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**ORIGINAL ARTICLE**

Carrier-mediated blends of Chitosan with polyvinyl chloride for different applications

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Compatibility

Abstract The current work aims at blending of PVC with Chitosan through simultaneous casting of their separate solutions in different proportions of PVC and Chitosan in suitable solvents. After dissolution, both solutions were added to each other while stirring at room temperature. The obtained mixture was left at room temperature to form the blend after evaporation of the solvent. Similar blends have been prepared similarly in presence of the organic ligand, dithizone, as a carrier-mediating material for different metal ions. PVC/Chitosan blends were characterized by thermal (TGA) and FT-IR Spectroscopic analyses as well as scanning electron microscopy (SEM). The obtained blends were found to have reasonable extent of compatibility between their components. Such compatibility depends mainly on the way with which the components have been blended with each other. The polymer-supported dithizone was investigated toward its ability to be used for removal of some metal ions from their aqueous solutions. Concentration of metal ions was determined by ICP-AES analysis.

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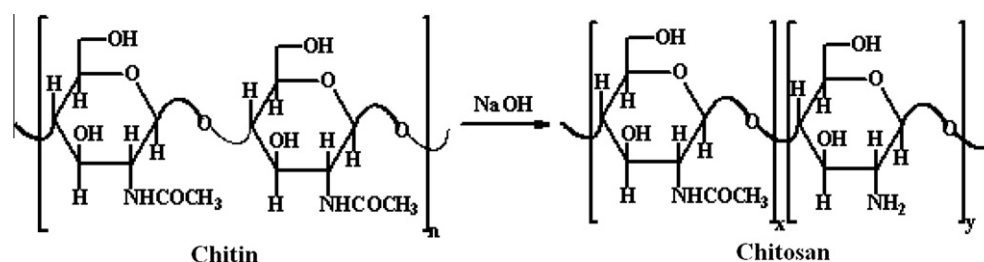
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1. Introduction

It is well known that the annual consumption of the different types of plastics is amazingly increasing. PVC is one of the most common types of plastics used in the daily life applications. Consequently, PVC waste has its environmental impact and a suitable method should be established to justify such wastes for environmental basis and for economical reasons. This may be achieved if PVC could be converted into value-added materials. In the field of ion exchange applications, styrene-based ion exchangers are the most common materials. PVC has been slightly introduced as a candidate in this field either in its native form as PVC or in a chemically modified form. One of the trials was conducted by Rinaudo to modify PVC with quaternary ammonium salts through physical mixing with lightly crosslinked PVC (Rinaudo, 2006). Although chemical



Scheme 1 Chemical modification of Chitin into Chitosan.

modification of the alkylene halide-bearing polymers is vastly achieved (Kubota and Eguchi, 1997; Aiba, 1991; Rinaudo and Domard, 1989; Rinaudo et al., 1999a, 1999b; Muzzarelli, 1973; Rhazi et al., 2002a; Kurita et al., 1979), the chemical modification of PVC materials is still relatively low (Rhazi et al., 2002b; Nieto et al., 1992). This, of course, is due to the sensitive nature of PVC terminal double bonds toward thermal effects during the different chemical modifications undertaken on PVC based materials including cross-linking.

Chitosan on the other hand is a polysaccharide in which the C-2-OH group is substituted by NH₂ functionality that can be produced by deacetylation of chitin in basic medium (Scheme 1). When the degree of deacetylation of chitin reaches about 50% (depending on the origin of the polymer), it becomes soluble in aqueous acidic media and is called Chitosan. Solubilization occurs by protonation of NH₂ function, whereby the polysaccharide is converted into a polyelectrolyte in acidic media. Chitosan is the only pseudo-natural cationic polymer and thus, it finds many applications that follow from its unique character such as flocculants for protein recovery, depollution, etc. It is largely used in different applications as solutions, gels, or films and fibers (Bhatia and Ravi, 2000).

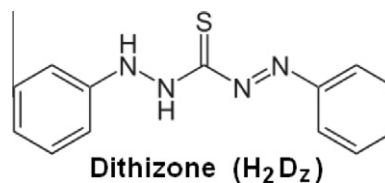
Solubility of Chitosan depends not only on its degree of acetylation but also on distribution of acetyl groups along the main chain beside the molecular weight (Sashiwa et al., 2003; Thanou and Junginger, 2005; Ravi Kumar et al., 2004). Deacetylation gives an irregular structure due the semi-crystalline nature of the initial polymer. The degree of ionization of Chitosan in different acids depends on pH and pK of the acid. Chitosan has good ability for complexation through the incorporation of NH₂ groups in specific interactions with metals useful for heavy metal recovery from waste water (Illum and Davis, 2005).

Toxic trace metals enter into natural waters through seepage from seleniferous soils and industrial waste and are liberated into the environment (in soil) through complex biogeochemical reaction forming organometallic compounds (Sitting, 1976; Adriano, 1992). These ions are absorbed by plants, e.g., cabbage, mustard, etc. (Adriano, 1992; Foster and Sumar, 1996). Thus, recent years have seen an upsurge of interest in developing novel methods involving chelating polymer as solid sorbents for the chemical speciation and separation of trace amounts of metal ions in water (Olivas et al., 1994; Afkhami et al., 1992; Kuban and Kuban, 2004; Safavi and Mirzaee, 2000; Abdelaal et al., 2000).

The chromogenic reagent 3-mercapto-1,5-diphenylformazan, namely dithizone (H₂D_Z) forms colored complexes with most metal ions. The produced complex species were extracted quantitatively into water immiscible organic solvent e.g.

n-hexane, chloroform, etc and their absorbance were measured at the optimum wavelength. The chemical composition of the extracted chelates involving the reagent H₂D_Z and their molar absorptivity at the optimum wavelength are well known.

Values of the extraction constants (K_D , K_{ex} , β) enable convenient applications of most of the liquid-liquid extraction procedures for the sequential spectrophotometric determination of traces of metal ions e.g. Hg (II), Bi (III) and chemical speciation of Se (IV) and/or Se (VI) after reduction of the later to Se (IV) with HCl (El-Shahawi and El-Sonbati, 2005; Marzenko, 1986; El-Shahawi and Al-Mehrezi, 1997; Kiwan et al., 1997). Most of these methods have sufficient sensitivity, selectivity and don't require careful experimental conditions or considerable time for the trace levels of metal ions in water, polluted water, plant material and steel plant dust. On the other hand, different polymeric materials have been used in this application through trapping of different ion chelating or ion exchanging agents (Bahaffi et al., 2006; Abdelaal, 2001).



Dithizone (H₂D_Z)

Specificity of Chitosan is strongly recognized in cosmetics in addition to the pharmaceutical and biomedical applications (Kanke et al., 1989; Abdelaal et al., 2007) including drug delivery applications such as oral, nasal, parenteral and transdermal administration, implants and gene delivery. Transmucosal administration of drugs has been discussed recently (Liu et al., 2003). Films of Chitosan incorporating prednisolone, formed by mixing have been tested for this purpose (Li et al., 2005). Chitosan gels and layer-by-layer polyelectrolyte capsules are often used for controlled release of drugs or proteins, as previously noted (Wang et al., 2002).

Chitosan and its derivatives have been used for gene transfection (Ito et al., 1998). Alginate/Chitosan systems have found applications as wound dressings and in bone tissue engineering (Wang et al., 2002; Ito et al., 1998; El-Zein et al., 2002). An interesting application concerns self-setting calcium phosphate cement by using Chitosan glycerophosphate mixed with calcium phosphate and citric acid to form an injectable self-hardening system for bone repair (Ito et al., 1998; El-Zein et al., 2002).

In the present work, modification of PVC and Chitosan by blending of them has been conducted through casting of their separate solutions in different proportions. Carrier-mediated

material such as dithizone was incorporated into the blends to enhance the ability of the blends toward metal ion uptake. The obtained products have been characterized with thermal (TGA) and FT-IR spectroscopic analyses in addition to the scanning electron microscopy (SEM) and investigated also toward their application in the field of ion exchange.

2. Experimental

2.1. Materials and techniques

PVC (M.Wt. 10,000) and High molecular weight Chitosan (CS) M.Wt. 10,000) were purchased from Aldrich. All other chemicals are from Aldrich unless otherwise mentioned. FT-IR Spectra were recorded by using JASCO FT-IR 310 Perkin Elmer FT-IR Spectrophotometer at KAU. Thermal analysis was conducted by using Shimadzu Thermal Analyzer with heating rate of 10 °C/min and the concentration of metal ions was determined by using ICP-AES instrument in the department. Electron Scanning Microscopy (SEM) was conducted using JEOL JSM-6360 L-Velectron microscope at Biology Department, KAU.

2.2. Preparation of the Chitosan blends

Chitosan (0.5 g) was suspended in the least amount of distilled water (≈ 50 ml) for 1 h. Few drops of acetic acid were added and few drops of ethanol were also added. The mixture was sonicated for further 2 h until homogeneity. About 0.5 g of PVC was dissolved in ≈ 50 ml of THF by stirring for 2 h and sonicated for further 1 h at room temperature.

The two solutions were poured simultaneously in another beaker portion-wise while stirring. The precipitated material was stirred for 1 h and sonicated for further 1 h then left to stand for 2 h at room temperature. The obtained product has been collected and dried in vacuum at 40 °C for 24 h. The same procedure was repeated by using different ratios of PVC and Chitosan, namely, 2:1 and 1:2, respectively.

2.3. Preparation of dithizone-mediated Chitosan blends

The two solutions of Chitosan in acidic solution and PVC in THF solution were prepared as above described. 0.1 g of dithizone (H_2Dz) was added to each solution with continuous stirring. The two solutions were mixed simultaneously while stirring for 1 h at room temperature. The dithizone-containing blend was collected by filtration and the product was dried in vacuum oven under reduced pressure and at 40 °C for 24 h.

2.4. Characterization of the modified Chitosan

The obtained blends were characterized by using thermal (TGA) and FT-IR spectroscopic analyses as shown in Figs. 1 and 2 to investigate the inter-chain homogeneity of the blend components. Such homogeneity reflects also the compatibility of the different components of the blends.

2.5. Treatment of Chitosan/PVC blends with solutions of metal ions

The obtained blend (0.1 g) was treated with 50 ml of 0.1 M solutions of $FeCl_3$ and $CuSO_4$, separately, to check the ability

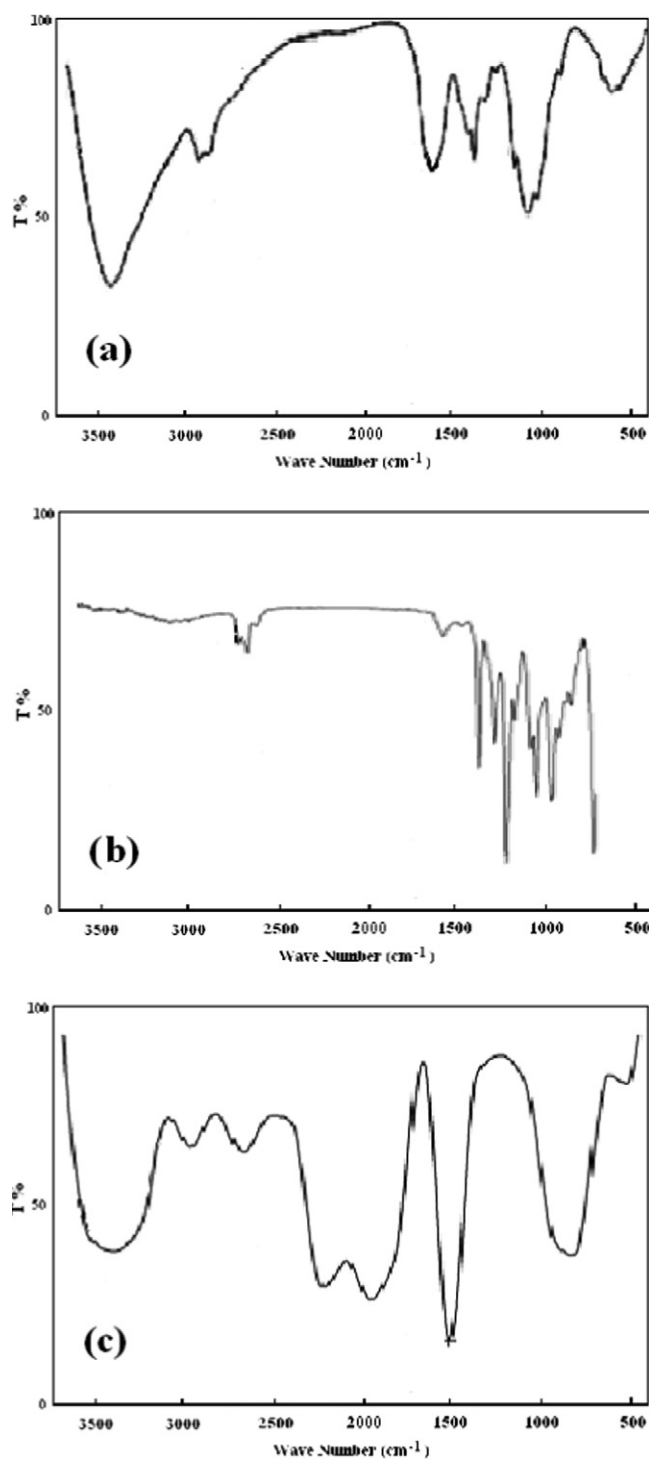


Figure 1 FT-IR Spectra for (a) blank Chitosan, (b) blank PVC, and (c) Chitosan/PVC blend.

of the blend to be applied in the field of metal ion removal. The concentration of the metal ion has been determined before and after the treatment with the obtained blends using ICP-AES. The difference in the amount of metal ion was considered as a function of the ability of the investigated blend to uptake metal ion from the aqueous solution. Polymer capacity in mg/g polymer was determined using Eq. (1) below:

$$W_p = [(W_f - W_o)/W_o] \times 100 \quad (1)$$

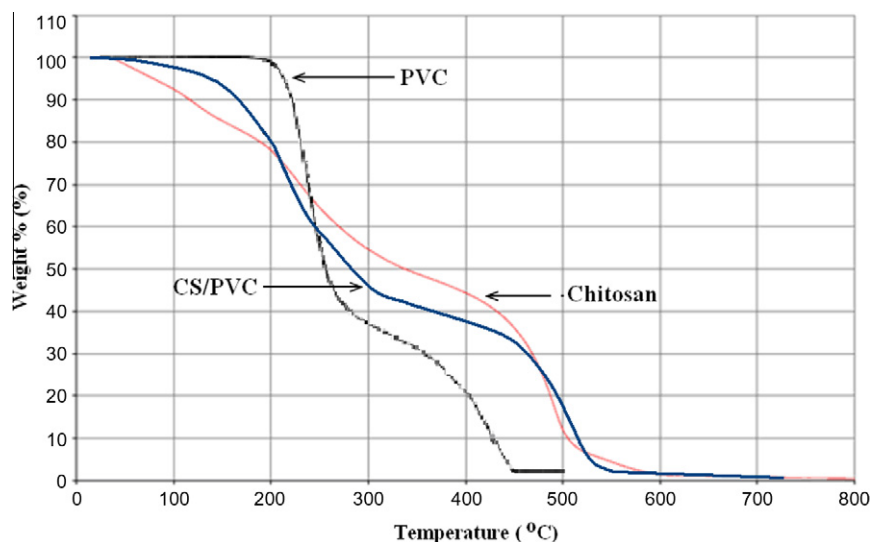


Figure 2 TGA analysis of Chitosan, PVC and Chitosan/PVC blend.

3. Results and discussion

3.1. FT-IR Spectroscopic analysis of Chitosan/PVC blends

FT-IR Spectroscopy is an important technique used to elucidate the changes in the chemical structure. FT-IR spectrum of the obtained blends in Fig. 1(a) showed the characteristic bands of Chitosan at 1089 cm^{-1} for C–O–C bonds, 1559 cm^{-1} for free NH_2 groups and 1658 cm^{-1} for the residual acetamido groups remains after deacetylation of Chitin during the production process of Chitosan. In addition, there is an absorption band at 2938 cm^{-1} attributed to C–H bonding. Also absorption bands are shown at 860 cm^{-1} and 2730 cm^{-1} corresponding to PVC beside broad bands at 1930 cm^{-1} and 2290 cm^{-1} which are observed neither for Chitosan nor for PVC.

This may be attributed to the partial inter-chain interaction or what so called dipole-dipole interaction between C–N bonds in Chitosan and C–Cl bonds in PVC. Such interaction may have some possibility to occur during the preparation process of the blends through casting of their solutions. Fig. 1(a) shows FT-IR spectrum of Chitosan while Fig. 1(b) shows the FT-IR spectrum for PVC. This concludes that a blend of Chitosan/PVC has been obtained with some inter-chain distribution of PVC and Chitosan chains. This leads of course to reasonable extent of homogeneity in the blend matrix and consequently in their compatibility.

3.2. Thermo-gravimetric analysis of Chitosan/PVC blends

Thermal behavior of Chitosan/PVC blends has been investigated in comparison with the thermal behavior of the blend components Chitosan and PVC over the temperature range from room temperature until $800\text{ }^\circ\text{C}$. Temperature was raised in a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and the results are shown in Fig. 2. It can be noticed that thermal behavior of Chitosan tends to be a gradual decrease in the weight of the investigated sample with no definite horizontal regions. PVC

showed a different behavior where the weight of the sample decreased mainly at the temperature range $220\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ in which $\approx 60\%$ of the sample weight has been lost. The rest of the sample has been thermally decomposed by heating up to $440\text{ }^\circ\text{C}$.

On the other hand, CS/PVC blends showed reasonable behavior where the sample weight started to decrease gradually up to $300\text{ }^\circ\text{C}$. After that the blend showed some stability against heating where a nearly horizontal region occurred up to $480\text{ }^\circ\text{C}$ with 25% remaining amount of the sample. This residual amount has been completely decomposed by continuous heating until the end of the measurement at $800\text{ }^\circ\text{C}$.

This thermal behavior reflects that both of the components have their own behavior in which PVC decomposes rapidly while blending with Chitosan retards the decomposition of PVC. This means the presence of some homogeneity or compatibility between Chitosan and PVC. This can be attributed to the dipole-dipole interaction between the C–N bonds in Chitosan and the polar C–Cl bonds present in PVC.

3.3. Scanning electron microscopy of Chitosan/PVC blends

Scanning Electron Micrographs (SEM) of Chitosan/PVC blends were compared with those of the blend components (a) Chitosan and (b) PVC as shown in Fig. 3.

Fig. 3 shows that PVC particles are distributed within the Chitosan matrix as domains of accumulated PVC particles. Micrograph (a) shows Chitosan as a noncrystalline matrix while micrograph, (b) shows PVC as small particles with certain diameter range. PVC particles occur within the Chitosan matrix in micrograph, (c) reflects that some of PVC particles disappeared within Chitosan matrix while the remaining particles of PVC are still appearing within Chitosan matrix as accumulated domains. This correlates more or less with the above mentioned conclusions derived from TGA thermal and FT-IR spectroscopic analyses regarding the inter-chain distribution of PVC and Chitosan domains. Such distribution may be enhanced on using a third component acting as compatibilizer.

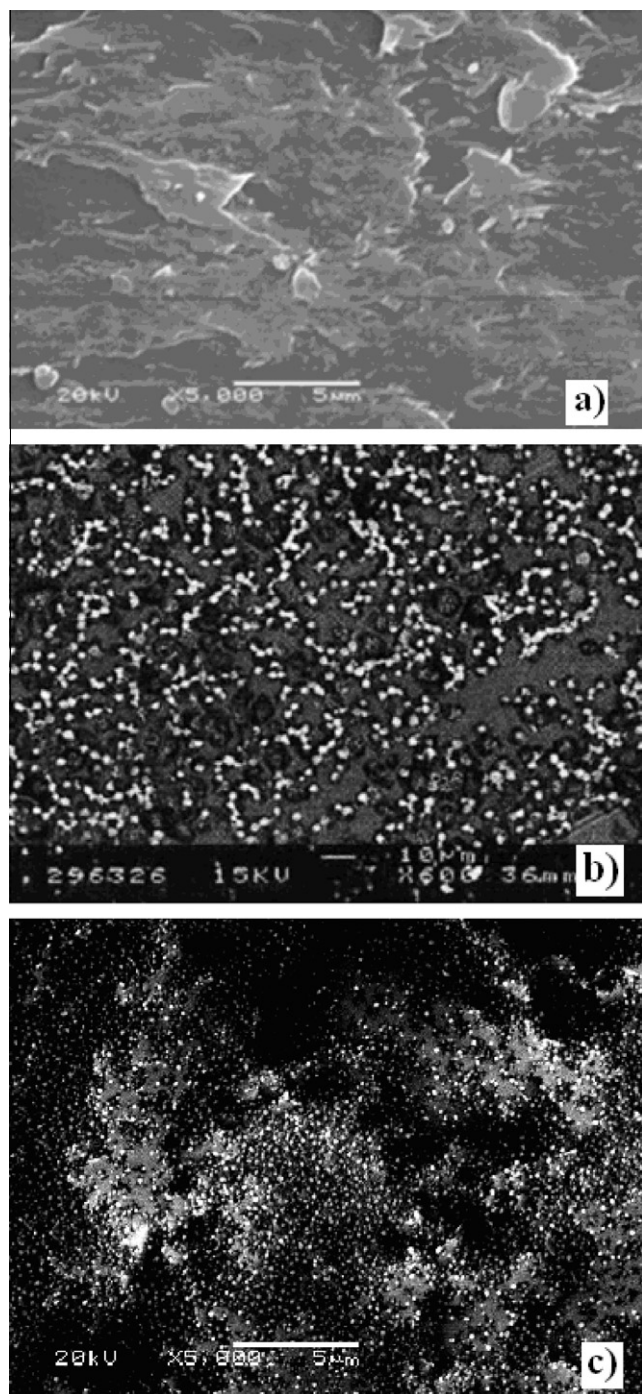


Figure 3 SEM of (a) Chitosan, (b) PVC and (c) Chitosan/PVC blend.

3.4. Treatment of Chitosan/PVC blends with solution of metal ions

Chitosan/PVC (CS/PVC) blends showed ability to uptake metal ions from their aqueous solutions. Different metal ions have been used in the current investigation including FeCl_3 and CuSO_4 solutions. CS/PVC blends showed better metal ion uptake than that showed by PVC while Chitosan showed the best results among the investigated samples. However,

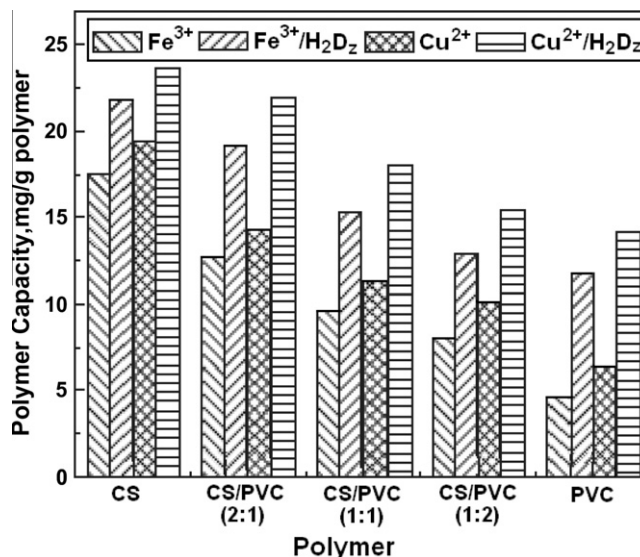


Figure 4 Metal ion uptake of Chitosan, PVC and CS/PVC blend in absence and in presence of H_2D_z using FeCl_3 and CuSO_4 .

CS/PVC blends would be more favorable in some cases in which the higher swelling ability of Chitosan in aqueous media is a strong drawback. Fig. 4 shows the metal ion uptake of Chitosan, PVC and CS/PVC blends by using aqueous solutions of FeCl_3 and CuSO_4 . From the figure, the polymer capacity increases directly with the content of Chitosan in the blend. This reflects that the main force affecting the polymer capacity in this case is the diffusion parameter of the aqueous solution of the metal ions into the polymer matrix in case of the dithizone-free blends.

The presence of dithizone in the polymeric blends enhances obviously the polymer capacity as shown in Fig. 4 which can be attributed of course to the presence of dithizone (H_2D_z). However, there are some drawbacks regarding dithizone which are mainly the insolubility of dithizone in the solvents used in the preparation of the blends and the ease of leaching from the polymer blend matrix during the chain relaxation. It is expected that utilization of nano-particles of dithizone may resolve at least partially the problem of homogeneous distribution during preparation of the blends while crosslinking of the blends may also resolve the leaching problems of dithizone from the polymer matrix. This would be the target in our future work.

4. Conclusion

The following conclusions can be derived from the current study.

- Modification of Chitosan with PVC can lead to promising materials in the light of their application directions.
- PVC/Chitosan blends need an external agent to enhance the compatibility of the blend components.
- Homogeneity of the blends and distribution of dithizone as well among the blend matrix can be enhanced by using nanoparticles of dithizone and utilization of different solvents to optimize the homogeneous mixing of the blend components.

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