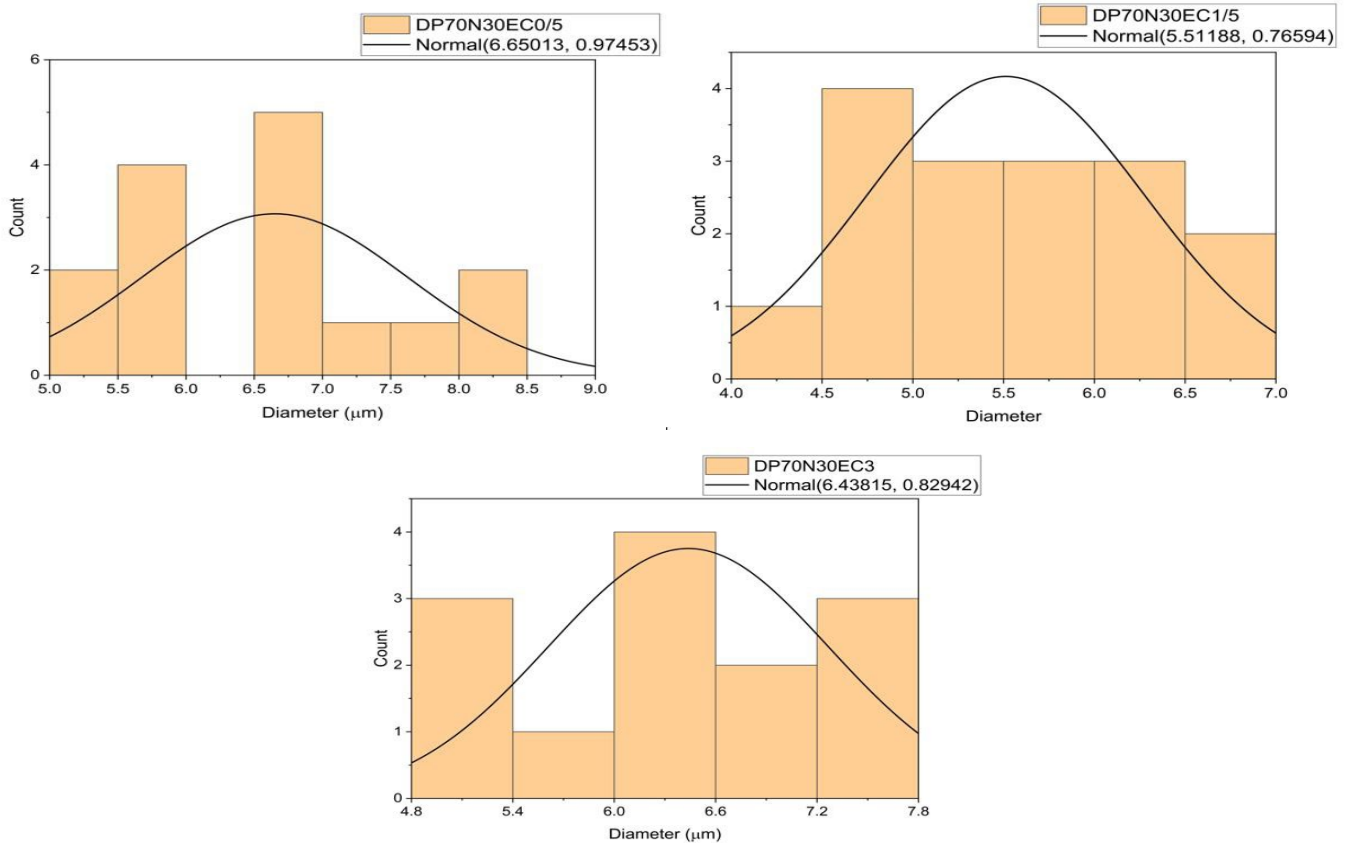


Figure 5: Rubber's size distribution in P70/N30 for various CNC content: 0.5, 1.5 and 3 phr.

Conclusion

In this work, to improve the brittle behavior of PLA, we blend it with natural rubber and used CNC as a reinforcer. As expected, a high reinforcing effect is observed even at low filler contents when using this nanofiller to prepare nanocomposites with a natural rubber (NR). Prediction of placement of CNC, in the blend studied, showed that CNC tends to be present in the PLA phase. By studying the effect of the presence and concentration of CNC on the tensile properties, it was observed that the addition of NR to PLA reduces the tensile strength and also the modulus; but increases the elongation at break and the area under the curve as well. Adding 1.5 phr CNC to this mixture increased the Young modulus and decreased the strain to failure and toughness. For instance, the elongation at break has increased 23.3 times higher than the pure PLA itself and 6 times higher than the simple blends. With the presence of 3 phr CNC, the modulus increased to some extent, the strength did not change much, and the elongation at break also decreased. The SEM tests exhibited the compatible effect of CNC. So, it can be concluded that the high phase ratio of the CNC is involved in the good mechanical results. An important contribution of this work is to highlight the importance of CNC in increasing the elongation at break and the compatibility of these two immiscible polymers. This polymeric system is expected to show great shape-memory behavior in future research.

Acknowledgments

We gratefully acknowledge Polymer and Color Department of AmirKabir University for providing the equipment and technical support and Labsnet for providing financial support for testing.

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