



Study on Preparation and Property of CaCO₃-filled SF/PVA Blend Films

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Abstract

In order to solve the problems of the poor binding capacity, forming the aggregate easily between the surface of calcium carbonate powder and SF/PVA blend system, causing the dispersion inhomogeneous in the organic blending system. The CaCO₃-filled SF/PVA blend films were prepared by blending solution with CaCO₃ treated with titanate coupling agent. According to IR, the introduction of titanate coupling agent was indeed to crosslink the CaCO₃ with PVA and SF. DSC showed that the compatibility of each component of blend films had obviously changed by adding of glycerin. When the content of calcium carbonate was 5wt%, the improving of the tensile strength, elongation at break mechanical properties and the stability of wet of blend films had obvious effect. In addition, when the content of titanate coupling agent was 0.3wt%, the blend films exhibited a breaking strength of 45.26Mpa and 832.78% elongation at break, dissolve-loss rates were 2.88%. After the content of titanate coupling agent increased, the mechanical properties decreased and dissolve-loss rates increased gradually.

Keywords: Titanate coupling agent, Calcium carbonate, Blend film, Mechanical properties, Dissolve-loss rates

1. Introduction

Silk fibroin (SF), a water insoluble fibrous protein from *Bombyx mori* silkworm, has been mainly used as textile fibers with an excellent performance. Though silk fibroin films in wet state are soft and extensible to some extent, SF films in dry state are hard and very brittle and different for practical use (Yamaura, K *et al*, 1985, p565-566). Therefore, SF has been blended with other polymers in order to overcome the drawback of SF itself by improving mechanical properties and to introduce secondary performance (Y. Sun *et al*, 1997, p1405, G. Freddi, M *et al*, 1995, p1563, M. Tsukada *et al*, 1994, p243-248, J. H. Yeo *et al*, 2000, p1220-1223).

Poly(vinyl alcohol) (PVA) is a widely used synthetic biomaterial that is a nontoxic, water-soluble, biocompatible, and biodegradable polymer with excellent film-forming properties, highly hydrophilic properties, and high mechanical strength, and has been studied as a membrane in various ways (M. Tsukada *et al*, 1994, p243, T. Suzuki *et al*, 1989, p491, K. Yamaura *et al*, 1990, p2029). Therefore, PVA can be used as a component in polymer blends with SF. Many studies have reported the preparation and properties of for improving the flexibility and the mechanical properties of SF (M. Li *et al*, 2002, p89-94, L. Dai *et al*, 2002, p2342-2347, M. Li *et al*, 2001, p529-534, T. Tanaka *et al*, 1998, p175-184, T. Tanaka *et al*, 1997, p107-111, M. Tsukada *et al*, 1994, p243-248); In order to improve the performance of blend films, many people have made great efforts in this respect and achieved positive results. However, many researches have been limited to using organic to crosslink, graft for polyvinyl alcohol or silk fibroin, and incorporate inorganic compound into the blend films for changing the performance was poor.

Recently, the preparation and properties of polymer filled with nanometer inorganic rigid particles have become one of the hot points of research in this field (Zhen J *et al*, 2001, p5-8). In general, the mechanical and physical properties of polymeric composites are related closely with the dispersion state of the filler particles in the matrix, especially for nanometer fillers because of the particle surface effect. Several researchers attempted to modify polymeric materials by filling with nanometer inorganic rigid particles, and discussed the dispersion property as well as its mechanisms, such as nano-calcium carbonate (Zhen J *et al*, 2001, p5-8), nano-SiO₂ (Zheng YP *et al*, 2002, p1-3) and nano-Mg(OH)₂ (Zhang Q *et al*, 2003, p88-95).

In most cases, calcium carbonate is used as a filler and additive. When handling this material as filler, the most important matter is the control of the interface between the powder particles and their media. In this study, we

characterized CaCO₃-filled SF/PVA blend films prepared by adding glycerin and titanate coupling agent to improve the mechanical properties of SF/PVA. The stability of wet of blend films had obvious effect and finally determined the content of titanate coupling agent.

2. Experimental

2.1 Materials

Poly (vinyl alcohol) (PVA; DP=1750±50) purchased from Beijing Organic Chemical Factory, was dissolved in deionized water by heating in a water bath at 95±2 °C, for 2h. After heating, it was filtered and stored at room temperature. The concentration of the ultimate aqueous PVA solution was 10wt%. The silk fibroin powder (SW=5000-6000) purchased from Huzhou Xintiansi Bio-tech Co. Ltd, was dissolved in distilled water at room temperature and a 3wt% silk fibroin aqueous solution was prepared. The glycerin with a concentration of 4wt% from Tianjin Standard Science and Technology Co. Ltd, was use as a compatibilizer, added into the SF/PVA blend solution. The fine precipitated calcium carbonate (1600 mesh), from Zibo Hainuo Chemical Co. Ltd, was dispersed in distilled water by ultrasonic vibration, for 1h. The water-based titanate coupling agent (TM-TET) purchased from Yizheng Tianyang Chemical Plant.

2.2 Preparation of CaCO₃-filled SF/PVA blend film

A suitable amount of PVA solution was put into a 250mL 3mouth flask and heated in a water bath at 80 °C. Then a certain amount of calcium carbonate solution was added for 30min. In the meantime, the titanate coupling agent was added dropwise into the blend solution for 1h. After the water bath temperature gradually dropped to 40 °C, with addition of silk fibroin and glycerin, the resulting solutions were mixed together at ratios of SF/PVA=20/80 and slowly and carefully stirred for 1h at 40 °C. Films of the SF/PVA blends (0.05-0.17mm thick) were cast from the aforementioned solution onto a polystyrene plate at room temperature until a dry film was made. The sample codes for the SF/PVA blends used in this work are show in Table 1.

3. Characterization

FTIR spectra were measured with Tensor37 series spectrometer (Bruker Optics Co. Germany) in the spectral region 3500-500cm⁻¹ to investigate the molecular conformation and molecular interaction of SF/PVA blend films.

Heat-flow differential scanning calorimetry (DSC) measurements were performed on a V3.7TA instrument. The scans were always under a nitrogen atmosphere at a heating rate of 10 °C/min. The range of temperature was 100-350 °C.

Tensile strength and elongation at break were measured using a tensile tester (Laizhou Electronics Instrument Co. Ltd China) with a 200N load cell, 10mm specimen length and 100mm/min extension rate. All samples were preconditioned at 20 °C and 65% (RH) for 24h before tensile testing. The tensile strength and elongation at break were calculated as follows:

$$\sigma = T / d \times w$$

$$\varphi = L / l'$$

Where;

σ = tensile strength (N/mm²)

T = absolute strength (N)

d = film thickness (mm)

w = film width (mm)

φ = elongation at break (%)

L = absolute length (mm)

l' = clamping length (mm)

The blend films (30mm×30mm) were measured their weight at W , and then the films were place at the adsorptional condition at 50 °C for 1h and bath ratio 1:100. Using ultraviolet spectrophotometer for detect the absorbance (A) of each solution at the maximum wavelength of 274nm. The dissolve-loss rates were measured by following equation:

$$C = KAV / W \times \%$$

C = dissolve-loss rates

K = UV-absorbing constant (8.49×10⁻⁴g/ml)

A = absorbance

V = solution volume

W = weight of blend films

4. Results and Discussion

4.1 Chemical structural analysis with FTIR spectroscopy

FTIR spectroscopy has been a useful tool for determining of structural change in function groups of polymer and investigating the molecular conformation of polymer. The 3500-500 cm^{-1} wave-number ranges of the FTIR spectra of CaCO_3 fillers treated with titanate coupling agent was presented in Figure 1, respectively. The CaCO_3 shows absorption bands at 1451.52, 873.18 and 712.74 cm^{-1} , which are attributed to the Ca-O Stretching vibration and bending vibration. However, as shown in Figure 1 (a), for CaCO_3 -filled blend films treated with titanate coupling agent, the band at 2916.65 cm^{-1} is attributed to the C-H stretching peak of long-chain alkyl group in titanate coupling agent structure. In addition, a broad absorption band at about 1087.26 cm^{-1} appeared in the treated sample, and was assigned to the P-O-C stretching peak of titanate coupling agent. All these facts indicated that the introduction of titanate coupling agent was indeed to crosslink the CaCO_3 with PVA and SF.

4.2 Thermal properties

The thermal behavior of CaCO_3 -filled SF/PVA blend films was characterized by DSC. The DSC curves of blend films with different content of titanate coupling agent are shown in Figure 2. When the content of titanate coupling agent was 0.2wt%, the films displays a major endothermic peak at about 223.8 and 261.1 which approach to the melting point of PVA and SF, respectively. This result means that the force between the two polymer is very small, just a simple superposition. As we know, if the compatibility of various materials increases, the glass transition region of each component would broaden and T_g move together with each other. Figure 2(b) showed the curves of blend films with the content of titanate coupling agent was 0.3wt%. Compared with Figure 2(a), the glass transition temperature of SF changed little, while the region of glass transition temperature of PVA was relatively widened. This indicated that the compatibility of each component of blend films had not obviously changed by increasing the content of titanate coupling agent. The addition of glycerin to SF/PVA blend film [Figure 2(c)] causes new endothermic peaks at about 224.7 and 252.1. The T_g of SF and PVA mutually close up, and the broad endothermic PVA peak became sharper and shifted to a lower temperature. This is because of the presence of glycerin induces the occurrence of intermolecular interactions between the two polymers. The polar hydroxyl groups of glycerin act with molecular chains of SF, preventing hydrogen combination between SF molecular chains. Similarly, the hydroxyl groups can act with PVA molecules, showing a nearly homogeneous single glass transition behavior.

4.3 Mechanical properties

Mechanical properties, particularly tensile strength and elongation at break, are important for evaluating the film performance for proper application. Figure 3(a) illustrates the typical tensile strength curves of each sample and the elongation at break of SF/PVA films with different calcium carbonate content and without addition titanate coupling agent. The blend films exhibited a breaking strength of 41.5Mpa and 794% elongation at break when the content of calcium carbonate was 5wt%. Under this kind of condition, the mechanical prosperities of blend films are just best. As the content increased up to 20wt%, tensile strength decreased to 33.9Mpa and elongation at break fell to about 718% simultaneously. This indicated that the calcium carbonate has the enhancement and reinforcement roles for the SF/PVA films after increasing the content of calcium carbonate. Therefore, the few filler may play an important role for enhancing mechanical properties of the SF/PVA blend films. However, the focal point of stress on material internal increased with increasing content of calcium carbonate, and the interaction between SF and PVA molecular will also be weakened due to the volume fraction of filler increased. So, the tensile strength and elongation at break of SF/PVA blend films decreased with increasing the calcium carbonate content. At the same SF/PVA blending ratio and different calcium carbonate content, the strength and elongation of the blend films decreased slowly [Figure 3(b)] with addition titanate coupling agent. This result indicates that chemistry coupling layer has formed in the filler and silk fibroin macromolecule as well as PVA and silk fibroin macromolecule due to the introduction of titanate coupling agent, which improved the interfacial state between the filler and silk fibroin macromolecule as well as PVA and silk fibroin macromolecule. Therefore, the trend of mechanical properties decreased slowly.

Because of titanate coupling agent has the unique chemical structure which one end reacts with organic and another end reacts with inorganic, the binding force between calcium carbonate and the blending system will be improved by using the function like "bridge", and the mechanical properties of blend films also increased. Figure 4 showed the influence of titanate coupling agent on SF/PVA blend film's mechanical property. The strength and elongation of blend films do not increase monotonously with increasing content of titanate coupling agent, but in 0.3wt% have peak values. Normally, the alkoxy of titanate coupling agent reacts with surface of inorganic powder, giving rise to the formation of organic monomolecular layers on the surface of the substrate. Because of the calcium carbonate particle surface and the polyvinyl alcohol surface have many hydroxyls, there is surely the chemical bonding reaction with them after adding 0.3wt% titanate coupling agent, finally forming Ti—O—Ca and C_{PVA}—O—Ti. In addition, the organic phase of titanate coupling agent and silk fibroin macromolecule induced intramolecular cross-linking reaction or generated entanglement effect by the van der Waals force to form a complete with organic compounds and inorganic compounds, and formed a

complete interface between calcium carbonate and SF/PVA molecular too. When suffering external force, the interface can pass the force to the calcium carbonate particle, and the mechanical properties of SF/PVA blend films increased correspondingly. Once the single molecule interfacial layer of titanate coupling agent formed, adding titanate coupling agent excessively again, the unnecessary titanate coupling agent will be formed multilayer adsorption or local enrichment in the calcium carbonate and SF/PVA macromolecule. Then, the mechanical properties of blend films are not only decided by the binding force among calcium carbonate-titanate coupling agent, PVA-titanate coupling agent and titanate coupling agent-silk fibroin molecule, but also restricted by binding size on titanate coupling agent molecule. The more addition proportion of titanate coupling agent, the restriction is more obvious. When the intermolecular binding force of titanate coupling agent is weak, it will be certainly decreased mechanical properties on entire blend films.

4.4 Dissolve-loss rates of the blend films

Dissolve-loss rates are one important means for evaluating film performance on the stability of wet. Figure 5 shows the influence of titanate coupling agent on SF/PVA blend films' dissolve-loss rates. The dissolve-loss rates of blend films do not increase monotonously with increasing content of titanate coupling agent, but in 0.3wt% have peak values. Under this kind of condition, the dissolve-loss rates of blend films have minimum value and the stability of wet is best. This indicated that titanate coupling agent itself has the two-phase structure of organic and inorganic. A small amount of titanate coupling agent can not only wrapped up a layer of coupling on the surface of filler, but also can take on the role of cross-linking of SF and PVA, reducing entanglement of SF intermolecular and promoting the reaction of SF and PVA. In addition, it also brings about regularized molecular arrangement in the interfacial films and increasing the stability of blend films in hot water. However, the excessive amount of titanate coupling agent will be formed multilayer adsorption or local enrichment in the calcium carbonate and SF/PVA macromolecule, reducing the reaction of SF and PVA. The prepared blend films express the poor compactness and higher dissolve-loss rates.

5. Conclusions

In this paper, CaCO₃-filled SF/PVA blend films treated with titanate coupling agent were successfully prepared. According to IR, the introduction of titanate coupling agent was indeed to crosslink the CaCO₃ with PVA and SF. DSC showed that the compatibility of each component of blend films had not obviously changed by increasing the content of titanate coupling agent. The force between the SF and PVA is very small, just a simple superposition when adding the titanate coupling agent. After adding glycerin, the presence of glycerin induced the occurrence of intermolecular interactions between the two polymers and formed a nearly homogeneous single glass transition behavior.

When the content of calcium carbonate was 5wt%, the blend films had good mechanical properties, the strength and elongation of the blend films decreased slowly with addition titanate coupling agent. In addition, when the content of titanate coupling agent was 0.3wt%, it had good membrane formation property, the improving of the tensile strength, elongation at break mechanical properties and the stability of wet of blend films had obvious effect. Therefore, the prepared SF/PVA blend films have great potential as biomedical material. The SF/PVA fiber prepared by a wet spinning method using blend spinning solution may be also as surgical sutures.

References

- G. Freddi, M. Tsukada, and S. Beretta. (1999). Structure and physical properties of silk fibroin/polyacrylamide blend films. *Appl. Polym. Sci*, 71, 1563.
- J. H. Yeo, K. G. Lee, H. C. Kim, Y. L. Oh, A. J. Kim, and S. Y. Kim. (2000). The Effects of PVA/Chitosan/Fibroin (PCF)-Blended Spongy Sheets on Wound Healing in Rats. *Biol. Pharm. Bull*, 23, 1220-1223.
- K. Yamaura, N. Kuranuki, M. Suzuki, Tanigami, and T. Matsuzawa. (1990). *Appl. Polym. Sci*, 41, 2029.
- L. Dai, J. Li, and E. Yamada. (2002). *J. Appl. Polym. Sci*, 86, 2342-2347.
- M. Li, N. Minoura, L. Dai, and L. Zhang. (2001). Preparation of Porous Poly(vinyl alcohol)-Silk Fibroin (PVA/SF) Blend Membranes. *Macromol. Mater. Eng*, 286, 529-534.
- M. Li, S. Lu, Z. Wu, K. Tan, N. Minoura, and S. Kuga. (2002). Structure and properties of silk fibroin-poly(vinyl alcohol) gel. *Int. Biol. Macromol*, 30, 89-94.
- M. Tsukada, G. Freddi, and Crighiton, J. S. (1994). *Polym. Sci, Part B, Polym. Phys*, 32, 243.
- M. Tsukada, G. Freddi, and J. S. Crighiton. (1994). Changes in the fine structure of silk fibroin fibers following gamma irradiation. *Polym. Sci. B: Polym. Phys*, 32, 243-248.
- M. Tsukada, G. Freddi, and J. S. Crighiton. (1994). Structure and compatibility of poly (vinyl alcohol)-silk fibroin (PVA/SF) blend films. *J. Polym. Sci. Phys*, 32, 243-248.
- T. Suzuki, S. Hayashi, M. Nambu. (1989). *Appl. Polym. Sci*, 38, 491.
- T. Tanaka, M. Suzuki, N. Kuranuki, T. Tanigami, and K. Yamaura. (1997). Properties of silk fibroin/poly(vinyl alcohol)

blend solutions and peculiar structure found in heterogeneous blend films. *Polym. Int*, 42, 107-111.

T. Tanaka, T. Tanigami, and K. Yamaura. (1998). Phase separation structure in poly(vinyl alcohol)/silk fibroin blend films. *Polym Polym. Int*, 45, 175-184.

Y. Sun, Z. Shao, P. Hu, and T. Yu. (1997). *J. Polym. Sci. B: Polym. Phys*, 35, 1405.

Yamaura, K., Tanigami, T, Matsuzawa, S. (1985). A single large bubble consisting of a very thin-film of native aqueous silk. *Journal of colloid and interface science*, 106, 565-566.

Zhang Q, Tian M, Wu YP, Liu L, *et al.* (2003). Dispersion property and mechanisms of nano-Mg(OH)₂/rubber composites. *J Compos Mater*, 20, 88-95.

Zhen J, Ding YF, Du JQ. (2001). A study of property of PP/nano-CaCO₃ composites. *Plast Proc Appl*, 23, 5-8.

Zheng YP, Wang B. (2002). Studies of TiO₂/epox nano-composites. *J Compos Mater*, 19,11-3.

Table 1. Sample Codes and Preparation Conditions for PVA/SF Blend Films

Preparation Condition	Sample							
	1	2	3	4	5	6	7	8
PVA (wt%)	80	80	80	80	80	80	80	80
SF (wt%)	20	20	20	20	20	20	20	20
CaCO ₃ (wt%)	1	3	5	10	15	20	25	30

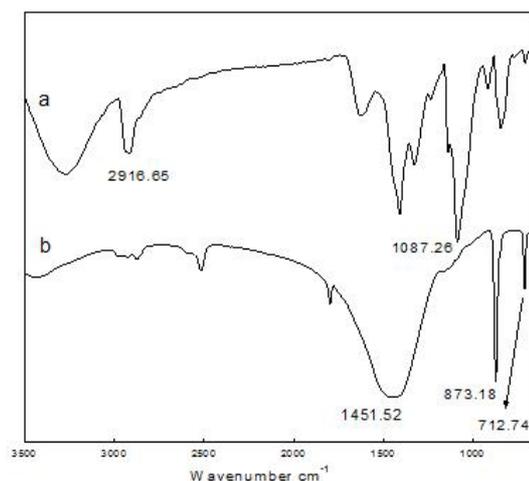


Figure 1. FTIR spectra of SF/PVA blend films:
(a) CaCO₃-filled blend films treated with titanate coupling agent. (b) CaCO₃

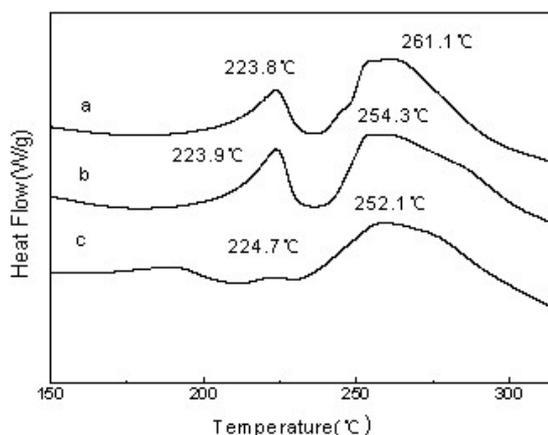
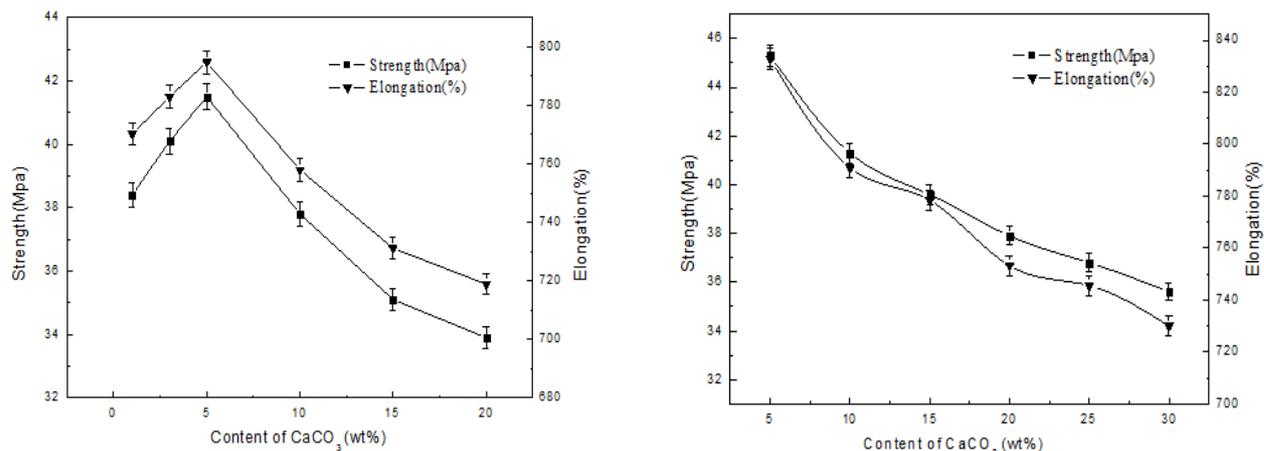


Figure 2. DSC curves of CaCO₃-filled SF/PVA blend films treated with different content of titanate coupling agent: (a) 0.2wt%; (b) 0.3wt%; (c) blend films with addition of glycerin



(a) without titanate coupling agent (b) with titanate coupling agent

Figure 3. The influence of CaCO₃ on SF/PVA blend films' mechanical property

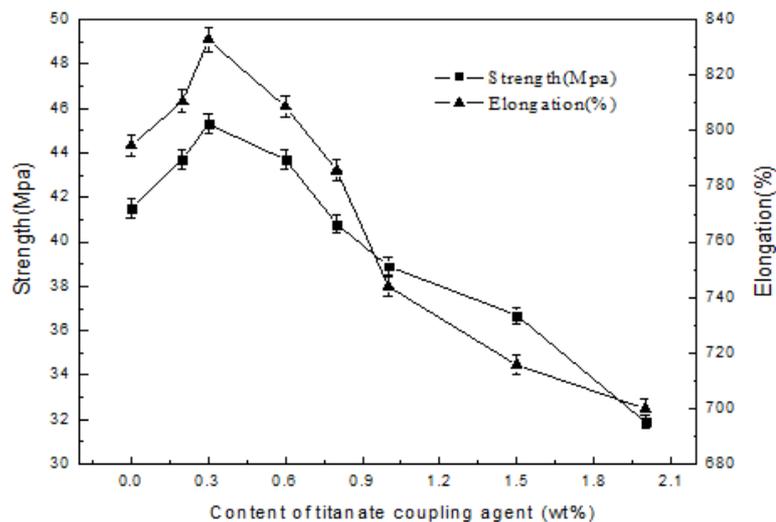


Figure 4. The influence of titanate coupling agent on SF/PVA blend films' mechanical property

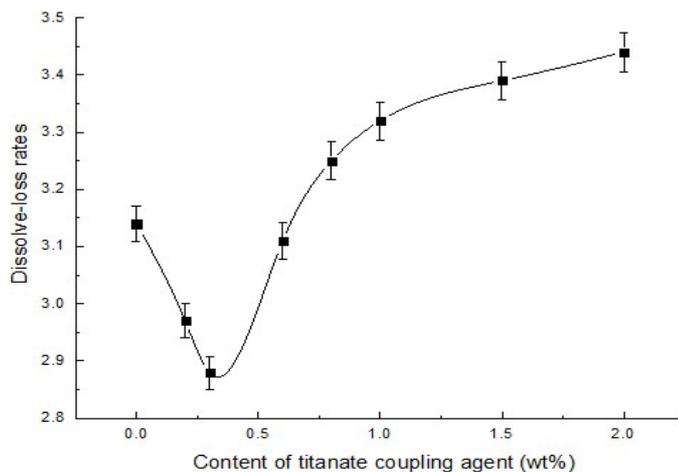


Figure 5. The influence of titanate coupling agent on SF/PVA blend films' dissolve-loss rates