RESEARCH ARTICLE

Mussel-inspired double cross-linked interpenetrating network with unique mechanical properties using di-diol complexation

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Abstract

Polymer nanocomposites with exceptionally high mechanical properties owing to strong interfacial attraction have garnered tremendous interest in the research community. In general, tough and robust polymer nanocomposites are usually obtained via dispersing a nano-flaky filler in the polymer matrix, although the strategy is only sometimes practically viable. To this end, in this work, a facile strategy has been adopted to achieve a strong and tough polymer nanocomposite. A novel mussel-inspired full interpenetrating polymeric network (IPN) consisting of polyvinylalcohol and polydopamine was prepared. This technique helped integrate the advantages of dopamine chemistry with forming a full IPN using Borax as a common crosslinker. The infusion of 1 wt% acid-modified carbon nanotubes (ACNT) in the IPN matrix helped greatly improve the current state-of-the-art. The synergistic effect of nano-reinforcement and formation of ester linkage through a substantial amount of di-diol complexation dominated and accounted for the significant enhancement of mechanical properties. This is further supported by decreased intensity of free —OH groups in the FTIR investigations, viscosity enhancement from rheological behavior, and temperature-dependent dynamic mechanical property analysis. Such an IPN structure is a promising way to enhance mechanical properties.

KEYWORDS

borax, carbon nanotube, interpenetrating polymeric network, mechanical properties, polydopamine, polyvinyl alcohol

1 | INTRODUCTION

Fabricating high-performing polymer-based composite is necessary to bridge the inherent gap between physics, chemistry, and polymer and explore engineering

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applications.[1] In the recent past, the incorporation of carbonaceous nanostructured materials such as graphene, graphene oxide, Carbon Nanotubes (CNTs), cellulose nanofiber, and so forth, bearing high aspect ratio, in the polymer matrix has gained popularity as an effective nano-reinforcement for the strategic formulation of stable polymer nanocomposite.[1] However, the maintenance of mechanical integrity is an inevitable requirement for the design of such high-performance polymer nanocomposites. Therefore, several attempts have been made to develop high-strength and easily processable polymer nanocomposites, infusing carbonaceous nanofillers in the polymer matrix.[2] Techniques such as covalent cross-linking,[3,4] organic–inorganic hybrid,[5] introducing cationic groups with bulky substituents, and so forth, have been thoroughly reported for formulating such nanocomposites.[6]

In this perspective, an interpenetrating polymer network (IPN) utilizing two or more polymers could effectively enhance mechanical properties.[7] In semi-IPNs, one linear polymer is entrapped within the cross-linked network of another polymer and utilizes the advantages of each component, which in turn synergistically improves the mechanical properties.[8] In full IPN each polymer component polymer forms a cross-linked network that is intertwined with the other polymer network and bears the properties of both polymers.[9] The utmost benefit of IPN-based systems is the highly entangled network resulting in mechanically strengthened composites.

To further explore the concept of full IPN in enhancing the mechanical properties, we have focused on the fabrication of doubly cross-linked IPN composites composed of poly (vinyl alcohol), dopamine, and Borax. The rationale for choosing PVA can be further justified due to its eco-friendly, bio-compatible nature along with hydrophilicity, good adhesion, high water content and most importantly high mechanical strength.[10] The final fabricated system is mussel inspired material since the chemical structure of dopamine is analogous to the mussel foot proteins. The proteins help the mussels to adhere to a wide range of substrates which is similar to the properties induced by dopamine when it is integrated with any system. The term "mussel-inspired" in the title, demonstrates how an advanced and highly multifunctional material can be engineered and developed using MIMs (mussel-inspired materials). However, for target-specific applications requiring mechanical strength several carbonaceous nanofiller like graphene oxide,[1] CNT, CNF, and so forth, have been incorporated into a neat PVA matrix.[1]

As discussed earlier, the fabrication of suitable IPNs is advantageous upon addition of one component while maintaining the key attributes of another which in turn
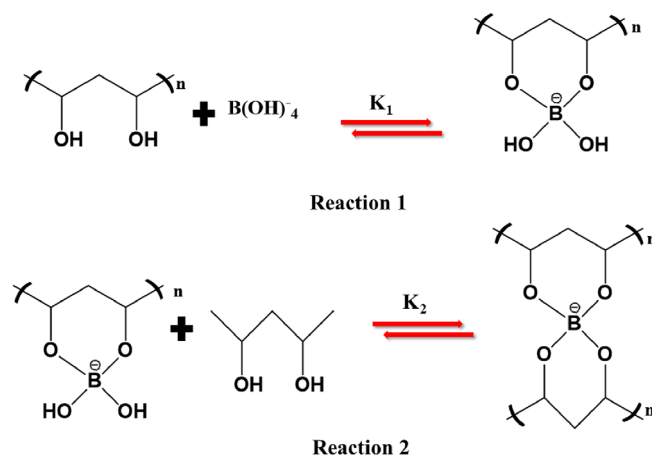

FIGURE 1 Di-diol mechanism of PVA and borax.

purposefully serve the enhancement of mechanical strength.[11,12] In line with this, poly(vinyl alcohol)/polydopamine (PDA) sequential IPN via in situ polymerization of dopamine in PVA matrix has been designed. Further, a common crosslinker Borax was used to confirm the formation of full IPNs where two independent networks of PVA and PDA can be cross-linked via di-diol complexation through the intra- and intermolecular hydrogen bonding. Along with this 1 wt% acid functionalized CNT (ACNT) was added to investigate the synergistic effect of the reinforcing filler in the mechanical properties of the full IPN composite film composed of PVA/PDA/Borax.

Usually, Borax is used as a crosslinker for PVA-borax hydrogels after dissolution in water to form equal amounts of boric acid ($B(OH)_3$), $[B(OH)_4]^-$ and Na^+ (Equation 1).[13,14]

$$Na_2B_4O_7 \cdot 10H_2O = 2B(OH)_3 + [2B(OH)_4]^- + 2Na^+ + 3H_2O \quad (1)$$
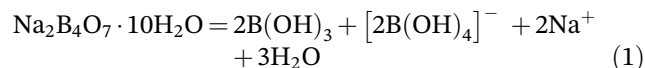
When Borax is mixed with PVA solution maintaining proper formulation, the crosslinking is anticipated to undergo two-step process, that is, firstly, two of the hydroxyl group of $[B(OH)_4]^-$ reacts with alternating —OH groups of PVA to form a monodiol complex; and in the second step the other two —OH groups of the boron atoms in the borate, react with another adjacent diol of PVA leading to di-diol complexation as schematically presented in Figure 1.[13] However, in the presence of PDA the catechol moieties of PDA can also take part in diol complexation in the second step to form a doubly cross-linked network where Borax acts as a common crosslinker or bridge between PVA chain and in situ polymerized PDA. Thus, introducing a common crosslinker has the advantage of forming a full IPN composed of

FIGURE 2 Schematic synthesis route of the PVA and PD film for dynamic mechanical testing.
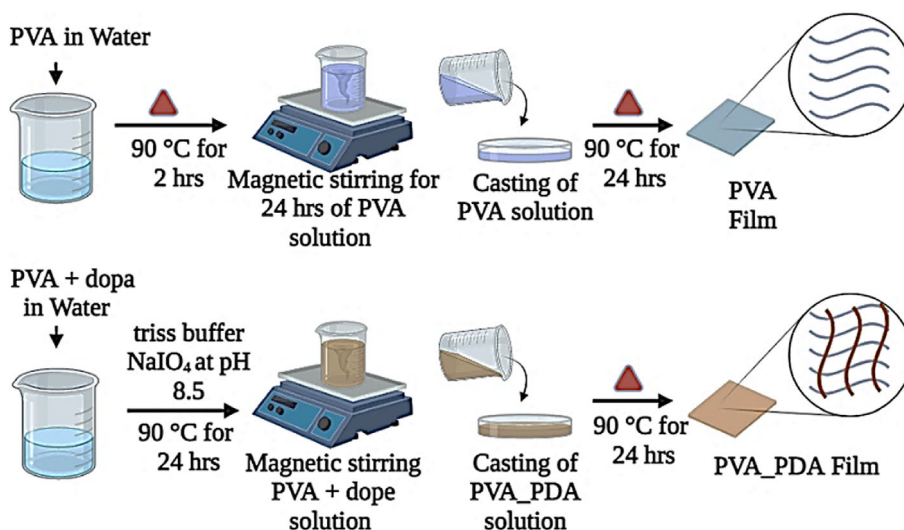
two cross-linked networks through their molecular-level interpenetration.[15] This novel strategy has not been reported so far. It is anticipated to lead to improved mechanical strength compared to single network sequential PVA/PDA or semi-IPN, which could be further strengthened from a rheological point of view and dynamic mechanical analysis (DMA).

2 | EXPERIMENTAL PROCEDURE

2.1 | Materials and methods

2.1.1 | Materials

A pristine multi-walled carbon nanotube (NC7000, length of 1.5 μm and diameter of 9.5 nm) was purchased from Nanocyl SA (Belgium). Dopamine hydrochloride (M_w = 189.64 g/mol), Poly (diallyl dimethyl ammonium chloride) (PDDA, avg. M_w = 200,000–350,000, 20 wt% in water) and di-sodium tetraborate decahydrate (Borax) were procured from Sigma Aldrich. Polyvinyl alcohol (PVA, M_w = 85,000–124,000 g/mol), and Sodium Hydroxide pellets (AR grade) were procured from SD Fine Chemicals Ltd. (SDFCL, Mumbai). Sodium periodate ($NaIO_4$, >99.8%) and Tris(hydroxymethyl)aminomethane (99.8%–100%) were obtained from Sisco Research Laboratories (SRL) Pvt. Ltd.

2.1.2 | Fabrication of PVA film

A facile method in which 6 g Polyvinyl alcohol (PVA) and 60 mL deionized water are taken in a 200 mL beaker. The resulting mixture is allowed to heat at around 90°C for 24 h in closed conditions, followed by pouring in a flat glass Petridis for easy water evaporation. After this, the

mixture is kept at 90°C overnight to get a translucent freestanding film. Figure 1 shows the schematic of the synthesis of the PVA film.

2.1.3 | Preparation of PVA-PDA film (PD)

To prepare the PVA-PDA film, 6 g PVA is dissolved in 60 mL of hot deionized water. In the hot viscous mixture, tris(hydroxymethyl)aminomethane (tris buffer) 485 mg, sodium meta periodate 22 mg are added, and the solution pH is maintained to 8.5, followed by the addition of dopamine hydrochloride 50 mg. The deep brown sticky solution is allowed to stir for 24 h and poured in a Teflon sheet. It was then kept at 90°C overnight resulting in a deep brown freestanding PVA-PDA (PD) film. Figure 2 shows the schematic of the synthesis of the PD film.

2.1.4 | Fabrication of PVA-PDA-BORAX (PDB) film

The schematic of the synthesis of PDB film is shown in Figure 3. For fabricating the PDB film, 6 g PVA is dissolved in 60 mL of hot deionized water. The viscous solution is then added with tris buffer 485 mg, sodium metaperiodate 22 mg, and pH 8.5 is maintained through the addition of sodium hydroxide 1 (M) solution. After the addition of dopamine hydrochloride 50 mg, it turned into a deep brown solution and then kept for stirring at 90°C for 24 h. Next, disodium tetraborate decahydrate (borax) solution 0.04 (M) is added dropwise. The resulting highly viscous solution is poured into a Teflon sheet and kept at 90°C in an air-circulated oven for 12 h. This finally results in brown-colored freestanding soft PVA-PDA-BORAX film.
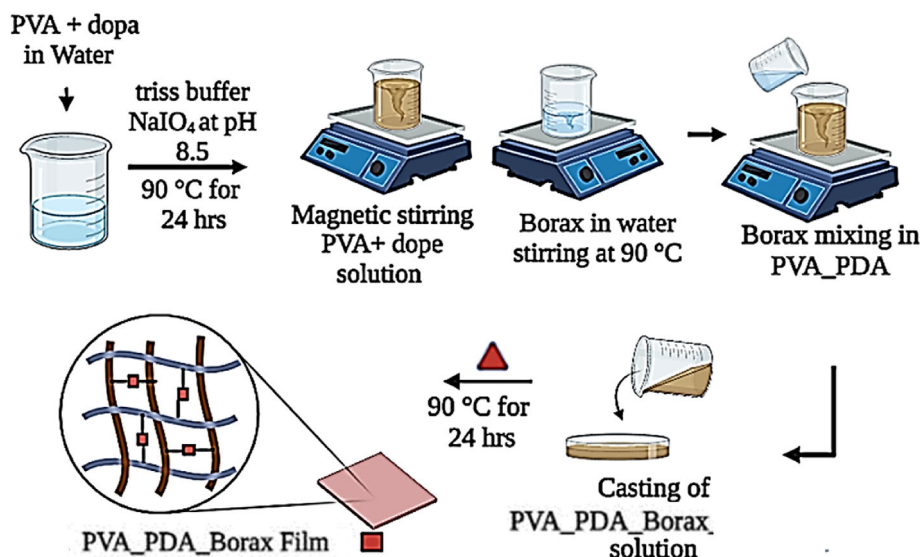
FIGURE 3 Schematic synthesis route of the PDB film for dynamic mechanical testing.
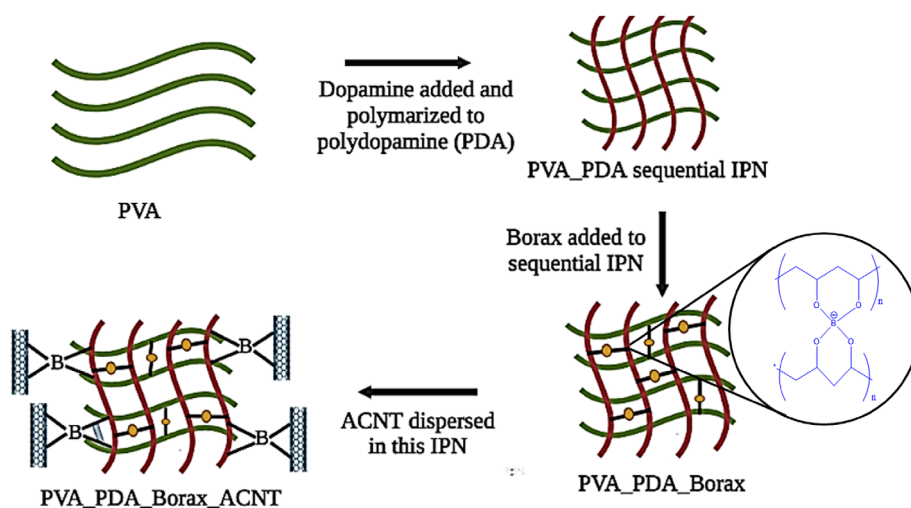
FIGURE 4 Formation of the hydrogen bond between PD-Borax film and covalent bond between PDB-ACNT film.

2.1.5 | Preparation of PVA-PDA-BORAX-ACNT (PDB-ACNT) composite film

To prepare the composite film, 6 g PVA is mixed with 40 mL hot water. After 3 h, tris-buffer 485 mg, sodium periodate 22 mg, and dopamine hydrochloride 50 mg are added to the solution. Prior to the addition of dopamine, the pH of the solution is maintained at 8.5. In another beaker, 1 wt% of acid functionalized carbon nanotube (ACNT) is dispersed in 20 mL deionized water through probe sonication followed by bath sonication. The well-dispersed ACNT solution was then mixed with the PVA-PDA solution mixture and allowed to stir at 80°C for 24 h. Next, 0.04 (M) borax solution is added to this mixture. The final viscous solution is poured into a teflon sheet and kept overnight in an air-circulated oven at 100°C. This results in a black freestanding PVA-PDA-BORAX-ACNT film.

Figure 4 shows the schematic of the synthesis of the PDB_ACNT film.

2.2 | Synthetic procedure of acid-functionalised of MWCNT

At first, a single neck round bottom flask is charged with concentrated sulfuric acid and concentrated nitric acid in 1:3 volumetric ratios to make final volume of 200 mL acidic solution, keeping the flask on the ice. 1.5 g pristine carbon nanotube is then added to the acidic mixture. The solution mixture is then allowed to stir at 80°C for 6 h followed by cooling at room temperature. Next, it is washed thoroughly with deionized water and filtered through Whatmann-1 filter paper. Finally, it is kept in the oven (~80°C) for 48 h, after which black flakes of acid functionalised carbon nanotube (ACNT) are obtained. The dried

black chunks are grinded to powder with the help of morter pastle.

2.3 | Characterization techniques

The fabricated and modified composites were characterized thoroughly via various material characterization tools. The presence of different functional groups in the fabricated film was confirmed by Fourier Transform Infrared Spectroscopy (FTIR). All the prepared films were obtained as 2 mm thick and evaluated through the transmittance mode of FTIR (Perkin Elmer). The spectra were obtained in the frequency range 4000–650 cm^{-1} during 64 scans. Ultra 55 FE-SEM Karl Zeiss scanning electron microscope (SEM) duly equipped with an EDX detector was used to evaluate and probe the morphological characteristics and the elemental compositions. The mechanical and viscoelastic behavior of the samples were analyzed using Dynamic mechanical analyzer Q800 tester (TA Instruments, Inc.) in film tension mode. Four samples, namely, PVA, PD, PDB, and PDB-ACNT, were subjected to a temperature sweep from 30*C to 150*C at a heating rate of 5*C/min. The sample dimension is 30 × 4 × 0.4 mm, and the test was carried out at a constant frequency of 1 Hz. The viscosity change with time was determined at room temperature in a TA rheometer. Three samples, PVA, PD, and PDB were analyzed in this condition. The aqueous suspensions were poured into a 25 mm parallel EHP aluminum plate at room temperature to analyze their viscosity change. The experiment procured a time sweep in the range of 0 to 3600 s at a strain rate of 1%, and the maintained frequency was 10 rad/s. According to ASTM D638 (type V) stress–strain properties of the compounds measured using Universal Testing Machine at room temperature. A gauge length of 7.62 mm, a preload force of 0.1 N, and a cross-head speed of 50 mm/min were used for every specimen. Each specimen with dimensions of around 9.53 mm (length) × 3.18 mm (width) × 3.2 mm (thickness) was measured at least five times for accuracy. Using the universal test machine, the specimen was placed between two clamps or grips with the edges of the specimen parallel to the direction of the load. The specimen grips were tightened to hold the specimen securely within the fixture. The test specimen was then pulled apart at tensile speed 50 mm/min until it was broken.

3 | RESULTS

3.1 | Fourier transform infrared spectroscopy characterization

Figure 5A shows all the characteristic peaks of various chemical functional groups which were obtained in the

FTIR analysis of the prepared films. A large, broad peak around 3500–3100 cm^{-1} is attributed to O—H stretching from intramolecular and intermolecular hydrogen bonding. The vibrational stretching of the alkyl C—H bond is obtained in the range of 2800–3000 cm^{-1}, and the low-intensity peak around 1723 cm^{-1} is due to the C═O bond remaining in a lesser amount in the PVA due to high dilution. CH$_2$ bending vibration is observed in 1427 cm^{-1}. The specific absorption peak at 1247 and 1089 cm^{-1} are attributed to PVA crystallinity and the symmetric C—C stretching, respectively.[16] Now, all the films and the composite have shown almost the same pattern in FTIR as the characteristic peaks of dopamine and Borax is masked by PVA due to a higher concentration of PVA.[17] Therefore, to understand the crosslinking density of the hydroxyl group of PVA upon the addition of Borax and acidified carbon nanotube (ACNT), a bar chart has been prepared. From Figure 5B it is clear that the intensity of free —OH is gradually decreasing with the inclusion of Borax and ACNT in PVA.

3.2 | Rheological analysis

The viscosity of PVA, PVA-PDA (PD), and PVA-PDA-Borax (PDB) changed with time and was analyzed by the rheological experiment, as shown in Figure 6. The time range of the experiment was 0 to 3600 s at room temperature. The viscosity change of PVA and PVA-PDA sequential IPN was ∼0.2 to 0.3 Pa s and ∼ 2.3 to 2.9 Pa s, respectively in this time range. This minor viscosity change in IPN was observed because of the presence of polydopamine in the PD system compared to only PVA film, where a single linear polymer was present. In the case of PDB, the viscosity gradually increases from ∼1847 to 2350 Pa s due to the formation of the hydrogen bond between the hydroxyl groups of PVA and Borax. The increasing number of hydrogen bonds form a complex network structure which can be attributed to the enhancement in the viscosity. PDB reached to vitrification point at 2070 s after which the chances of extended hydrogen bond formation is very less. Effect of polydopamine and the presence of hydrogen bond in the main chain synergistically augment the high viscosity of PDB in comparison to PVA and PD.[18]

3.3 | Dynamic mechanical analysis

Figure 7 depicts the storage modulus, loss modulus and tan delta vs temperature plot for the four samples, namely, PVA, PD, PDB, and PDB-ACNT subjected to temperature sweep from 30*C to 150*C at a heating rate of 5*C/min. The increase in storage modulus for PD
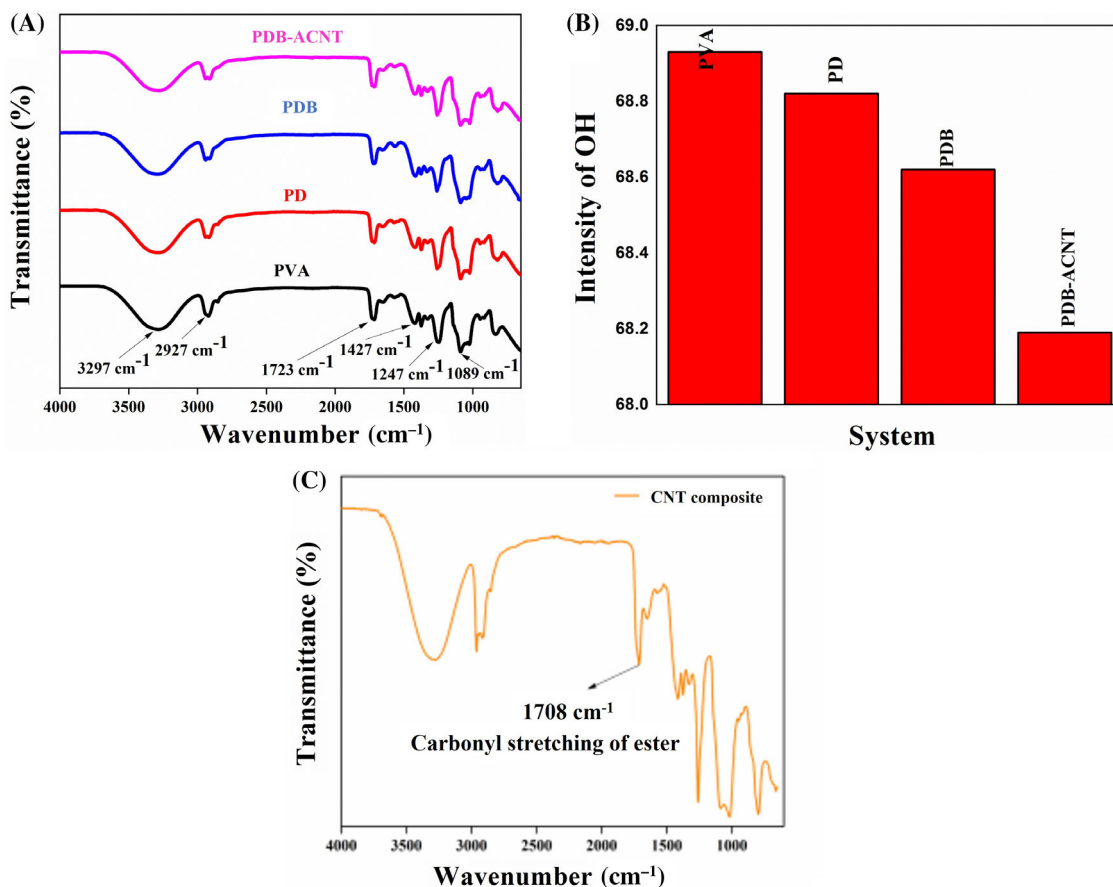
FIGURE 5 (A) FTIR spectra of PVA, PD, PDB, and PDB-ACNT film (B) change of the hydrogen bonding intensity from PVA to PD to PDB to PDB-ACNT film. (C) FTIR spectra of molded composite for ester linkage.
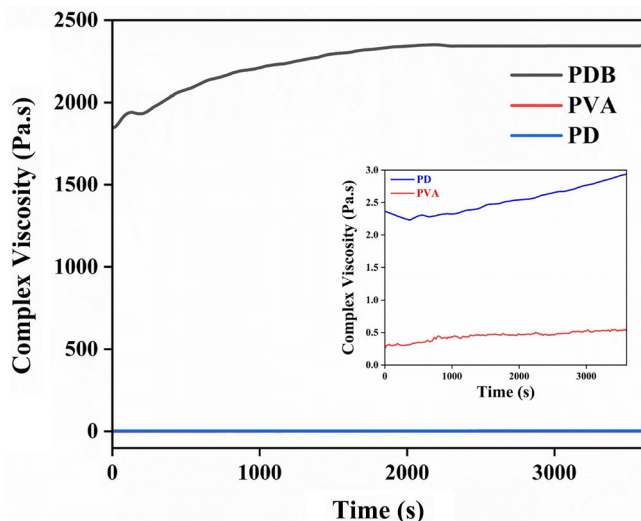

FIGURE 6 The rheological behavior of PVA, PD, and PDB shows that viscosity changes due to adding polydopamine and forming the hydrogen bond in Borax.

(16%) compared to initial modulus of PVA at room temperature can be attributed to the formation of a sequential IPN of in situ polymerized PDA and PVA. The

incorporation of Borax in the PD system resulted in the development of a full IPN with Borax forming H bonds with the —OH groups present in PVA and PDA; this further strengthened the network structure, improving the storage modulus by 21%. The best performance was seen in the case of ACNT reinforced PDB full IPN (57%) owing to a positive synergetic effect arising from filler-induced mechanical reinforcement and possible ester linkage formation between the —COOH groups of ACNT and the remaining —OH groups present in the full IPN system. Tan delta represents the ratio of viscous to elastic response of a viscoelastic material, that is, the ratio of loss modulus to storage modulus. It is used to define the glass transition temperature (Tg) of the material. It can be seen from the figure that the Tg of PVA, PD, PDB, and PDB-ACNT is attained at 87, 84, 97, and 102°C, respectively. The rightward shift in Tg for PDB can be attributed to the formation of H bonds between Borax and —OH groups of PVA and PDA, leading to a more cross-linked network. The incorporation of ACNT in PDB further shifts the Tg to the right as the ACNT nanoparticles hinder the segmental mobility of polymer chains due to the
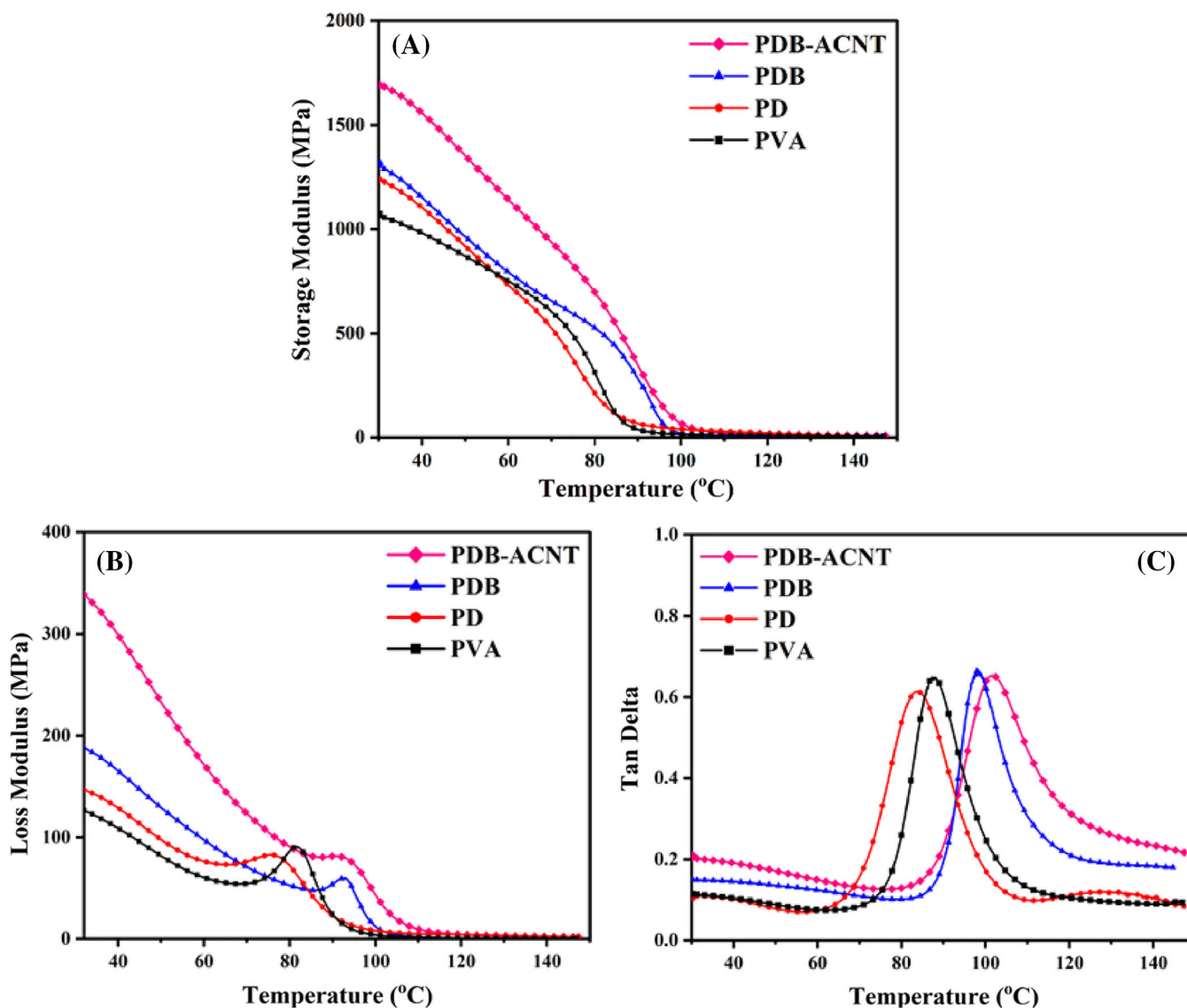
FIGURE 7 DMA graph of PVA, PD, PDB, and PDB-ACNT (A) Storage modulus vs. temperature, (B) loss modulus vs temperature, (C) tan δ versus temperature.

adsorption of polymer chains on the surface of these nanoparticles, the ester linkage formation between ACNT and hydroxyl groups in PDB also aids in improving the interaction between the nanoparticles and the polymer system. The FTIR data corroborates the strengthening mechanism discussed, where moving from only PVA to PVA and in-situ polymerized PDA sequential IPN to full IPN and finally, ACNT reinforced full IPN, the free —OH intensity progressively reduces, which is an indication of improving cross-linking in the system.

3.4 | Mechanical property

As we can see from Figure 8 and Table 1, the tensile strength of PVA film increased sharply from ∼38 to

54 MPa when 50 mg dopamine and 0.04 molar of borax were added. Similarly, the elastic modulus increases from 0.9 to 1.4 GPa of this modified PVA film compared with only PVA film. The reason could be the formation of a network structure during the reaction of borax with the hydroxyl group (—OH) of PVA and polydopamine chain, and it formed a fully interpenetrating network of PVA, polydopamine, and borax. Therefore, ductility, characterized by elongation at break, decreased and enhanced the tensile strength of this film. Further ductility decreased when one wt% ACNT was added to the PDB film, and the elastic modulus and tensile strength increased to 2.12 GPa and 71 MPa. Here ACNT acts as a nanofillers in the film, which prevent chain slippage during mechanical loading, and the presence of functional groups on the basal plane of ACNT played an important role in the
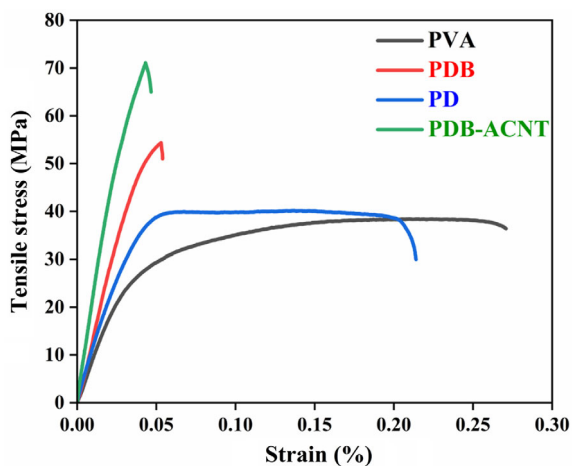
FIGURE 8 Tensile stress versus tensile strain curve of PVA, PD, PDB and PDB_ACNT.

TABLE 1 The effect of polydopamine, borax, and ACNT on the tensile strength and elastic modulus of PVA film.

Samples	Tensile strength (MPa)	Elastic modulus (GPa)
PVA	38	0.9
PD	40	1.07
PDB	54	1.4
PDB-ACNT	71	2.12

enhancement of the mechanical property that these functional groups could react with this IPN and can form covalent bonds and hydrogen bonds. So, chain flexibility is reduced, and stiffness increases sharply, which is reflected in Figures S1 and S2 is representative of the chemical stability of the composites at harsh chemical en. Only polydopamine in the PVA film did not affect much compared to the above modifications.

3.5 | Scanning electron microscope

The SEM micrographs (Figure 9) of the synthesized full IPNs were probed in order to evaluate the structural and morphological changes induced upon the introduction of 1 wt% ACNT into the PDB hybrid architecture. As evidenced by the surface (Figure 9A,B) and cross-section images (Figure 9C), the typical thread-like structure of ACNTs seems to disappear. A possible insight into this finding can be the fact that polymer-filler interaction dominated filler-filler interaction,[19,20] due to which all the ACNTs got wrapped via the polymeric matrix, which in turn enhanced the mechanical integrity of the Full IPN composite (corroborated by the DMA values). Additionally, the absence of agglomerates of ACNT further

ascertains their strong affinity toward participating in the cross-linking process. If filler-filler interaction had dominated the full spectrum acquired, ACNTs would have been clearly visible. However, the strategic absence of such a thread-like structure supports the mechanism of mechanical integrity enhancement.[19,20]

4 | DISCUSSION

Mussel-inspired doubly cross-linked interpenetrating polymeric network (IPN) composites provide a facile pathway for integrating the advantages of dopamine chemistry and IPNs in general. Full IPNs aid in suppressing macroscopic phase separation and provide processing advantages. Herein, the formation of full IPN was realized with the help of PVA, dopamine, and a common crosslinker, that is, Borax. This technique allowed for the in situ polymerization of dopamine to polydopamine, hence providing precise control over the desired extent of polymerization. Borax, on the other hand, forms hydrogen bonds with the abundant —OH groups present both in PVA and in polydopamine (PDA). Such bonds strengthen the network structure and prevent chain slippage, which in turn augments the mechanical properties of such doubly cross-linked IPNS. These hydrogen bonds are inherently reversible in nature, and hence this strategy can act as a yardstick of methodologies in the field of self-healing composites. The addition of ACNTs further reinforces the full IPN and the reinforcement depends primarily on its state of dispersion,[21,22] and the mechanical property of the filler-infused full IPN surpasses the ones without filler. Upon processing the solution cast composites, the moisture present in the system evaporates and leaves behind a very sturdy full IPN composite film. For the one filled with ACNT, higher temperatures likely facilitate the formation of ester linkages in between the acid-functionalized CNTs and the remaining —OH groups present in the system. Overall, on moving from simple PVA film to a sequential IPN consisting of PVA and in-situ polymerized PDA, to a doubly cross-linked IPN, and finally to an ACNT-filled full IPN, a steady increment in mechanical properties is recorded owing to the formation of more and more covalent and hydrogen bonds. The highest jump for the ACNT_PDB composite resulted from a synergistic effect of filler reinforcement and ester linkage formation. These composites are robust, practicable, feasible to synthesize industrially, and have long-term service life owing to their superior mechanical properties. With the mere presence of hydrophilic polymers such as PDA and PVA, these composites are bound to be endowed with superior surface hydrophilicity, which in turn can affect their performance. With the

FIGURE 9 SEM micrographs of 1 wt% ACNT-PDB Full IPN composites (A, B) surface morphology (C) cross-section morphology. (D) Zoomed image of cross-section morphology depicting network-like structure.
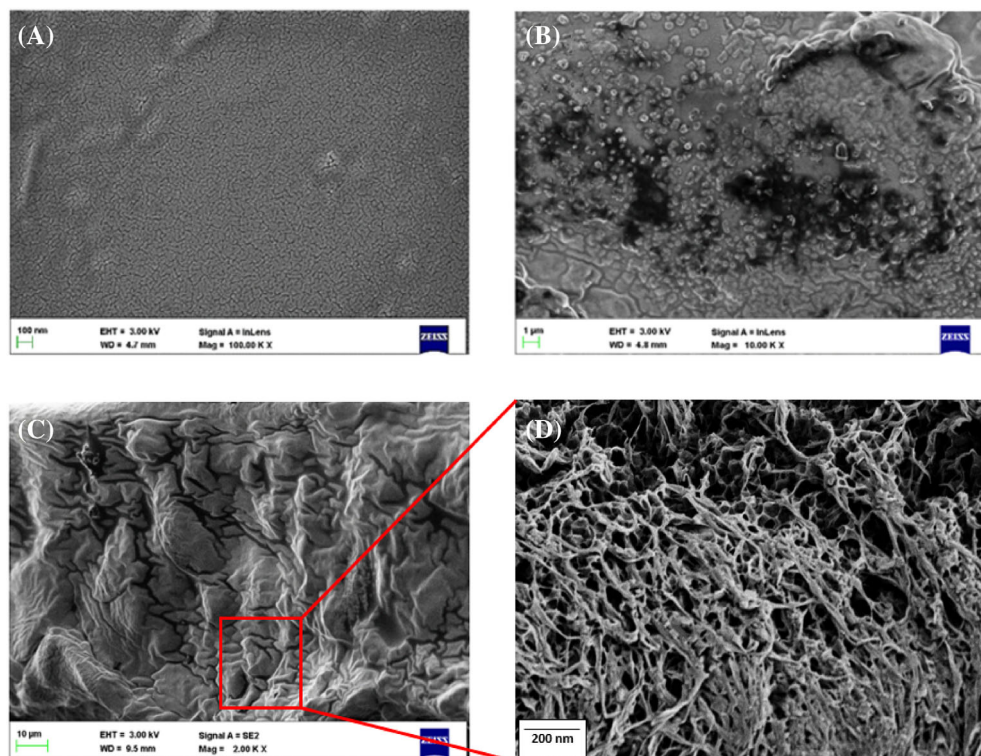
mentioned attributes in place, these full IPNs have the potential to emerge as candidates for next-generation materials where high mechanical properties are required in combination with lightweights.

5 | CONCLUSION

A simplistic synthetic method for engineering full IPN nanomaterial composite possessing superior mechanical properties has been explored. The gradual increment in the cross-linking density upon inclusion of Borax and ACNT clearly reveals the holistic improvement in the strength of the composite. This augmented behavior is through the formation of hydrogen bonds which remain stable even after exposure to elevated temperatures. The findings were further corroborated by DMA evaluations. Simultaneous enhancement in viscosity of the systems going from PVA to PD to PDB (from rheological studies) was attributed to the presence of PDA and Borax, both of which were instrumental toward the formation of hydrogen bonds in tandem. With the attributes mentioned above, the fabricated composites demonstrate superior behavior as compared to the ones reported in the literature in terms of enhanced mechanical, and potentially thermal, and chemical resilience.

DATA AVAILABILITY STATEMENT
Data sharing not applicable

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