

*Chapter 1*

## **DOING BUSINESS IN CHINA: FROM THEORY TO PRACTICE**

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### **FOREWORD**

#### **Introduction**

The purpose of this handbook is to try to identify the differences in behavior between Western and Chinese people, with its impact in the business life and to analyze the various steps towards the realization of a typical industrial project in China, to put in evidence what is peculiar and which difficulties are specific in the Chinese environment.

I do not expect reporting anything which cannot be found in the many books published on this very fashionable and trendy subject, the difference is that I will report only facts based on my personal experience.

So let me start confirming that it is right: we are different. According to recent anthropologists' studies, we are 40 thousand years far each other.

The human stream who reached China left the African/European area 40 thousand years ago, which means during the Medium Paleolithic period, 15 thousand years before the paintings in the caves of Lascaux in France or Altamira in Spain.

By the way, we can immediately distinguish a Caucasian and an Asian due to somatic differences and we have to expect that same differences impact the mental processes, the behavior and the body language.

These differences can be occasion of a lot of fun and wonderful relationship or could be the premise of misunderstandings and failure: that is just up to us.

I remember that in Latin the words "guest" and "enemy" share the same root: "hostis" or "hospes" (in English we still have "hostile" and "guest"). Let me recommend that the balance between the "guest" and "enemy" approach has to be carefully watched all the times. Nevertheless my experience confirms that a positive approach is extremely helpful.

So let start dealing with the business issues with positive mindset.

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## **PART ONE: INTERPERSONAL RELATIONS**

### **1. Working with a Chinese Team**

A Westerner parachuted in China to take managing responsibilities normally is not prepared to face the cultural shock. Often he would think that to deal with Chinese subordinates or colleagues is only matter of:

- Language (we mean English)
- Education (we mean them to learn our culture)

Unfortunately this would not be fair and for sure is not enough.

As far as languages, I do not mean that we have to learn Mandarin to be able to do business in that language, this is a full-time job; nevertheless I personally found extremely useful the time I spent to realize the structural differences between Mandarin and our Western languages. Mandarin lacks agreement in gender, number and case, lacks declension and conjugation and only cares to establish the sequence of the events more than their exact position in the time continuous. Syntax, on its turn, has to compensate the lack of grammar tools and, as a consequence, obliges to strict rules in the organization of the sentence. The use of ideograms influenced the language, which is still based on syllables: one syllable, one word, one concept, one ideogram. Another interesting effect of the Chinese ideogram writing is that a middle culture Chinese can read what was written centuries in the past: Chinese people live in contact with their history and this for sure has an impact on their “being Chinese” feelings. I could conclude that the study of Mandarin, even if limited to the basics, is a useful and also pleasant way to try to penetrate the mental processes, on which the behavior are normally based, of your Chinese counterpart.

As far as the behavior it is essential to pay attention to the different ways of communication. Semeiologists say that only 30% of men communication flows through the oral language, the rest goes through other means like the body language for example: we have to realize that all those means show differences in use and meaning as compared to western ones.

By the way I anticipated talking not theory but reporting personal experiences and then let me give some of this.

When I was president of a company in Taiwan I realized that anything you ask to a Chinese subordinate the answer is always “yes“. Then you start waiting for the follow-up, which will not come. From this behavior originated the Western legend that Chinese are not reliable or are lazy.

The matter is that if the Chinese colleague or subordinate does not understand you, he will never admit it in order not to lose his face. Also worse, if you ask something stupid or impossible, he will never tell you in order not to make you lose your face. I will develop later in this manual the concept of “face” so specific in Chinese culture.

Anyway after some time in Taiwan I learned how to manage.

First of all you never have to take as a given that your counterpart understands English, even if you know that he studied it and so is reported in his CV. This is true even

if your counterpart can speak good English. English pronunciation is tricky: when I first arrived to the USA from Italy to work I was able to talk good English but I did not understand in the same way. I had to pretend not to be able to talk to obtain from the American counterpart the use of simple words and a slow talking. For Chinese this situation is also worse and I learned how to politely ask people, before they leave my room, to repeat the conclusions of our meetings and to anticipate to me the means that they were planning to use to perform the task.

If you stay there enough time you will be also able sooner or later to understand the body language and to tell the difference between the various kinds of "yes" some of which simply mean "no way" or "forget it".

### ***Anecdote 1: Moving the Headquarter***

After few month from my arrival in Taipei as C.E.O. of XXX, I realized that would have been possible to move the headquarter from Taipei downtown to the same premises where the plant was located in the industrial zone of Kaohsiung, the second town in Taiwan. No technical reason, no Unions interference (unemployment in Taipei was and still is about 4 to 5% would have prevented me from implementing the idea, enjoy nice savings and deserve good bonus. Moving the few key people, even if expensive, still would have been convenient considering the very high cost of the Taipei location. I could not understand why my predecessor didn't think to it but I was too proud to ask. So I called the Vice President in charge of the Human Resources and I asked him to develop the project and to take care of the details.

Of cause the answer was: yes.

After some weeks I asked the Vice President for the status of the project and the answer was: we are working. After some additional weeks I called a meeting to complain for delay in taking action on the project. Fortunately the good personal relationship with the person in charge allowed him to be open with me and this is what I learned:

- In China the family concept is extremely important. The old people are always taken care by the sons' families and they almost always live together with them. In addition to the obvious difficulty of moving the old people from their environment, there was the problem of finding a job in the new location for the various members of the extended family, so typical in China. As a consequence to move the headquarter would have meant to loose all the key people, who, being senior, are normally in charge of large families.
- As far as the other employees, they would have not been damaged in their income, considering the low level of unemployment, but they would have felt betrayed by the Company, showing so poor interest for their experience to renounce to it only for money. This would have had a negative impact on the Company image and on the motivation of everybody. All this comes from a very typical company/employee relationship in China, which will be clear later in this manual when dealing about Confucianism and organization.
- The Chinese shareholder, a local tycoon owning a significant percentage of the company, was informed about my purpose and recommended to discourage the project. In Taiwan for a big company like ours is a must to have the headquarter in the Capital for connections and prestige reasons: moving the headquarter would have damaged, may be, the stock value.

I got enough to give up and so I did.

This example of real life allows various considerations on various aspects of the Chinese mentality, but one thing hit me immediately which is that nobody was ready to object to my request about moving the headquarter: no the Vice President in charge nor the big shareholder. On the contrary, during one of the periodical personal meetings with this gentleman, an old person enjoying great prestige in his Country, I was encouraged, with benevolence, to pursue all my ideas.

Now it is clear to me: I should have understood by myself or I had to get tired and give up. Meanwhile they would have judged me.

As far as *education*, I could experience that many of those confusing differences in behavior clarify a lot if we really try to understand the Chinese culture. And Chinese culture has its roots in Confucianism. At this point, even if it is not a subject to be discussed in a manual, moreover written by a business person, nevertheless I need to try a definition of Confucianism to enlighten my experiences and my interpretations.

I could realize that Confucianism is a high profile philosophy aimed, like other high profile philosophies, to overcome the individual interests in favor of the community and I think that one of the tool Confucianism adopted to pursue this goal is the concept of Organization.

I would say that the Organization plays for a Chinese the same role that Charity or Solidarity play for a Western Christian person and, according to this conclusion, I will use since now the capital initial when mentioning organization with such meaning.

This is the reason why Chinese, and Japanese people as well, are extremely loyal to the organization they belong to, which includes their Companies and their friends.

This is the reason of the strong importance of the personal relationship, the famous "*guan xi*", for all Chinese.

But I am afraid that for the same reason they do not feel obligated to anybody who is not part of their environment or their "*guan xi*". I will add some words later on the "*guan xi*" concept.

All above has a big impact in the business life. Consider for example the value that a Westerner and a Chinese recognize to the same contract or any other formal or informal agreement. Another Western legend flourished about that subject, always leading to the conclusion that Chinese are unreliable and not ready to comply with signed agreements.

Actually what counts for a Chinese is the personal relationship: if you enjoy good personal relationship with your counterpart you do not really need a formal contract, in fact an MOU would be enough. If you do not have any personal relationship, no formal contract will be able to protect you. Such behavior, apparently so strange, clarifies if you consider that for a Chinese person any agreement with a Westerner concerns the outside of his Organization, his entourage and at the end his Country. As a consequence any agreement should, and must, be disregarded at the minimum suspect of conflict with the Organization in all its meanings. Let me spend some words on this particular subject.

The concept can be summarized in this scheme, only apparently ironical:

Personal relationship in place		No personal relationship
<i>you do not need a formal contract</i>	/	<i>no contract will protect you</i>

NOTE: you will not know when and if you have a personal relationship or not, particularly if you are a foreigner.

Another personal experience could help to understand the big difference in value of the same contract, or even clause, for a Chinese and a Westerner.

I was negotiating in Beijing a contract to realize a petrochemical plant. As the technology was also involved, the usual secrecy agreement clause had to be drafted.

It took me six months to reach an agreement on the confidentiality clause. I was very worried as, at this rate, considering the complexity of the project, it would have taken years to conclude. Later I understood how important was that clause for the Chinese mentality. The reason is that such clause would have created barriers and constraints in the flow of information in their system of relationship, in their "*guan xi*", in their Organization, and then had to be carefully considered. Eventually the clause was signed but are we sure about its solidity in case of request from some Authority, may be connected with some of your competitors? Certainly not.

To keep all above into account, I recommend to be very cautious in providing sensitive information and to let them go only step by step accordingly with the progressing of the identification of your interests with those of your Chinese counterpart.

To conclude on this subject about Confucianism, and Organization as its tool, I would list some typical aspects of the Chinese culture which are directly consequence of the importance of the concept of Organization.

Let say that we can expect from Chinese people the good and the bad things of a culture based on organization:

- Sense of duty
- Reliability
- Respect for hierarchy
- Respect for old people

But also expect:

- Total disregard for whom is perceived as not being part of their world, which means all the Foreigners, the non Chinese
- Tendency to bureaucracy
- Tendency to gerontocracy
- Communication system heavily hierarchical

About this last point, I would comment that also in Europe the communication *top-down or bottom-up* was and still is an issue. In the 90' in Boston a *guru of business consulting*, Mike Hammer, faced that problem analyzing the organization structures in place in that moment, matrix organizations included. From his work the all theory on *Reengineering* was developed and seriously taken into consideration all over the Western business world. I did not find any traces of this studies in the Chinese environment and I deduct that this is due to the fact that a discussion on *horizontal communication* would be against their cultural roots.

***Anecdote 2: Introducing the “Management Committee“***

After some while in my position of CEO, and after having absorbed the first hit from the new culture, I started getting out from my office segregation with the idea to apply some of the rules that a good boss is supposed to apply everywhere in the world. One of this rule is to call regular meetings with your first line people to discuss the most important issues and reach shared decisions. After some of those meetings I realized that there was something wrong. Nobody during the meeting ever gave any suggestion; nobody ever challenged my opinions or decisions. After some efforts with my friends I understood that for a Chinese person to criticize the authority is a bad behavior and, also worse, to show up in public and in presence of the boss with proposals is considered an act of unforgivable arrogance. Was surprising to me to learn that in Chinese schools never and never a student would raise his hand, like in our countries, to offer an explanation or to ask for a question. By the way the “Management Committee” issue was easily resolved as I started asking each person his opinion before revealing mine. After some while things looked like normal. Except one thing which now makes me laugh, and also makes me feel some nostalgia but in those moments made me mad. One of the vice presidents, when unhappy for something or in disagreement with me or with some colleagues, was used to get up and leave the room for a while with some pretext. Later I learned that it was too difficult for him to face any conflict and that I had to fix the issue through person to person meetings.

**2. Rewarding a Chinese Employee**

Just a few words on how to reward a Chinese employee. The compensation in China, more than in Western countries, has the purpose of motivating people and of keeping the good ones, preventing them to go to your competitors as soon as they are trained in your shop.

What I report on this subject is obviously consistent with the insight on their culture, which I developed so far.

The tools available are the same as everywhere else but the meaning for Chinese employees is different. As a consequence is different the relative importance and effectiveness of the same tools and the mix of them which is convenient to apply case by case.

Let me comment the most common compensation means and their Chinese *translation*.

- Salaries and social success has to do with their specific concern about "face". Of course they like it very much but in any case we have to pay attention not to damage the equilibrium or the harmony in the organization. A promotion or a bonus or a salary increase can not be kept confidential in China and if it is not more than justified the reward will charge the incumbent with very high responsibility and will make his colleagues to loose a bit of their face.
- International exposure has to do with their perception of un-justified inferiority to Westerners which inferiority they want to cancel fast. Management courses or training programs are very popular and well accepted as a form of reward. I enjoyed big success offering free English lessons at the end of the working time.

- Training in creativity is necessary to free them from residual mental constraints due to the planned economy environment.

But the most important tool to make your employees happy and loyal to your company is to make them feel part of China and working for China development and benefit, not as part of a Western company aiming only to export the profit, may be competing with other Chinese companies.

Of course if this is the strategy of your company, you cannot change it. If this is the case, then be ready to a big turnover or to react with big benefits and salaries.

### 3. Negotiating with a Chinese Counterpart

Everything I mentioned so far about Chinese culture applies to the relationship with third parties, in particular to the conducting of negotiations.

Focusing on negotiations let me first anticipate a premise: Chinese are smart and tenacious negotiators. This should be surprising considering their recent history, which shows the Chinese locked inside their borders; but in fact this is recent history.

Chinese started trading in Asia very early in the history and their skills were well recognized in the Region. In XIV century they had the most developed navy in the world.

In XII century, in certain sculptures on the walls of Angkor temples in Cambodia, it is easy to recognize Chinese ethnic people, traits and hairdo indicate this on purpose, in the act of trading and shopping with the local Khmer ethnic people in the middle of a Khmer town. (figures 1,2 and 3)



Figure 1. Bayon, external gallery, South side, East wing. Angkor, Cambodia. End of XII century.



Figure 2. Bayon, external gallery, East side, South wing. Angkor, Cambodia. End of XII century.



Figure 3. Bayon, external gallery, South side, East wing. Angkor, Cambodia. End of XII century.

This happens at the end of the XII century and the Chinese presence is not only noticed but its trading role is emphasized. By the way, Khmer people were too busy fighting with Siamese, as you can easily note from the same sculptures in figure 4.





Figure 4. Bayon, external gallery, South side, East wing. Angkor, Cambodia. End of XII century.

Many events took place since then and it is not the purpose of a manual to investigate those, provided that you remember: no matter the way a Chinese appears, his chromosomes are those of an old traders' and travelers' culture.

There is a motto, I do not know if it is Western or Chinese, saying: no matter the way a Chinese appears, if you scratch the surface you will find a farmer. That is true but if you scratch a bit deeper you will find the trader and better you realize this before it is too late.

With this concept in mind let us never undervalue the hard task of negotiating with a Chinese counterpart, also considering that most negotiations take place in China where the Chinese counterpart is inevitably favored.

After this long but necessary premise, let now consider some specific traits of Chinese culture and their impact in conducting a negotiation.

- Patience

Patience is a stereotype about Chinese. Let me confirm that the stereotype corresponds very much to the reality.

We need to be prepared to accept that in the middle of a crucial negotiation the Chinese counterpart disappears. This could happen not only because the counterpart wants to challenge your negotiation strengths but sometimes simply because the passing of time has a different value for the Chinese. Sinologists say that the elapsing of time is linear for Westerners and circular for Chinese. To me it is enough to note that it is normal that in a negotiation the time factor had a different value for the parts involved but that in a Chinese environment to the business differences cultural differences overlap.

If you show yourself nervous you give a weakness signal also in the Western environment but in China this would be a disaster. For us, Western people, you can invoke the "sense of urgency", for the Chinese this concept do not exist at all. If you show sense of

urgency this means that you are not high enough in your organization: more urgency means more bosses to answer to.

To our mentality this is difficult to understand but urgency would really reduce your dignity and make you loose a bit of your face.

By the way also in the Western culture "sense of urgency" was not as popular in the past as it is now.

I remember a verse of a famous Italian poem "La divina Commedia" where Dante and Virgilio, having been reproached by Catone, had to accelerate their steps. When eventually they stopped this is the verse which comments the situation:

"Quando li piedi suoi lasciar la fretta che onestade ad ogni atto dismaga"  
(when their steps gave up the hurry which always reduces dignity)

On the subject of urgency and patience I also remember an old and very Chinese proverb: "Riding the horse you can not feel the smell of the flowers".

### ***Anecdote 3: Secretaries Chatting***

I was in the Taipei office and I needed to reach Kaoshiong, where the factory is located, to lead the monthly management committee. I had to catch a plane and I was very late. Nevertheless I asked my secretary to call the Kaohsiong hotel just to check if the reservation was ok.

The lady called and then started a long conversation with her counterpart in Kaoshiong hotel.

I was getting nervous and nervous but I resisted. At last the conversation finished and my secretary told me that the reservation was ok.

I was just running out of the office when the lady told me: "Mr. Ballada, in Kaoshiong now it is raining heavily and in addition there is a demonstration in progress, may be you will find difficult to get a cab". This allowed me to call immediately the factory in order to have the company car picking me at the airport, which normally I did not ask being the hotel and the airport close together and both far from the factory.

This saved me a lot of trouble, as a reward for having been patient and having accepted the two ladies to talk enough to consolidate their relationship and to share useful information, as good friends are supposed to do.

- Temper

Chinese people do not like conflicts. They killed each other by the millions just like the Europeans in the past centuries, nevertheless in the personal relationships they follow certain behavioral rules, which we need to adapt or at least to know.

A blunt "no" would be impolite and loosing your temper at a negotiation table would be a barbarism.

The consequences in practical terms are bad. If you loose your temper they will tell you anything you like just to save their faces and your face.

You go home with the impression that you concluded something good and start thinking to the big bonus, instead you will realize soon that you have to start everything from the beginning the next time.

This circumstance adds also some additional explanation of the legend about Chinese disregarding previously reached agreements.

- Face

Face is very important for Chinese in every circumstance.

“Face” is the perfect translation of the Chinese word *mien zi* which, by the way, means exactly face and also is written by an ideogram being the stylization of a face. But this is not enough: it is always difficult to translate a word from a complex culture in the language of another complex culture and this is the case.

For Chinese people Face means dignity (which has to do with the individual values), prestige (which has to do with wealth), and recognition from the others. The importance of Face in the Chinese environment has probably to do with the high importance of the organization for their society and the role that a person plays in it. For a Chinese person Face is like money for us: something you can gain, you can lose, you can trade, you can share, you can inherit or you can leave in heritage.

In any case we never, never have to take advantage of a favorable situation to weaken our counterpart challenging his image or his Face.

This behavior will create for us a tough enemy and will make us to lose the esteem of the others, including those in our side.

I strongly recommend instead to apply this old and nice Chinese proverb: "Give Face and you will receive Face".

#### ***Anecdote 4: Complicated Contracts***

This experience has to do with face and contracts in the same time. The Licensing department of my company needed to ask to a Chinese company a very special favor.

They needed to ask permission to the Chinese company to allow some technicians to be trained in their plants, as only in those plants was in use a certain process technology. Unfortunately in the same Chinese plant certain innovations had been introduced and, to make things complicated, such innovation belonged to a different Western company.

The situation was enough complicated and my Licensing department decided to go to visit the Chinese company to explain and negotiate.

Negotiations progressed very well and, so they reported to me, the agreement in principle was reached fast enough being the all matter based on reciprocal good faith.

The two delegations took advantage to touch also other subject about technologies to share and the all mission was accompanied by big dinners and concluded with friendship declarations.

When back from China my company Licensing department sent to the Chinese company a draft of contract and started waiting for the answer.

Time passed, mails were sent to ask for explanation about the delay but no any sign from the Chinese “friends”.

After six month of frustration my colleagues asked me for opinion.

Of course I wanted to see the draft contract which was sent after the visit and after having seen it I could guess an explanation for the Chinese behavior. The all matter, considering the specificity of the deal, was about confidentiality and trust. My colleagues prepared a draft not less than one pound of difficult legal English wording which would have costed to the Chinese party months to read and understand.

Moreover I am convinced that the reason why the Chinese did not answer is also another one, having to do with face. The Chinese counterpart would have had difficult time to explain to the bosses that, after a good and happy negotiation, they did not succeed to conquer the Western counterpart reliance, obliging them to send such insulting draft. So I recommended making an exception to the rules, prepare a slim draft agreement and go back to China to apologize and enjoy additional dinners.

### ***Guan Xi***

Anybody dealing with China has to learn soon about this concept.

Chinese manage the business through relationship. They are strongly interconnected and they pay attention to you only after you are properly introduced.

There is a sentence that I heard somewhere depicting perfectly this situation: "Chinese business people do not invest on a project, they prefer to invest on a person".

This is not good business practice of course and probably costed them very much in terms of development, but this is the situation we have to adapt to.

Some analysts say that one of the biggest problems for Chinese future development is the huge bad debt in the Banks books. It easy to conclude that such bad debts has to do with the rules applied in granting the loans. Frequently network, family and loyalty concepts prevail on discounted cash flow considerations and the result are inevitable.

Of course *Guan Xi* has also many good effects.

As a foreigner it is not easy to penetrate the Chinese *Guan Xi*, but staying in China long enough and using the right approach it is possible to get close to it. When this goal is reached the life in China becomes very pleasant and easy.

All friends will do their best to help to cope with big and small problems and to enjoy life; only one warning: friends can ask important favors on their turn and a refusal, with no serious excuse, would be considered very impolite and totally unacceptable.

We have to keep in mind that Confucianism and the concept of Organization, which I mentioned earlier, make everybody to be part of a complex network with rules, not written but highly respected.

Just to give an example: it is considered very impolite to ask for a favor to a higher level person in your *Guan Xi* before having tried with the lower level one, but would be also impolite to ask to the lower level person a favor if only can be done at a higher level in the same *Guan Xi*.

## **PART TWO: INDUSTRIAL PROJECT IMPLEMENTATION.**

So far I elaborated about people. Now I would like to develop some concepts about the real and typical business issues considering, step by step, the realization of a industrial project.

## 1. Planning Phase

In this section I will try to identify what makes different in China the planning activity and the forecasting which is needed for a conscious and wise planning exercise.

- In China we cannot take advantage of the **many production or export statistics** as we normally do in Europe or in the US.

So it is extremely difficult to evaluate competitor's market share and then to plan a target market share. The same happens with the analysis about planned suppliers and customers which makes in turn difficult to predict the overall competitive position.

- As far as the **market forecasts** the situation is also more confused. China developed at an Average Growth Rate of 8.5%-9% from 1995 to now (including in the average the big Asian Crisis in 1997 and 1998). Is that reasonable to extrapolate such performance? Till how long? I do not try any answer as in the specialized press you can find already all the opinions any also their contrary. Nevertheless I will report one of those opinions as it recalls some of the aspects of the Chinese culture I discussed about in this manual.

Niall Fergusson, professor of International History at Harvard Business School, in one of its recent reports foresees the risk of collapse in the Chinese economy as a consequence of the two networks which represent all over the world basilar key institutions: the credit network and the global information network. The credit network could collapse under the load of the bed debts inherited by the Government owned companies and anyway unable to disregard the *Guan Xi* pressure in the selection of the projects to be financed; the global information network as it opens the world to whom was so far excluded, priming the comparison between what is reported by the official sources and what is internationally accepted. This situation could bring large sectors of the population to an identity crisis with a consequent social protest of unforeseeable effects.

- Another big risk comes from the **big attracting figures** you get extrapolating the Chinese demand.

A typical way or reasoning in the past was for example: one billion Chinese do not have the telephone, so sooner or later they will absorb one billion telephones. This kind of predictions can be wrong for many reasons, in case of the telephones, to remain in the example, was wrong because the Chinese are actually absorbing millions of telephones but portable and not table version.

In this situation would be useful to use the old Michael Porter graph about the dimensions of a business, trying to forecast the future of each dimension: technology, customers, suppliers, etcetera.

- Another issue which has not being taken under enough consideration by the copious literature about "Business in China", is the **change in the trade pattern**. Since few years ago Western countries were used to import from China raw materials and to export finished goods Now it works the other way around. Actually everybody is aware of this new situation so much so that the area between Canton and Hong Kong has been named the "factory of the world". Nevertheless trade patterns take long time

to change and to adjust. Logistic infrastructures, commercial relationship had to adapt to the new situation.

Again let me report my personal experience. As a consultant with relationship with China, I am frequently approached by companies or traders looking for raw materials from China to feed their established channels and customers, producing, in Italy or Europe, finished or semi finished products. Very difficult to satisfy those requests as all chemicals, steel and cement stay in China. Everybody is aware of the difficulties now hitting this sector of the industry, I just want to emphasize that the same difficulties are hitting throughout all the supply chain.

Why I emphasize this particular aspect discussing about “doing business in China”? Because when planning a production in China we need to carefully consider that the raw materials availability could be a serious issue. In fact the supply chain to feed a Western project in China from other sources could not exist yet, or it is not yet consolidated, and Chinese raw materials will stay in China with an allocation priority list dictated by the *Guan Xi*.

After having listed the difficulties now would be nice to suggest the tools to overcome such difficulties.

Unfortunately I can not recommend any recipe except to watch the Chinese behavior and try to follow their example. This conclusion looks like banal, nevertheless it is the synthesis of what is repeated in many reports on this subject, which is: if Chinese make money in their environment this should be possible also for Westerners provided that they are able to adapt to the environment. This, in fact, is the actual challenge.

Once again I have to refer to the *Guan Xi*. Chinese business people tend to involve the constituencies of a future project since the planning phase of the same project. They take advantage of their *Guan Xi* and tend to create a new one around the planned project.

I try to translate such behavior in practical recommendations:

- Set a local office as soon as possible and start lobbying.
- Be generous in pre-marketing.
- Create relationship and if convenient also partnership with some key customers or suppliers.

It is obvious that following above recommendations means to reduce the independence of the project but this is exactly what I mean and what I would like to emphasize as a conclusion: it is not wise to invest in China without big connections and the balance between independence and relationship is the name of the game. More: this is true for Chinese business people among themselves.

Before to live the subject of planning and forecasting I would like to report a more general reflection about the Chinese market predictability.

Just because of the fast development, the Chinese Authorities have to balance the following factors:

- the growth of the various business segments;
- the allocation of the limited available financial resources for investment;
- as alternative to local investment, the growth of import, which means need for foreign currency.

Let us make an example. Let imagine that we created in China a company to process plastic materials, PVC for example. Could happen that the companies producing PVC are encouraged to invest in other segments (energy shortage reasons, environment reasons?) or even that the Authorities favor investments in segments different from Plastics: pharmaceuticals for example. The reasons of such decisions would be in any case unpredictable. The outcome for your company would be the need to turn to import to feed your extruders. At this point a foreign currency squeeze could take place. The PVC segment will be penalized and so all private investments in the same segment.

Can you bear this kind of risks?. A normal company can not afford to be caught in the middle of such big Government decisions.

As a consequence it is advisable to progress by steps even if this could not optimize the scale of your assets.

In case it is really necessary to start big (a refinery, for example) than it is better to associate the Chinese Government owned companies in the venture. In fact this is what the major oil company did in order to safely enter in China.

For those who like history, I recall that what I described as a potential risk already happened in the Chinese history. In the sequence of events that I will report a Central Government decision had the greatest consequences not only on a business sector but eventually on all China.

As I already mentioned earlier, in XIV century the Chinese Navy was the strongest in the world. Chinese had invented the compass and anticipated Europe in the use of multiple masts and separate holders in their big boats. This technology allowed them to build the largest boats in the world. Trading flourished and their admirals reached, in those years, the coast of Australia and Africa.

Unfortunately the Ming government in Beijing decided to withdraw support, and indirectly the investments, from the trading activity as it was perceived more important in that moment to convey all the Country resources to some big projects to consolidate the territory. Was considered vital to protect the fields and the population from the recurrent disastrous floods from the big rivers and to protect the Country from the equally recurrent invasions from the northern nomadic populations.

So the Emperor Court was moved from Nanjing to Beijing, big canals were built to connect the Yellow River with the Yang Zi and the Yang Zi with the Pearl River in Canton and also the Great Wall was restored and completed to resist to the pressure from the same northern populations who took over anyway two centuries later.

The consequences were enormous.

- The navy with no support converted into piracy, making unsafe the traveling in the South China See and more and more isolating China from the rest of the world.
- The coastal areas as well became unsafe and people started withdrawing to the internal areas. Somebody said that also the Chinese mistrust for bathing activities and sports has this origin.
- Anyway the biggest of the consequences of the above described Central Government decision is that only few years later the Dutch came with smaller boats and bigger guns and with full support from their Government to colonize the Region and this was the beginning of the end.

## 2. Project Phase

Once completed the planning phase we are ready to start to project the plants.

In this section I describe the specificity in the Project Phase for projects requiring an investment higher than 30 millions US\$ and involving a Chinese partner, which is the most common case, particularly for big investments.

- *Negotiations with partners and authorities.* Also in the Western world we need to negotiate with the partners the reciprocal contribution to the venture and both have to negotiate with the Authorities environment specific issues. What is special in China? At least three very important things.
  - First **the alliances.** In the Western world the two partners are normally allied to negotiate from the Authorities the best conditions for the common venture, in China the partner and the Authorities are frequently allied to obtain the maximum contribution from the Western partner.
  - Second **the transparency.** In the Western world we normally know what it is going on between the partners and the Authorities. Needless to say that in China you will never have access to this kind of information. It is true that becoming member of WTO Chinese Authorities accepted epoch-making conditions as far as the transparency in regulations but, just for the newness and importance of such changes, we have to be careful in taking as a given their compliance. Just think that so far the Administrative Authorities had the right to issue some regulations, called “to internal circuit”, not to be communicated to everybody but of cause applicable to everybody. This kind of practices have been abrogated by the WTO membership, but few years are really sufficient to modify a consolidated practice, moreover in such a big and diversified territory?
  - Third **the relative importance.** In the Western world the most important negotiation is between you and the partner or the suppliers or the customers. In fact the negotiation between the partners and the Authorities are supposed to take place in the frame of accepted and well known rules. In China the most important negotiation is between you and the authorities. As the rules are not existing, or flexible, or unknown.
- **Regulations.** What is the problem with regulations? The fact that they change frequently and suddenly and unpredictably. In any case as a “foreigner” you will be the last to know. It happened to me to work for more than one year on a joint venture with one of the two big Companies in the petrochemical business with no result only because of an unforeseeable change of the rules. The project was based on a fifty-fifty approach, officially agreed in an Memorandum of Understanding duly signed by the two top level people of the two Companies involved. Just after one year of negotiations we have been informed that Authorities do not allow any more fifty-fifty deals in the segment we were negotiating, as the same segment became strategic for the Country. In that case my company could not accept the new situation, due to intellectual property reasons, and we had to drop the project. Our Chinese counterpart was unhappy more than us for the lost business opportunity and, for sure,



everybody was in good faith. Nevertheless, at the end of the day, my Company lost money and time, not to talk about sensitive information that were made available during the negotiations.

We celebrated the funeral of the big project in a wonderful restaurant in Beijing and I lost one year of my career.

To make the point about regulations, and their changes now taking place, I take as an example the regulations concerning the liberalization in the trade of goods and services.

Up to the approval of the new Trade Law , in 2004, only a certain number of trade companies, Government owned and holding a special license, were allowed to import, export and operate on the international markets. The liberalization took place through various steps. First was allowed also to foreign Companies to conduct trading activities provided that strictly connected to the same Company manufacturing activity. Second everybody was allowed to trade but only in the Special Trade Zones. Lately all over the Country, but limited to Joint Ventures and lastly to everybody. Of cause expect that all above procedure was dressed by exceptions as far as the business segment, plus or minus strategic to the Country, delays in communication and the application of the many “non tariff barriers” invented on purpose to make unprofitable the trade of certain goods.

Moreover we have to keep in mind that any liberalization process in China has to cope with the vastness of the Country, the fast and irregular development of the economy and the resistance to the change of a system used to years of interweaving between business and beaurocracy.

As a consequence of all above, it is logical to recommend caution and insist on the concept that we need to have available all the tools and the appropriate assistance, also legal, before to feel “ready for China”.

- **Administrative steps.** In this case makes a big difference if we are dealing with a big project (beyond 30 millions US\$ investment) or a smaller project. In the case of a big project we have to follow an established procedure.

MOU signing with the Chinese partner.

Project Proposal (a preliminary study) presentation for approval to the relevant Government Planning Commission.

Negotiation and preparation of the Feasibility Study report.

Negotiation and preparation of the JV contract and the Articles of Association, if this is a JV, or in any case negotiation and preparation of the many contracts for the supply of Utilities, Facilities and Technology, even if it comes from your same company.

Presentation for approval of all the above to the SDPC (State Development Planning Commission) and the other affected Authorities like the Environmental Bureau.

Presentation for approval to the MOFTEC (Ministry Of Foreign Trade and Economic Cooperation).

Application for Enterprise Registration.

Now you can relax and wait for the Business License...

I reported the above boring list with the purpose of emphasizing the importance of being equipped with the necessary tools when projecting a big investment in China: time and money, both patient. May be the above procedure has already changed while I am writing this manual, but anyway something similar would have replaced it.

Last year in 2006 the first petrochemical plants in China, part of the Nanhai project, started up North of Hong Kong.

The project started in 1988 (it is not a typo, I really mean nineteen eighty eight), and Shell opened an office in Beijing to take care of the project.

Generations of managers worked on that project, including myself, and eventually retired before seeing the plants running.

That one is a big project with an investment of four billion US\$, but things work in the same way also for smaller projects.

In the case of a medium size fully owned enterprise the project phase can be fast enough but then we have to be prepared to face all unexpected events and to cope with them using our own, and our *Guan Xi*, resources.

Above arguments are not supposed to discourage those who are planning to invest in China. Many already did it and many of them successfully.

So how to face those difficulties if a company is determined to invest in China because it wants to take advantage of a good technology, has already identified a good partner and perceives the need to protect the domestic market in Europe?

It is not impossible, provided that the main rules are followed.

- To make available enough money and time to support the long lasting project phase.
- Create a team sitting in China or familiar enough with Chinese environment. Give to that team enough decision power.
- Build strong relationship with the local partner, or in case you are going “stand alone”, with the other constituencies: suppliers, customers, local authorities.
- Retain a local advisor for legal and regulatory matters.

### 3. Construction Phase

In this section I will consider some issues typical of the plant construction phase.

Some of these issues are well known and common to all developing countries. In fact when planning a plant construction in a developing country looks like reasonable to expect the following conditions to apply.

- Manpower cheap and available everywhere.
- Variety of equipment available from foreign JV and now also from local producers.
- Plenty of land available.
- Good and skilled Engineering Companies ready to provide their service cheaper than in developed countries.
- HSE to be less expensive.

Unfortunately the reality is quite different. Actually, considering one by one the above listed expectations, we discover the following.

- **Manpower cheap and available everywhere.** The labor is not necessarily cheap where you need it. In China the differences among the various regions are huge under all standpoints: climatic, cultural, economic, logistic, industrial, commercial

and fiscal. There are regions very developed and regions still very poor and other big factors have to be taken into consideration when selecting a site for your initiative. The final decision has to optimize many factors and you can find yourself obliged to select a place where the labor is not cheap as expected.

- **Variety of equipment available.** this is not true for many reasons. First of all some special items or laboratory equipment are not yet so commonly available and, second, in some cases the import of certain materials could be heavily discouraged by tariff or non tariff barriers. As a conclusion about this item, I recommend to **always ask the engineering company in charge to detail the origin of all the items** in their investment estimation.
- **Plenty of land available.** Even if the land is available, normally the site requires significant investments in infrastructures. Local authorities are interested and happy to cooperate to the upgrading of the area, for social or propaganda reasons. Sometimes the local authorities are also available to contribute to the investment but in any case the impact on the schedule of the overall project, could be heavy. In some cases the site preparation involves local residents relocation and, even if the local authorities commit to take care, the schedule can not be kept under control. In practice the only caution to apply is to plan the investment with great care to the “financial charges under construction“. This approach requires a different mindset from the Western approach. In Europe, for exempla, we are normally ready to order the so called “long delivery time items” well in advance not to delay the project progress. In China this could be a big risk. To conclude on this item I would say that the PERT chart of a project in China must follow the Chinese concept of time not the Western one.
- **Good and skilled Engineering Companies.** The Engineering Companies are normally controlled by local downstream companies and, at the end, by the Government, so we need to be careful and obtain everybody’s agreement before getting to much involved in a project. I was offering to a big company in Beijing a very unique technology and my only competitor was a Japanese company. I was happy and very comfortable to reach an agreement, particularly considering that Chinese do not like to deal with Japanese if they have an alternative. Nevertheless the negotiations were slow and I perceived that there was something wrong. Later I realized that the all matter was about the fact that I put as a condition the engagement of a Western engineering company, while the Chinese were committed to appoint there own. Fortunately I had not contractual obligations with the Western company, which I was proposing only for the fact that I was comfortable about the performance of such well known company. So I could easily resolve the problem accepting the Chinese engineering company with some additional conditions about their expected performance. It is clear that in case I had contractual obligation with the Western company I would have lost the deal. Only an additional remark on the engineering companies subject. In case we are obliged to use a Chinese engineering company, like in the case I reported above, we need to be prepared to see our technology to be copied soon. Again, this could be a problem or not, but in any case we need to know it in order to adopt the right measures.
- **HSE to be less expensive.** May be HSE costs are low for a Chinese producer, not necessarily for a Western investor. Actually the Western investor is expected, by all

the business community and the local authorities, to apply in China the same standard that are applied in the West. This is for many reasons: for “face” reasons but also because the Chinese industrial community wants to learn from the Western initiatives also about this specific side of technology.

## 2. Operations

In this paragraph I consider the issues that normally have to be taken care of when running the plants. Many of these issues are common to the construction phase plus some new others:

- **The supply of the utilities could be a problem.** Even in the case that our plant owns independent utilities supply equipment, still we have to be very careful with the back up requirements. In case of out of service of your utilities plants we do not have to expect the back up from the local infrastructure to be a given. In fact utilities are normally short everywhere in China and in order to be allocated for emergency supply we need to deserve it. Again it is a matter of *Guan Xi*.
- **Logistic costs could be a problem.** Even if the logistic aspect has been considered carefully in the planning phase, still we need to continuously monitor this aspect of the business all the way long. In China the situation is changing very fast in terms of traffic and infrastructures and the balance between them is totally unpredictable. It has been reported that in the Western countries the cost of logistic represents 4% of the total product cost. In China this value reaches 16%. Some analysts predict that, despite the continuous construction of new roads, the traffic could increase more than expected and in the future the logistic costs could probably increase with potential impact on the competitive position of those companies which did not equip on time. The recommendation here is to be very flexible in managing the business and to be continuously updated on the evolution of the area where the plants are located.
- **An additional warning about Quality.** It is not yet an issue except if our production is aimed for export. In this case Quality is more expensive than in Western countries and would be probably necessary to budget important costs to train the operators. An other warning about quality: keep in mind that also quality is an aspect of technology and incorporates important know how. So be careful not to see your quality manager leave your company as soon as he will be able to sell the training received in your factory to some competitor’s shop.
- A recurring question about running a company in China is the **management structure**. Western CEO and Chinese Vice-Presidents or Chinese CEO and some Western VP?

In my experience it is very important to have a Western CEO. But not a bureaucrat and not necessarily a technician. We need an aged and experienced person able to gain reputation and to cultivate the relationship, then he will enjoy subordinates loyalty and environment support. The VP’s must be local and able to manage the nuances of the day by day business.

The other way around, Chinese CEO and Western technical people, would be a disaster.

The Chinese CEO will soon short circuit with the Chinese subordinates and will isolate the Western employees. In addition the Chinese CEO will be less able to resist to the Chinese

environment pressure in case of any conflict of interest between your company and some Chinese constituency.

A personal experience clarifies this point perfectly. I wanted to replace two old extruders with a new one with larger capacity. I immediately anticipated to everybody that the purpose was not to reduce the personnel, actually right in that period the company was recruiting to cope with a debottlenecking in an other section of the factory. So I was surprised when the local Environment Protection Office refused to release the necessary permits. You do not need to be an engineer to understand that when you replace two old machines with a new one with the same total capacity, you do not increase pollution but instead you reduce it. So what was the problem? I must admit that I do not know, even now. When I realized that probably somebody was asking for some favor, I immediately passed the problem to the Manufacturing VP and the Finance and Administration VP asking them to take care together keeping me out of the loop. I had to wait some time but eventually the permits were released. And no evidence in the balance sheet of any cost connected to such issue.

#### ***Anecdote 5: The Japanese Vice president***

The experience I want to report here refers to a Japanese person and took place in Italy and not in China. Nevertheless I think it is very instructive also for our subject here.

Many years ago I was appointed as the Controller of an Italian-Japanese JV producing certain plastic parts. The headquarter was in Milan and the plant in Southern Italy.

The production was based on Japanese technology and the Japanese partner made available the Manufacturing and Technology Vice President while the Italian partner had the CEO position. Looks like very obvious isn't it?

Unfortunately at a certain point the situation in the plant started to be very difficult and the fixed costs got out of control. The two partners began bouncing the responsibility. One blaming the Japanese technology the other the Italian management. At the end my boss, the Italian shareholder of the JV, gave me a flight ticket and asked me to go to the factory and not to come back without an explanation. Fortunately I didn't need much time and I didn't need either to be too smart. The explanation came to me very soon.

The Italian CEO was totally in the hands of the local constituencies: he was obliged to hire unnecessary manpower, obliged to accept extra costs for participation to any kind of local fake social initiatives and so on. The Japanese Vice president was not in a position to perceive all this but he was not able to impose any rule or discipline to the operators and then the plant efficiency and the production quality went fast out of control.

The gentleman was psychologically destroyed and saw in the task I received from the big boss the way out from his situation.

So I learned from him all the details and sent quickly a report to Milan. Eventually I got a career advancement and I was appointed to sell to the Japanese the Italian share of the company.

## 5. CONCLUSIONS

Let me now try to distil some conclusions.

Why to invest in China if it is so difficult and risky?

At this point comes to me very useful an analysis which has been developed by Valeria Gattai of Bocconi University in Milano last year in 2006.

Such analysis refers to the Italian investments in China during the last few years and reports the main motivations which led such investments. Italy is a small country and Italian investments in China are also smaller but, based on my experience, it will not be wrong to extrapolate the results from this sample.

These are the reasons the Italians invested in China:

- 38% to enjoy the large market;
- 23% to take advantage of the cheap manpower;
- 21% to escape the tough competition on Europe;
- 11% to take advantage of an occasion which was offered to the company;
- 4% to by pass the European restrictions in matter of environment protection.

Those who were so patient to read this manual can easily guess how those motivations got to those investors bitter disappointment.

In fact the same analysis reports that only 10% of those investors did not suffered bad surprises either due to the cultural gap, or the communication difficulties, or the invasive bureaucracy, or the legal system, or the corruption and the lack of infrastructures.

Nevertheless the reasons to invest in China are very convincing if you have a good technology and you want to exploit it before it is too late. The same if you want to protect your market share in the West from Chinese competition (tomorrow also Indian), producing at Chinese costs.

In my opinion, in many cases to invest in China it is not an option but a strategic necessity. Nevertheless I recommend to undertake such move, both psychologically and practically, as a defensive need instead then as a aggressive attack. This will avoid you to cherish illusions and in case of failure to reduce the damage.

Said that, I can add that many success cases are also reported.

The overall conclusion is that to invest in China looks like a gamble but it is not if we are culturally equipped and ready to follow the rules. This is also the reason that encouraged me to write this simple manual: to try to describe such rules, which I want to summarize as follows:

- appropriate cultural approach;
- personal relationship, with all constituencies;
- patience and patient money;
- appropriate human resources and management policies;
- in depth risk analysis;
- great flexibility.

I would not consider completed the task I took writing this manual without mentioning also the exceptions which I had the chance to observe to the rules I described so far. I insisted very much on the important heritage of Confucianism in Chinese behavior, and I confirm this, but I want to add a warning. Chinese culture is exposed since some decades to the Western culture to an extent never experienced before in their history. In the next years we can expect the Chinese behavior to slowly mix the Confucian roots with the Western habits, the good ones and the bad ones. This process is already perceived by Chinese themselves and from this they created the derogatory appellation *Xiang Jiao* (banana) for those Chinese who are yellow outside but white inside.

I anticipated at the beginning of this manual to only report personal experiences, so let me confirm that can happen, and actually happened to me, to meet people combining some bad aspects from both cultures. For example the “*mafioso*” behavior coming from the *Guan Xi* concept and the aggressiveness coming from the Western need of straightness and celerity.

So, the overall recommendation is to adopt great flexibility in dealing with everything related to the Chinese world, including this manual.

## APPENDIX: LIVING IN CHINA

In a manual addressed to those who are prepared to go to stay in China can not be missing a paragraph about living in China as an expatriate with the family and children.

Here I am not addressing to the case of a wise traveler by profession or to a journalist, who are equipped by profession with the necessary cultural tools; here I am addressing to those like me, business people, only equipped with the video that the Human Resources guy gave you as a welfare before to leave to China.

Here in some pills what I learned as an expatriate:

- take advantage to learn about the other side of the moon. This will make you a real global business person;
- train yourself in managing new and fast changing business scenarios which is the most important skill required to a business person everywhere not only in China;
- learn to practice the "cultural relativism" from the field instead of from the sociology books;
- in case you have children, take advantage of this opportunity to make them citizens of the world not only of one half of it.

Of course there is also a typical "wrong approach". Let me give you some examples:

- spending your holidays in traveling back to your Country;
- spending your free time in the local American (or anyway Western) club;
- leaving part of your family in your Country because "schools are better";
- and, last but not least, looking for Italian food where Italian ingredients do not exist, instead of devoting yourself to discover the real Chinese food, of which the many Chinese restaurants all over the world give a totally wrong idea.

I had the chance to see many colleagues taking this approach and feeling miserable instead of enjoying this outstanding experience.

Let me complete this manual with this last anecdote.

***Anecdote 6: Why to Use the Chopsticks?.***

I mentioned the "cultural relativism". Let me give an example from the field about this very sensitive issue.

When first arriving in China the first things that we have to manage are the chopsticks. Then after having dirtied your tie and your only business suit in the luggage, you start asking yourself: "How come that this people so proud of their civilization did not decide to switch to fork and knife"? You know the comment I got from a Chinese friend about this subject? "How come that you foreigners (Chinese people call all the non-Chinese foreigners) so civilized, show up at the table with all those complicated tools? Why you accept to work to get what you deserve from a lobster, a crab or a good stake instead of letting the job to be done for you in the kitchen, where there is people more skilled, more equipped and paid for that? At the table you should not need more than the chopsticks".

This is a good lesson about cultural relativism, so I learned fast to use the chopstick. Now, when having breakfast in the morning in the hotel in China, I can eat using only one hand and hold the paper with the other without being obliged to lean the newspaper to the bottle or to the glass like the other Western colleagues.

## **BIBLIOGRAPHY**

I will not add any bibliography as this manual is addressed to people who need very fast and practical information which are available from Internet more than from a bookshelf.

## **ABOUT THE AUTHOR**

Antonio Ballada was born in Milano Italy on 1944. With a degree in Industrial Chemistry from the Milano University and a Master in Business Administration from Bocconi University, he covered many top positions in the chemical and pharmaceutical business in Italy and the USA.

Since 1996 he works with Greater China, first in Taiwan as CEO of a public company with an affiliate in Hong Kong, later as responsible of the projects in China for a European Multinational.

At present Antonio is running a consultant activity aimed to Medium Small Companies looking for Internationalization of their business. Antonio is based in Milano, Italy.

He is lecturer at Bocconi University and Istituto per gli Studi di Politica Internazionale (ISPI) on various subjects related to the business management in China and is member of the Board of two companies in Greater China: Minerals Co. Taiwan and China Catalyst Ltd. Hong Kong.



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*Chapter 2*

## PREPARATION OF POLY(LACTIC ACID) AND PECTIN COMPOSITE FILMS INTENDED FOR APPLICATION IN ANTIMICROBIAL PACKAGING

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### ABSTRACT

Pectin and poly(lactic acid) (PLA) composite was compounded by extrusion. A model antimicrobial polypeptide, nisin, was loaded into the composite by diffusion. The incorporation of pectin into PLA resulted in a heterogeneous biphasic structure as revealed by scanning electronic microscopy, confocal laser microscopy, and fracture-acoustic emission. The incorporation of pectin also created a rough and cragged surface, which was hydrophilic and facilitated the access and absorption of nisin. The nisin-loaded composite suppressed *L. planturam* growth, as indicated by agar diffusion and liquid phase culture tests. The incorporation of pectin in the amount of ~20% total mass did not alter the Young's modulus of the film from pure PLA. The composite materials were able to retain their tensile strength, flexibility, and toughness to an extent, which

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† Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

satisfies the requirements for packaging materials. Results from this research indicate the potential of Pectin/PLA composite for the application of antimicrobial packaging.

**Keywords:** pectin, poly(lactic acid) (PLA), film, nisin, composite, packaging.

## INTRODUCTION

New concepts and new materials for food and non-food packaging result from flourishing manufacture and trade and are promoted by economic globalization. It was reported that the global packaging market was \$300 billion in 2004, and 1/3 of it was spent in the U.S. market. Food packaging is a large sector in the packaging industry. Among the \$100 billion generated by the U.S. packaging industry, \$60 billion was contributed by the food industry; and it will reach a new milestone of \$74 billion by 2008.[1,2] Petroleum-derived thermoplastics with great advantages in performance and cost have dominated the packaging market to a major extent for years. Nevertheless, interests have shifted to biobased materials derived from agricultural or forestry resources because of increasing environmental concerns arising from non-biodegradable plastics and an awareness of the limitation of petroleum resources.

Biobased materials include polysaccharides, proteins, lipids, and their polymeric extracts. They also include polymers that can be chemically synthesized from biobased monomers or produced by microorganisms or genetically modified bacteria. PLA is a biodegradable polymer, made from the condensation polymerization of lactic acid. The monomer, which is also the final degradation product, can be derived from the fermentation of carbohydrate feedstocks. PLA, in the form of rigid structures, films, porous scaffolds, and micro/nanospheres, has been used for biomedical applications and disposable plastic products.[3-6] As a packaging material, PLA is attractive because it exhibits a tensile strength comparable to petroleum-derived thermoplastics, degrades under commercial composting conditions, and can be sealed at low temperature. Furthermore, PLA is resistant to oil, is a good water vapor barrier, and has relatively low gas transmittance.[7-9] PLA also has demonstrated an antimicrobial activity, when it is used in a solution of oligomers or in combination with some organic acids or antimicrobial agents.[10-13] Although there are countless publications on PLA-based drug delivery systems, less study has been done on PLA as an antimicrobial carrier for food and non-food packaging. This could be imputed to its drug release mechanism, by which the release of drugs from PLA matrices depends on PLA degradation. Another obstacle is the hydrophobic nature of PLA, to which hydrophilic antimicrobials are less accessible.

Pectin is a film forming agent. Pectin films have shown applications in coating, encapsulating, and thickening for food and pharmaceutical uses. Pectin macromolecules bind with proteins and some organic or inorganic substances via molecular interactions. Pectin can be constructed as matrices to absorb biologically active materials and deliver the pre-absorbed bioactive substances in a controlled manner[14,15]. It is expected that the incorporation of pectin filler with PLA matrix may result in a new complex material, which inherits the advantages of the parent polymers, such as biodegradability, mechanical strength, water resistance, and accessibility to hydrophilic substances. Antimicrobial proteins can be loaded into the complex simply by diffusion-absorption method with higher loading efficiency and biological activity. In this study, we present a new composite material extruded from PLA

and pectin. The composite was evaluated for use as a packaging material and for its antimicrobial activity after loading with an antimicrobial polypeptide, nisin.

## MATERIALS AND METHODS

### Materials

Poly(lactic acid) (dl-PLA) was obtained from Dow Cargill (Minneapolis, MN). The average molecular weights were  $M_w = 148,000$  and  $M_n = 110,000$ ; the glass transition temperature ( $T_g$ ) was 55-60°C. Nisaplin (containing 2.5% nisin) and pectin sodium salt were purchased from Danisco (Danisco Cultor USA, New Century, KS), the average molecular weight of pectin was  $M_w = 90,000$ , the degree of esterification was 60% and the water content was 7.8%. Dichloromethane and acetone were from Sigma-Aldrich (Milwaukee, WI). Deionized water (D.I. water) was prepared using a Barnstead E-pure water system (Dubuque, IA).

### Composite Preparation and Physical Characterizations

Compounding was performed using a Werner-Pfleiderer ZSK30 co-rotating twin-screw extruder (Coperion Corporation, Ramsey, NJ). The barrel was comprised of 14 sections, giving a length/diameter ratio of 44:1. The screw configuration was reported earlier.[16] The screw speed was 130 RPM. PLA was fed into barrel section 1 using a gravimetric feeder (Model 3000, AccuRate Inc, Whitewater, WI). After melting the PLA, pectin was fed into barrel section 7 using a loss-in-weight feeder. In all cases, the total feed rate was approximately 75 g/min. The barrel was heated using eight heating zones. The temperature profile was 135°C (zone 1), 190°C (zone 2) and 177°C (zone 3-8). A die plate with 2 holes (4mm diameter) was used. The melt temperature of the exudate at the die was approximately 155°C. Residence time was approximately 2.5 minutes. Die pressure and torque were allowed to stabilize between formulations before sample was collected. Strands were pelletized using a Laboratory (2 inch) Pelletizer (Killion Extruders, Inc, Cedar Grove, NJ).

Thin PLA and Pectin/PLA formulations were prepared with a Brabender single-screw extruder with four temperature zones (150°-170°-170°-150°C). A 3:1 high shear mixing zone screw was employed. Ribbons were extruded using a hangar-type die at 150°C. The thickness of resultant materials was measured by a micrometer (Ames, Waltham, MA).

The appearance of the resultant composites was recorded by a camera, Nikon, Dix, equipped with a 100 mm Nikon macro lens. The resultant composites were characterized for water, PLA, and pectin content by measuring the weight loss after drying and extraction with dichloromethane.[15,17] Briefly, specimens of Pectin/PLA or PLA (~200 mg for each) were weighed, chopped to smaller pieces, placed in a 5.0 ml volumetric flask containing dry-acetone, capped with a pennyhead stopper, and gently shaken at room temperature for 8 h. The acetone was refreshed three times, and then pipetted out; the flask with the contents was vacuum-dried (20  $\mu$ mHg) at room temperature for 24 h. The weight loss due to the drying process was considered as the water content of the sample. An extraction solution, dichloromethane, 5.0 ml, was added to the flask, which was gently shaken at room

temperature for additional 8 h to complete the dissolution of PLA. The extraction solution was removed, the solid phase, pectin particles colored brown, were washed with fresh dichloromethane ( $3 \times 5$  ml) and dry ethanol ( $5 \times 5$  ml), dried under a dry  $N_2$  jet, and weighted immediately. The weight loss due to the dichloromethane extraction reflected the amount of PLA in the composite.

The composites were cut into ASTM D638-99 Type I tensile bars ( $16.42 \times 1.91$  cm,  $w \times l$ ) for mechanical property tests, strips ( $7.0 \times 38.1$  mm,  $w \times l$ ) for dynamic mechanical thermal analysis, discs (1.6 cm in diameter) for nisin loading and antimicrobial activity assay. The bars, strips and discs also were examined microscopically. All sample specimens were stored in a desiccator over desiccant at  $4-7^\circ\text{C}$ .

### **Scanning Electron Microscopy (SEM)**

Fractured surfaces of PLA and Pectin/PLA samples were examined for morphology and pectin distribution. Fractured surfaces were created either by freeze-fracture using liquid nitrogen or by separating into two parts by a destructive force during tensile testing. Sample fragments were mounted with adhesive to specimen stubs, and the edge was painted with colloidal silver adhesive and sputtered with a thin layer of gold. SEM images were made in a high-vacuum/secondary electron-imaging mode of a Quanta 200 FEG microscope (FEI, Hillsboro, OR). Digital images were collected at  $500\times$ ,  $2500\times$ , and  $25000\times$ .

### **Confocal Laser Microscopy (CLM)**

For CLM, specimens were glued to a  $1 \times 3$  cm microscope slide and placed on an IRBE optical microscope with a  $10\times$  lens integrated with a model TCS-SP laser scanning confocal microscope (Leica Microsystems, Exton, PA). Images were made at 633 nm for confocal reflection and at 425/475 nm (ex./em.) for autofluorescence at two channels.

### **Dynamic Mechanical Thermal Analysis (DMA)**

The dynamic mechanical analysis was performed on a Rheometrics RSA II analyzer (Piscataway, NJ). Storage modulus ( $E'$ ) and loss modulus ( $E''$ ) were measured as the function of temperature. The gap between two jaws at the beginning of each test was 23 mm; a nominal strain of 0.1% was used with an applied frequency of 10 rad/s (1.59 Hz). Each sample was equilibrated in the sample chamber under dry nitrogen at  $-100^\circ\text{C}$  prior to running the test, temperature was increased at the heating rate of  $10^\circ\text{C}/\text{min}$ ; data was collected from  $-100^\circ\text{C}$  to  $200^\circ\text{C}$  and analyzed using Rheometric Scientific Orchestrator software, version 6.5.7.

### **Mechanical Test and Acoustic Emission**

The mechanical property measurements were performed with a tensile tester, which enabled us to obtain tensile strength, Young's modulus, and toughness of the samples. Tensile strength is defined as the maximum stress to fracture composite specimens. Young's modulus is a physical quantity representing the stiffness of a material. It is determined by measuring the slope of a line tangent to the initial stress-strain curve from the origin to 10 percent strain. Toughness (also called fracture energy) was determined by measuring the energy required to fracture samples, which is the area under the stress-strain curve. Properties were measured at 21°C and 65% RH with a gauge length of 102 mm. An upgraded Instron mechanical property tester, model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this investigation. The strain rate (cross-head speed) was set at 50 mm/min. The tensile tester was programmed to perform a cyclic test. Samples were loaded into the jaws and the samples were then stretched to 2 % strain at 50 mm/min and then back to 0% strain; once 0% strain was reached the samples were again stretched to 2% strain and then back to 0% strain. A total of 5 cycles were tested and the peak stress was recorded for each cycle.

Acoustic emission (AE) measurements and tensile stress-strain tests were performed simultaneously for the samples previously described. A small piezoelectric transducer was clipped against the samples. This transducer resonates at 150 kHz (Model R15, Physical Acoustics Corp., Princeton, NJ) and is 10 mm in diameter. AE signals emanating from this transducer when the Instron stretched the samples were processed with an upgraded LOCAN-AT acoustic emission analyzer (Physical Acoustics Corp.). The upgraded LOCAN AT, which exceeds the 20 MByte limit of old LOCAN's, is connected to a PC base with enhanced graphing and data acquisition software with all the features and options of the SPARTAN 2000. This AE system has been used in our research center for studying the deformation and fracture mechanisms of bio-composites, fabrics, and leather.

### **Nisin Loading and Antimicrobial Activity Test**

Nisin was loaded into Pectin/PLA and PLA by soaking samples in a nisin solution. Briefly, 5 specimens were placed in a Petri dish (60 × 15 mm) containing 10.0 ml of nisin solution (1%, w/v; pH 2), and shaken at room temperature at 80 rpm for 18 h. The specimens were removed from the nisin solution, washed 3 times with 10 ml of 1 N NaCl (pH 2), and 3 times with D.I. water by shaking in the solutions for 1 min for each time. The washed sample specimens were dried in a fume hood for 30 min. and stored at 4-7°C in a refrigerator prior to examining for antimicrobial activity.

For the agar diffusion test, each specimen was placed on surface-inoculated MRS agar plate, on which  $10^6$  CFU/ml of *L. plantarum* was seeded. The agar plates with the specimens were incubated at 35°C for 48 h. The diameter of the growth inhibition zone was measured with a caliper. The ratio of the diameter of inhibition zone to the diameter of the specimen was used to determine antimicrobial activity. Specimens of PLA, Pectin/PLA with and without nisin loading were tested. Each sample was tested 5 times.

For the liquid culture test, 3 pieces of specimens from either Pectin/PLA composite or PLA (total surface area of ~12.0 cm<sup>2</sup> for each) were immersed in a glass tube with 10 ml

MRS broth. The medium was inoculated with 100  $\mu$ l *L. plantarum* culture and then transferred to a shaker (Innovas 3100, New Brunswick Sci. Inc., Edison, NJ) at room temperature and shaken at 200 rpm. The culture was sampled (1.0 ml) at time points of 0, 2, 16, and 24 h. *L. plantarum* in the culture was serially diluted by sterile phosphate buffer, then pour plated onto MRS agar. Plates were incubated at 35°C for 48 h. A specimen-free inoculated MRS medium served as a control.

All measurements were performed on five samples and data was expressed as the mean  $\pm$  SD. Significance was determined with the use of a Student's *t*-test.

## RESULTS AND DISCUSSION

The physical features of pectin particles were characterized by SEM and CLM and shown in figure 1. The pectin particles were irregular in shape, rough in appearance, and varied in sizes ranging from a few to several hundred micrometers. Images of CLM revealed a strong autofluorescent emission colored as green that outlines the shape and size of pectin particles. The intrinsic fluorescence of pectin was used as a tool for pectin identification in Pectin/PLA composite films through this study.

After composite compounding, PLA and Pectin/PLA specimens were characterized initially for PLA, pectin and water content, thickness, appearance, and surface characteristics. As shown in table 1, the composite contained ~20% pectin and ~7% water. The appearance of PLA and Pectin/PLA composites is shown in figure 2, pectin particles were evenly distributed within the PLA phase. The optical transparency of the composite was inversely reduced with the addition of pectin particles (figure 2A and B). The thin PLA and Pectin/PLA composites displayed negligible change after being bent into circular shape, showing their high flexibility (figure 2C and D) as packaging materials. The surface characteristics of the composites were further identified by CLM and SEM.

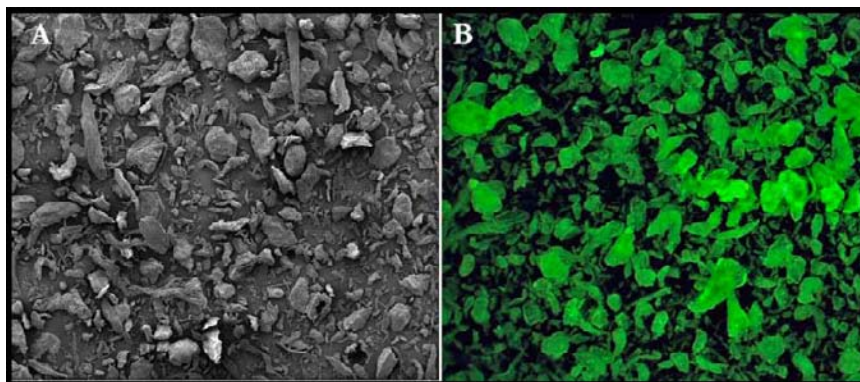


Figure 1. SEM (A) and CLM (B) images of pectin particle prior to extrusion. Field width: 2.6 mm.



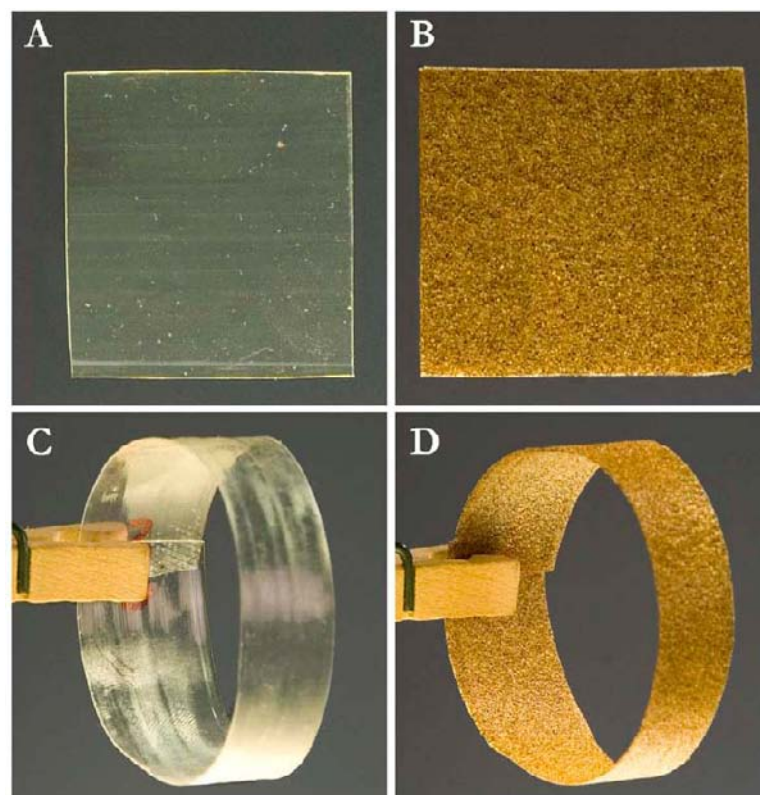


Figure 2. Photographs of PLA samples (A and C) and Pectin/PLA composites (B and D) containing ~19% pectin particles (w/w). A and B: top view; C and D: side view in circular shape. Field width: 6.0 cm.

**Table 1. Components and thickness of PLA and Pectin/PLA composites**

	Thickness (mm)	PLA content (%)	Pectin content (%)	Water content (%)
PLA	$0.54 \pm 0.02$	100	0	< 0.01
Pectin/PLA	$0.55 \pm 0.02$	$75.2 \pm 3$	$19.1 \pm 6.2$	$6.7 \pm 1.5$

Data are expressed as mean  $\pm$  SD (n = 5).

Confocal fluorescence and confocal reflection microscopy were used in a correlated mode to determine the composite structure. As shown in figure 3A, images of reflection and fluorescence in stereo projection revealed an integrated structure of the two components. The reflection areas colored red contain PLA fibers. Green fluorescence images indicate even distribution of pectin particles, which is consistent with the results shown in figure 2B. Confocal reflection microscopy revealed a continuous, smooth surface for pure PLA sample (figure 3B). Confocal fluorescence indicated a discontinuous morphology for the specimens containing pectin particles. The images of the green pectin areas also revealed a relatively rough morphology, showing a cragged layer of 20-30  $\mu\text{m}$  in thickness laying on the film surfaces (figure 3C). Furthermore, some particles were aggregated to form blocks or penetrated with PLA components (figure 3A). This was confirmed by SEM. Figure 4A shows

the image of a vertical section of a composite specimen. The pectin aggregates were located on the surface and extended deeply into the sample. In some areas, the pectin aggregates stretched about 300  $\mu\text{m}$  below the surface, which was 2/3 of the thickness. Higher magnification shows a porous structure of pectin particles embedded in the PLA phase (figure 4B). In comparison with the pectins prior to extrusion (figure 1), the embedded particles showed some changes in appearance, such as more porosity, containing crevices and folds. Since the composites were extruded at high temperature and pressure, the process might cause broken particles and/or adhesion of particles to each other. The melted PLA also could migrate into the pectin particles. As a result, the extruded composites provide a highly porous structure consisting of pectin, which is favorable for the diffusion, adsorption and storage of hydrophilic components. On the other hand, the reduction in the size of the PLA phase (figure 4A) may have an impact on the mechanical properties of resultant composites. All these will be discussed in detail later in this study.

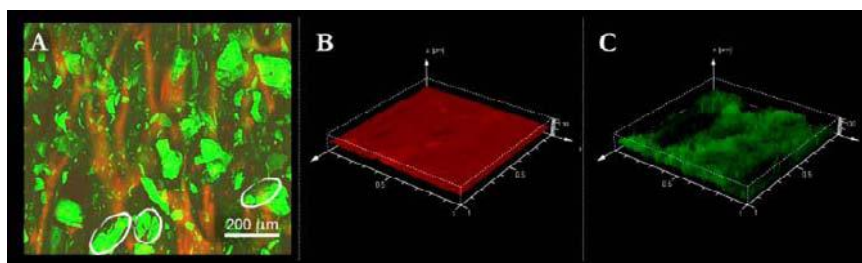


Figure 3. CLM images of (A) Pectin/PLA composites by confocal reflection and confocal fluorescence in two channels, (B) pure PLA samples by confocal reflection, (C) pectin zones by confocal autofluorescence. Areas marked by white circles in 3A indicate pectin aggregation.

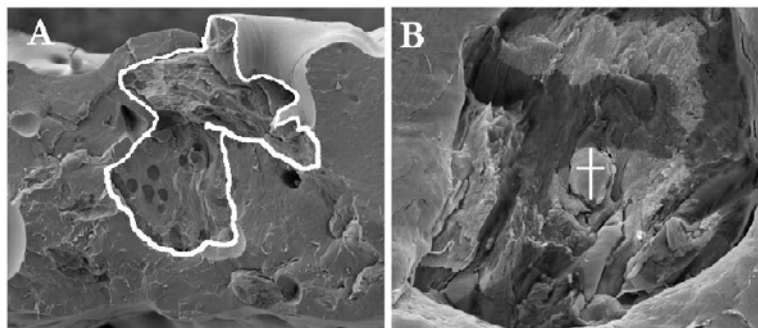


Figure 4. SEM micrographs of the composites indicate that pectin particles were located on the surface and extended into the deep of the specimens (outlined by a white curve), and the penetration of melted PLA into pectin aggregates (+). Field width: A 530  $\mu\text{m}$ , B 56  $\mu\text{m}$ .

As a complement to structural studies, samples were analyzed by dynamic mechanical analysis under a small deformation force. DMA measures the temperature-dependant storage modulus ( $E'$ ) and loss modulus ( $E''$ ). Comparisons of typical DMA curves of PLA and Pectin/PLA composites are shown in figure 5. There was a sharp decrease in  $E'$  beginning at 54°C for both PLA and Pectin/PLA composites, showing a glass transition temperature ( $T_g$ ) at about 57°C for the two films, which was consistent to the  $T_g$  of 55-60°C for PLA as

provided by the manufacturer. The blend of pectin with PLA did not alter the  $T_g$  value of pure PLA. This indicates the good miscibility of pectin with PLA and no chemical interactions between the two phases. Above  $T_g$ , the  $E'$  of PLA samples decreased as the temperature increased, and no response to the force could be recorded at about  $120^\circ\text{C}$ , indicating the specimen melted. For composites, a small amount of energy is required to overcome the resistance of pectin macromolecules to thermal movement. The addition of pectin seems to enable the composites to retain certain integrity at a higher temperature. The loss moduli data of PLA are similar to that of Pectin/PLA composites, and show a trend similar to that of the storage moduli.

Samples were then subjected to a destructive analysis for mechanical resistance. Acoustic emission was investigated simultaneously to collect information on structural changes during fracture. At the end of the test, the fractured surfaces of composites were examined by SEM.

Figure 6 shows the fractured surface of composite specimens. A clear and smooth, plate-like image is evidence of the breakdown of both PLA and pectin particles under stress, indicating adhesion between the two phases. However over all fractured surfaces, some pectin pullout also could be observed (data not shown). A decrease in tensile strength of about 19% and fracture energy of about 40% for the composite was recorded (table 2). These decreases are mainly attributed to the reduction of the PLA phase.

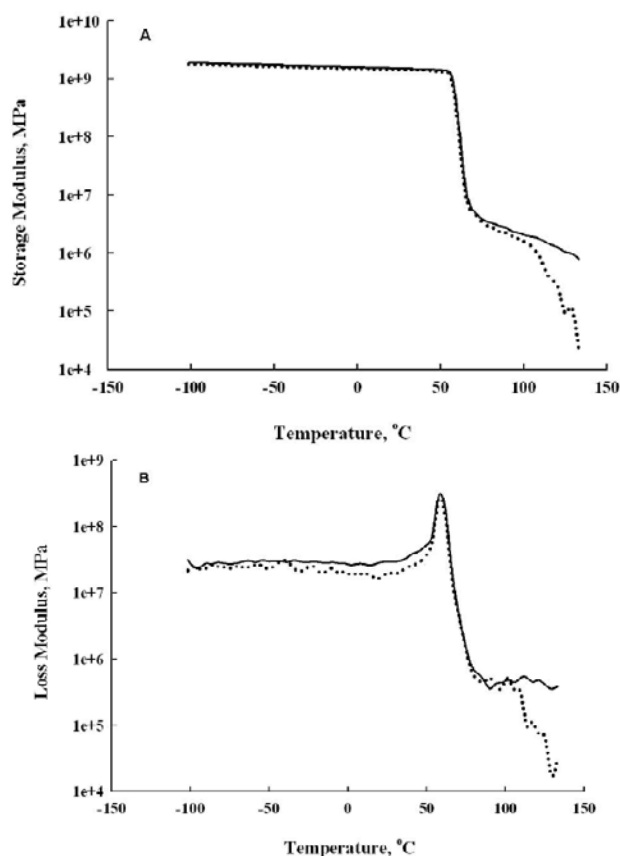


Figure 5. Typical plots of (A) storage modulus and (B) loss modulus as function of temperature. Solid line, Pectin/PLA composites; dotted line, PLA samples.

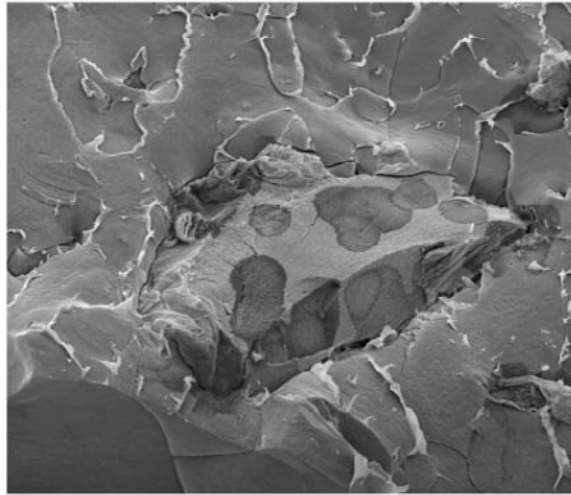


Figure 6. SEM photomicrograph of the Pectin/PLA tensile fracture surface. Field width: 134 μm.

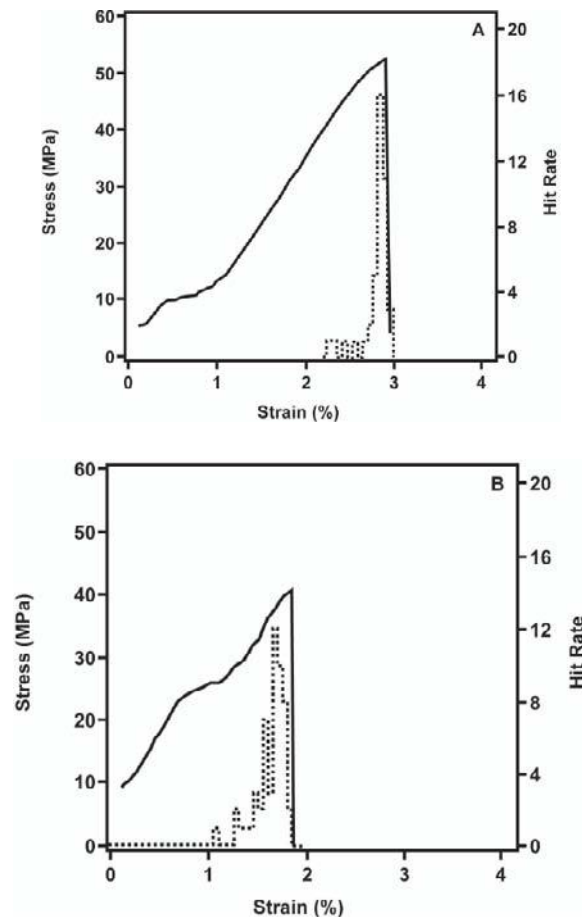


Figure 7. Correlation of strain-stress curve (solid line) with AE hit rate (dotted line). (A) PLA samples, (B) Pectin/PLA composites.

**Table 2. Mechanical Properties of PLA and PLA/Pectin composites**

Samples	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Fracture Energy (J/cm <sup>3</sup> )
PLA	2482 ± 99	53.4 ± 3.5	3.00 ± 0.21	0.63 ± 0.11
Pectin/PLA	2598 ± 100	40.2 ± 1.1	1.98 ± 0.07	0.35 ± 0.02

Data are expressed as mean ± SD (n = 5).  $P < 0.01$ .

Figure 7 shows the correlation between the stress-strain curve and strain-AE hit rate pattern. Both PLA and Pectin/PLA composites behaved as linear elastic materials. When the samples were stretched, strain and stress increased simultaneously. For PLA samples, the major AE activities occurred at peak stress when the sample completely destructed, although a few minor AE events were also detected right before destruction, indicating the homogeneous structure of PLA samples. Pectin/PLA composites, unlike pure PLA samples, emitted sound at much earlier stretch. The early occurrence in AE hit correlated to the increase in the slope of the stress-strain curves. This behavior indicated the early defect formation probably due to separation between some pectin particles and PLA at lower stress. Composites fractured at maximum stress, where the largest AE event was recorded. Such behavior is typical for a two-phase composite.

As shown in table 2, the Young's moduli of PLA and Pectin/PLA were similar, ~2500 MPa, indicating that the two materials are similar in stiffness. To fully understand the effects of adding pectin to PLA matrix, we also investigated the mechanical behaviors of composite samples subjected to a cyclic stretch, particularly, the hysteresis that is the energy loss during each cycle of the cycling test. It was calculated by subtracting unloading energy from loading energy. Hysteresis may have a close relationship to resiliency, which governs the dimensional stability of packaging products. Figure 8 shows the stress-strain curves as a function of the number of stretch cycles. We observed that the pure PLA samples (figure 8A) had a higher stress at loading compared to the Pectin/PLA composite samples (figure 8B). These stress-strain curves reveal the mechanical behavior differences between these two samples. Particularly, in the first cycle, the loop (hysteresis) for the composite sample is significantly bigger than pure PLA samples. Figure 9 shows the relationship between hysteresis and stretch cycle. At the first cycle, it was evident that the hysteresis for the composite samples was greater than that of the pure PLA samples. Presumably, adding pectin to PLA led to a decrease in elasticity of samples, therefore increasing the hysteresis (energy loss) in cyclic tests. However, after the first cycle, there appeared to be little difference between the pure PLA and Pectin/PLA composite samples. Figure 10 demonstrates the stress as a function of stretch cycles. For the pure PLA sample, figure 10A shows very little change in peak stress, whereas figure 10B clearly demonstrates that the peak stress steadily decreases as number of stretch cycles increase. This behavior implies that the addition of pectin weakened the composites and caused more permanent deformation at the first stress, therefore less force is needed to further stretch the sample. On the other hand, pure PLA samples have a homogenous structure, and have a higher peak stress than the Pectin/PLA composites. This higher stress indicates that PLA samples are structurally more resistant to a deformation than the Pectin/PLA composite. Because of its high resistance to deformation, the peak stress for PLA samples remains constant through various stretching cycles.

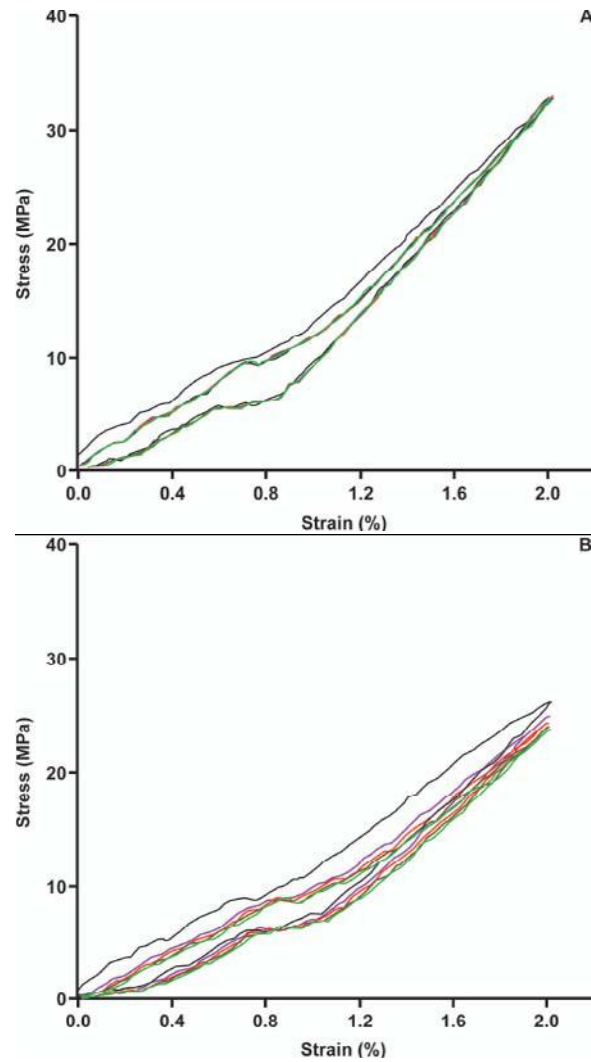


Figure 8. Stress-strain curves observed for cyclic tensile tests; (A) PLA samples and (B) Pectin/PLA composites. Cycling #1-#5 in sequence colored as black, purple, red, brown, and green. (Color figure can be only viewed in the online issue).

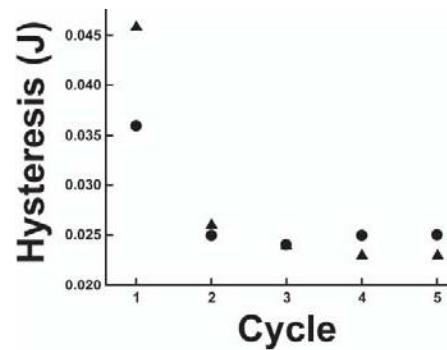


Figure 9. Energy loss (hysteresis) as a function of cycle. PLA samples ●, Pectin/PLA composites ▲.

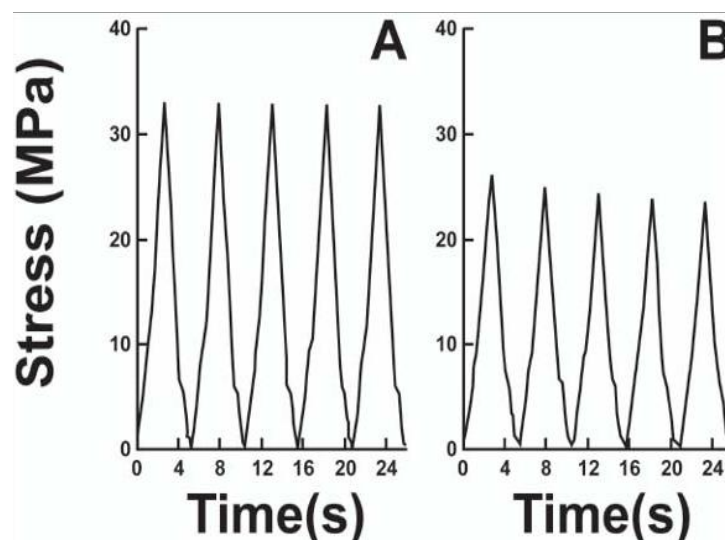


Figure 10. Stress curves as a function of time; (A) PLA samples and (B) Pectin/PLA composites.

The inclusion of pectin reduced the tensile strength and elongation to break of PLA. Nevertheless, the Pectin/PLA composites are still strong enough to serve as a packaging material, if one compared their tensile strength with other polymeric packaging materials, such as biodegradable blends from soybean flour protein and carboxymethylated corn cob, 29 MPa,<sup>17</sup> or non-biodegradable polyvinyl chloride, 35 MPa, and polystyrene, 55 MPa.[19]

Samples were tested for antimicrobial activity by two methods: one is the agar diffusion method and the other, liquid phase culture. Figure 11 shows the images taken from the agar diffusion test. Without the pre-treatment of nisin solution, PLA (sample #1) and Pectin/PLA (sample #2) samples showed no antimicrobial activity. With the pre-treatment of nisin solution, PLA samples (sample #3) also showed no antimicrobial activity. Probably, it could be attributed to the hydrophobic nature of PLA surfaces that limits the nisin binding, while facilitating the loss of bound nisin during the washing process. In contrast, the Pectin/PLA composite samples that were pre-treated with nisin solution (sample #4) demonstrated a significant antimicrobial activity against *L. plantarum*. No bacterial growth could be detected on the agar that was covered by sample #4. Furthermore, the diameter of inhibition zone around sample #4 was  $2.41 \pm 0.05$  cm, whereas the ratio of the diameter of the zones of inhibition to the diameter of specimen was 1.5. This indicates that nisin was released from the composite film into the agar layer and inhibited the microbial cells growth on the agar.

To confirm this result, the samples were tested by incubation with a liquid medium containing same bacterial under standard condition. As shown in figure 12, there were no differences in microbial counts between sample #3 and the control at time points of 0, 2, 16, and 24 h. However, sample #4 exhibited a strong activity against *L. plantarum*. At 2 h incubation time, sample #4 had already reduced the cells from 5.1 logs to 2.5 logs. No colony in sample #4 was detected at a  $10^{-1}$  dilution level ( $<10$  cfu/ml) at 16 h and 24 h, whereas sample #3 had 9 logs and 9.2 logs of the cells, respectively.

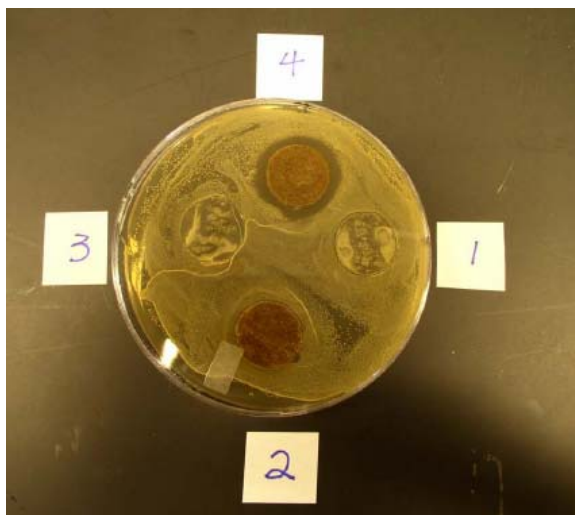


Figure 11 Antimicrobial effect on *L. Plantarum* growth by the agar diffusion method. Samples #1 and #3, PLA samples; #2 and #4, Pectin/PLA composites; sample #1 and #2, specimens without nisin solution pre-treatment; #3 and #4, with nisin solution pretreatment.

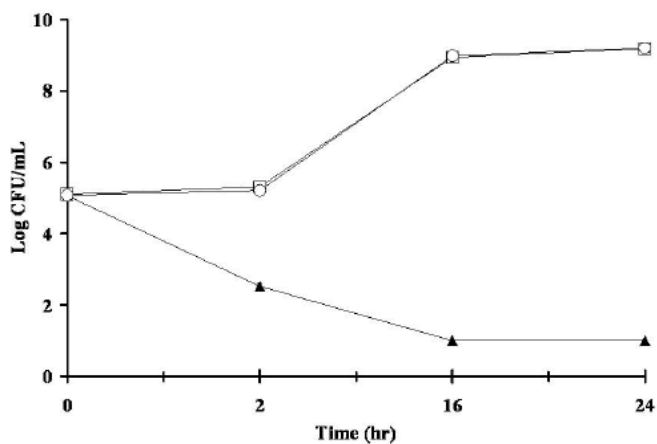


Figure 12 Antimicrobial effect on *L. Plantarum* growth by the liquid culture method. ▲ Pectin/PLA composites with nisin solution pre-treatment, ○ PLA samples with nisin solution pre-treatment, and □ control.

## CONCLUSIONS

By the incorporation of pectin particles into PLA matrix, we have prepared a composite that can absorb and store hydrophilic antimicrobial compounds, such as nisin. The resultant composite was able to inhibit bacterial growth in aqueous or gel phases by releasing the absorbed nisin. The incorporated pectin particles were located on the surface and extended deep into the materials, facilitating access and absorption of nisin into the composites. Although the mechanical properties of the composite were somewhat poorer than the films



made from PLA alone, they were sufficiently good to produce a viable packaging material. Further research is needed to optimize the ratio of pectin to PLA. The goal is to balance absorption of antimicrobial reagents and retention of mechanical properties. Furthermore, the diffusion and release kinetics of nisin into and out of the films needs to be evaluated.

### ACKNOWLEDGMENT

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*Chapter 3*

## **PECTIN COMPOSITE FILMS**

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### **ABSTRACT**

Blends of pectin with starch or proteins, or with synthetic hydrocolloids were investigated to characterize their ability to form strong self-supporting films. Microscopic analysis indicated that the blends were biphasic structure, except for pectin/proteins composites. Pure pectin films exhibited no thermal transitions, whereas the inclusion of plasticizers introduced a glass transition temperature to the pectin blends, as revealed by dynamic thermal mechanical analysis. The variation in composition, ratio and plasticizers determined the thermal transition property and mechanical properties of the blends, such as storage modulus, loss modulus, tensile strength and maximal elongation. Treating the pectin/proteins composite films with glutaraldehyde/methanol induced chemical cross-linking with the proteins and reduced the interstitial spaces among the macromolecules and, consequently, improved their mechanical properties and water resistance. Furthermore, antimicrobial reagents can be loaded onto the composite films, the resultant films can be used for food packaging or wrapping. The article summarizes the research results on pectin films conducted at the Eastern Regional Research Center, Agricultural Research Service, USDA, exploring the new utilities of pectin.

### **1. INTRODUCTION**

Pectin is a cell wall polysaccharide. It consists of one third of the cell wall dry substances of higher plants, and occupies a much less proportion in lower plants such as grasses.

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Mention of brand or firm name does not constitute an endorsement by the U.S. Department of Agriculture above others of similar nature not mentioned.

Commercial pectin is mainly derived from citrus peels and apple pomace, also from sugar beet pulp and sunflower heads. All those are the products, coproducts, or byproducts of agricultural processing. Thus, the production of pectin and the research and development on pectin derived non-food products address two important issues in agribusiness: the use of surplus and the development of value-added materials.

The majority of pectin structure consists of homopolymeric partially methylated poly- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid residues (“smooth” areas), but there are substantial “hairy” areas of alternating  $\alpha$ -(1 $\rightarrow$ 2)-L-rhamnosyl- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonosyl sections containing branch-points with mostly neutral side chains (1 - 20 residues) of mainly L-arabinose and D-galactose (rhamnogalacturonan I). Pectins may also contain rhamnogalacturonan II with sidechains containing other residues such as D-xylose, L-fucose, D-glucuronic acid, D-apiose, 3-deoxy-D-*manno*-2-octulosonic acid and 3-deoxy-D-*lyxo*-2-heptulosonic acid attached to poly- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid regions. The types and amount of substructural entities in pectin preparations depend on their source and extraction methodology. Commercial extraction causes extensive degradation of the neutral sugar-containing side chains. Pectin molecule does not adopt a straight conformation in solution, but is extended and curved with a large amount of flexibility. The carboxylate groups tend to expand the structure of pectin. Methylation of these carboxylic acid groups forms their methyl esters, which are much more hydrophobic and have a different effect on the structuring of surrounding water. Thus, the properties of pectin depend on the degree of esterification (D.E.). High D.E. pectin (> 40% esterified) tends to gel by the formation of hydrogen-bonding and hydrophobic interactions at low solution pH (pH  $\sim$ 3.0, to reduce electrostatic repulsions) or in the presence of sugars (> 70% esterified); while, low D.E. pectin (< 40% esterified) gels by calcium di-cation bridging between adjacent two-fold helical chains forming so-called “egg-box” junction zone structures so long as a minimum of 14-20 residues can cooperate [1-4].

Closely related to the gelling properties, pectin is a well established film forming agent. In cell wall, pectin associates with cellulose, hemicellulose, lignin, proteins and metal ions to form a physical barrier, which conducts mass transportation, signal transduction and protect the cells from environmental invasion. In isolated form, pectin readily reassociates or aggregates to form networks, and interacts with proteins, other polysaccharides and synthetic hydrocolloids via hydrogen bonding, ionic or hydrophobic interactions. This character has led to applications of pectin in encapsulation, coating, packaging and wrapping for food and pharmaceutical products.

In this review article, we summarized the recent work in our laboratory on the fabrication and characterization of pectin composite films. Materials used for blending with pectin include high-amylose starch [5-7], fish skin gelatin (FSG), soybean flour protein (SFP) [8, 9], poly(vinyl alcohol) (PVA) [10,11], and poly(ethylene oxide) [12]. The resultant pectin composite films have demonstrated to possess diverse physical, biological, and chemical properties, which can be tailored to satisfy various applications. Starch, gelatin and oilseed proteins have demonstrated a good film-forming property and have a long history of safe use in the food and food packaging industries, and so the synthetic hydrocolloids of PVA and PEO [12-14].

## 2. PECTIN/STARCH FILMS

Pectin/starch composite films were prepared by mixing solutions of pectin and glycerine with gelatinized starch solutions, casting them on a LEXAN plate using a Micro film applicator (Paul N. Gardner Co., Pompano Beach, FL), and allowing the films to air-dry overnight. After air-drying, the samples were vacuum-dried for 30 min at room temperature. Films were removed from the coating plates with a razor blade. For comparison purpose, other pectin composite films discussed in this article were also prepared by the same method. The resultant films were tested for structural and mechanical properties and other properties. Small deformation analysis, using a Rheometrics RSA II solids analyzer (Piscataway, NJ), was performed as a complement of microscopic examination.

In general, the pectin/starch films showed a two-phase structure. The pectin formed a homogeneous smooth matrix phase, within which the starch particles distributed and embedded. The size and distribution of the filler phase highly depended on the degree of starch gelatinization. The more the starch granules gelatinized (i.e., treated with microwave oven for a longer time), the more homogeneous films could be obtained.

The presence of the starch had an effect on the mechanical properties of composite films. The film containing 35% starch was noticeably more brittle than films containing less starch. As the amount of starch present increased from 0% to 35% by weight, both the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of pectin/starch composite films gradually decrease. At 35% starch both moduli were one-third lower than for the sample containing no starch. These differences were consistent over the temperatures ranging from 25 °C to 210 °C. In comparison with some commercially available thermoplastics, all samples tested had values of  $E'$  and  $E''$  at room temperature that were approximately an order of magnitude higher than those for polyethylene. While the high film moduli were encouraging because they open up many potential uses, the films were too brittle for use in many applications. Therefore, plasticizers were added to the system to obtain films which were more flexible and less susceptible to brittle failure. Four plasticizers were used: urea, glycerine, poly(ethylene glycol) 300, and poly(ethylene glycol) 1000. Glycerine was distinguished from the others. The glycerol breaks intermolecular pectin-pectin hydrogen bonds through preferential solvation (i.e. substitution of pectin-pectin hydrogen bonds with pectin-glycerol hydrogen bonds), and thereby facilitates chain slippage when pectin films are stressed. The level of glycerine present in the films had a noticeable effect on the tenacity and elongation to break of the films. Both elongation and tenacity roughly doubled as the glycerine content was raised from 9% to 19%. No further increase was seen at 27% glycerine. Significantly higher plasticizer levels may be necessary to obtain large increases in elongation to break.

It was also noted that films containing only pectin were slightly tacky. This tackiness seemed to be reduced or eliminated in the samples that contained starch. Increasing the glycerine content increased the tack of the films; however, this was overcome at higher starch levels. It appears that the starch is a useful additive to control or eliminate tack in these films.

In conclusion, plasticized pectin/starch blends can be made into strong, fairly flexible films with tensile strengths on the order of  $3 \times 10^8$  dyn/cm<sup>2</sup>, approximating those of commercial plastic films, and elongations of 1-3 %. The room temperature storage and loss moduli of the films were  $1.5-6 \times 10^{10}$  and  $1.3-5 \times 10^9$  dyn/cm<sup>2</sup>, respectively, depending on composition. This is equal to or higher than what is found in many commercial films.

### 3. PECTIN/PROTEINS FILMS

Pectin/protein composite films were prepared from pectin with several proteins, such as bovine serum albumin (BSA), chicken egg albumin (CEA), type B bovine skin gelatin (BSG), type A porcine skin gelatin (PSG), fish skin gelatin (FSG), and type I soybean flour protein (SFP). The pectin and protein composite films possess diverse physical, biological, and chemical properties, which can be tailored to satisfy various applications.

The inclusion of protein promoted molecular interactions, resulting in a homogeneous structure, as revealed by scanning electron microscopy, confocal laser scanning microscopy, and fracture-acoustic emission analysis [8, 9]. The treatment of pectin/protein composite films with glutaraldehyde/methanol resulted in a well organized microstructure (figure 1). The glutaraldehyde treatment introduced protein interactions via bridging of their  $-NH_2$  groups. The resultant protein packs (with the size of 100-300 nm scale) were arranged into fibers; the fibers were then parallel to each other to form a tightly packed, non-woven structure. The micrographs also showed there were gaps between adjacent packs with the size of  $<5$  nm (figure 1, indicated by arrow), forming closer connections, and crevices ranging from 50 to 100 nm between parallel fibers (figure 1, indicated by triangle), forming relatively loose connections. Since under the experimental conditions, the glutaraldehyde-mediated reactions only occurred between the active aldehyde and primary amines of the proteins and could not be referred to the hydroxyl groups of polysaccharides [15], the "free" pectin macromolecules, supposedly, were packaged within or penetrated through the protein packs [16]. Although the glutaraldehyde does not cause pectin-pectin or pectin-protein cross-linking, the methanol, as a dehydrate reagent, could reduce the free spaces between macromolecules and, consequently, enhance the polysaccharide chain-chain interactions, such as hydrogen bonding and hydrophobic interactions.

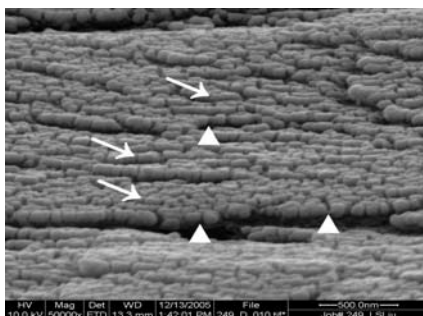


Figure 1. SEM photograph of frozen-fractured pectin/FSG film pretreated with 0.1% glutaraldehyde in methanol, showing gaps (arrow) between adjacent packs with the size of  $<5$  nm, and crevices (triangle) with the size ranging from 50 to 100 nm between parallel fibers.

To verify this hypothesis, the pectin/protein films were immersed in solutions at three different pH, their swelling behavior and the amount of released pectin and proteins were measured. It was found that the chemical treatment suppressed protein release, but not pectin release. The dissolution of pectin/proteins composite films was pH-dependent. The dissolution rate increased in the sequence of  $pH\ 4.0 < pH\ 7.2 < pH\ 8.5$ . The pectin-FSG and pectin-SFP films did not dissolve at any pH tested, but did display a pH-dependent swelling behavior. Both composite films swelled least at pH 4.0. As the solution pH increased, the

composite films were more swelled. Measurements at the same pH revealed that pectin films containing SFP swelled into a larger size than pectin films containing an equal amount of FSG. The effect of pH on the dissolution of the paired biopolymers could be referred to the electrostatic interactions between the two biopolymers. These electrostatic interactions are responsible for the mechanism of the formation-deformation of the electrostatic complex. Accordingly, the values of  $pK_a$  or  $pI$ , respectively, are around 4 for pectin, 4.8-5.2 for FSG, and 4.5-5.1 for SFP; electrostatic complexes between pectin and proteins could be formed at pH 4 solution. This may stabilize the films and suppress their swelling. For the composite films without chemical treatment, about 50% of pectin or proteins were released into the dissolution buffer at pH 4.0 in 48 h, whereas the values increased as the solution pH increased and reached the highest decomposition around 80-90% at pH 8.5. The chemical treatment did not influence the release of pectin from composite films, but did suppress the release of protein. This was more pronounced for the films containing FSG than SFP; less than 20% of the incorporated FSP released into the three dissolution buffers, whereas the SFP release seemed to be more pH-dependent even after chemical treatment. This could be attributed to more primary amine being available in FSG than in SFP, which generated more cross-linked bonds with FSG films than with SFP films.

The effects of protein blending and the following chemical treatment on other water resistant properties of resultant pectin composite films, such as water adsorption and water vapor transmission were summarized on table 1. The protein-free pectin films showed the highest values in both water adsorption and water vapor permeability. The chemical treatment showed little impact on water adsorption of pectin films but dramatically reduced the water vapor permeability of the films. As discussed in the above section, film dehydration in anhydrous methanol may enhance the level of chain-chain packing and reduce interstitial spaces among the pectin molecules. However, this is a reversible process. After conditioning in a more humid environment for a longer period, that is, at 95% relative humidity for 2 weeks as in this study, the dehydrated films could gradually be re-hydrated; thus, their water adsorption capability could be partially recovered. For pectin-FSG composite films, both water adsorption and water vapor permeability were suppressed. The smaller values of water adsorption and WVTR were obtained at higher FSG content. The chemical cross-linking further suppressed water adsorption and water vapor transmission; these values were even lower than those obtained for transglutaminase-modified protein and pectin-protein films [16, 17]. The blends of SFP with pectin and the subsequent chemical cross-linking showed an impact on water adsorption and penetration, which had the same trend as the inclusion of FSG but smaller. It is consistent with the results from the dissolution studies.

The structural characteristics have an impact on the mechanical properties of the blend. Table 2 shows the stiffness, strength, and flexibility of some blends. The inclusion of FSG or SFP remarkably enhanced both the tensile strength and the elongation of pectin films. The chemical treatment further strengthened the films. The chemical treatment also has a tendency to produce a stiffer composite as indicated by the increase in tensile modulus and the decrease in elongation. Adequate tensile strength is very important in manufacturing polymeric films, where the material is often subjected to a force during mechanical stretching. In a variety of end uses, products must be capable of resisting considerable stress without fracture. The pectin-protein composite films exhibit tensile strengths as high as 24-59 MPa (table 2). By comparison with the tensile strength of 29 MPa for biodegradable blends from SFP and carboxymethylated corn cob [17], 35 MPa for non-biodegradable polyvinyl chloride, and 55

MPa for polystyrene [18], the composite materials presented in the current study appear to be promising candidates for biodegradable wrapping and packaging materials.

**Table 1. Water Resistant Property of Pectin/Protein Films**

material	water adsorption <sup>b</sup> (%)	WVTR <sup>c</sup> (g × m <sup>-2</sup> × day <sup>-1</sup> )
pectin	47 ± 6	226 ± 11
pectin-gt <sup>d*</sup>	42 ± 7	178 ± 23
FSG	28 ± 4	98 ± 11
FSG-gt	6 ± 2	112 ± 15
pectin-FSG (0.1) <sup>e,#,†</sup>	32 ± 4	147 ± 7
pectin-FSG (0.1)-gt <sup>‡</sup>	12 ± 2	103 ± 12
pectin-SFP (0.1)	37 ± 5	196 ± 16
pectin-SFP (0.1)-gt <sup>‡</sup>	17 ± 6	158 ± 17
pectin-FSG (0.2)	26 ± 4	121 ± 10
pectin-FSG (0.2)-gt <sup>‡</sup>	8 ± 3	114 ± 9
pectin-SFP (0.2)	29 ± 6	184 ± 15
pectin-SFP (0.2)-gt <sup>‡</sup>	11 ± 2	161 ± 18

<sup>a</sup> The following symbols indicate statistical significance ( $p < 0.01$ ):  $\boxtimes$ ,  $\boxdot$ ,  $\perp$ ,  $\ddagger$ ,  $\diamond$ ,  $\ddagger$ ,  $\cdot$ ,  $\blacktriangle$ ,  $\blacklozenge$ . <sup>b</sup> Measured by weight gain after conditioning at 95% relative humidity at room temperature. <sup>c</sup> Determined by ISO 2528 (1995E). <sup>d</sup> -gt\* indicates the treatment of films with 0.1% glutaraldehyde/methanol solution. <sup>e</sup> Data in parentheses indicate the weight percent of protein in composite.

**Table 2. Mechanical Properties of Pectin/Proteins Composite Films<sup>a</sup>**

material	tensile modulus (MPa)	tensile strength (MPa)	elongation (max) (%)
pectin <sup>•,‡,‡</sup>	1082 ± 168	17.0 ± 3.4	2.5 ± 0.6
pectin-gt <sup>*b</sup>	4139 ± 766	59.2 ± 11.1	1.7 ± 0.5
FSG <sup>‡</sup>	1906 ± 34	71.8 ± 0.9	6.4 ± 2.4
FSG-gt <sup>‡</sup>	3132 ± 319	99.2 ± 6.1	3.6 ± 0.6
pectin-FSG (0.1) <sup>c,#,‡</sup>	1825 ± 43	43.5 ± 7.6	3.0 ± 1.5
pectin-FSG (0.1)-gt <sup>‡,‡</sup>	3306 ± 86	54.2 ± 6.9	2.1 ± 0.4
pectin-SFP (0.1)	1213 ± 286	24.0 ± 3.0	2.9 ± 0.9
pectin-SFP (0.1)-gt <sup>‡</sup>	2158 ± 113	33.0 ± 1.7	1.7 ± 0.4
pectin-FSG (0.2)	2178 ± 224	59.1 ± 12.4	3.2 ± 1.1
pectin-FSG (0.2)-gt	3016 ± 58	58.9 ± 1.8	2.6 ± 0.3

<sup>a</sup> The following symbols indicate statistical significance ( $p < 0.01$ ): #,  $\ddagger$ ,  $\ddagger$ ,  $\blacktriangle$ ,  $\bullet$ ,  $\blacklozenge$ ,  $\boxtimes$ ,  $\boxdot$ . <sup>b</sup> -gt\* indicates the treatment of film with 0.1% glutaraldehyde/methanol.

<sup>c</sup> Data in parentheses indicate the weight percent of protein in composite.

During a tensile test, composite deformation and fracture are accompanied by a rapid movement, relocation, or breaking of structural elements such as fillers, fibers, matrices, and their interfacial areas. As a result, sound waves are produced that can be detected by an acoustic transducer and converted into electronic signals named as “hit” using an acoustic emission (AE) analyzer. Figure 2 showed the relationship between the total elastic energy released by an acoustic event in response to the



maximal stress that specimens were subjected to. There is a clear correlation between the tensile strength and AE energy released at fracture. However, some spreading is also observed. For instance, the AE energy released for composite films with 10% proteins was detected lower than those of protein-free pectin films [comparing pectin film (●) with the composite films of 10% SFP (◐) or FSG (□) shown in figure 2]. The energy loss could be attributed to some structural factors, such as signal attenuation due to scattering or absorption losses during sound wave propagation from the AE source to the transducer and internal energy dissipation by the friction and toughening mechanisms. The preliminary results suggested that proteins might function as a lubricant in the blend structure. Observations indicated that the composite films, after blending with an adequate amount of protein, might be able to abate wave propagation. Moreover, data also showed AE energy increases with protein content.

We also studied the correlation between the stress-strain curve and AE hit rate pattern by referring one to another in order to get better understanding on the fracture mechanisms and how the structure changes effect the property of a sample. For films consisting of a single component, there were no acoustic events before the peak stress; the AE activities occurred exclusively at the peak stress when the specimens completely fractured. This behavior is due to their homogeneous structure, in which the single component specimens were able to transfer the stress evenly. In contrast, the composite films emitted sound at an earlier strain due to the micro-structural movement of individual components, which was correlated to the increase in the initial slope of the stress-strain curves (data not shown). Observation also revealed that a sudden increase in

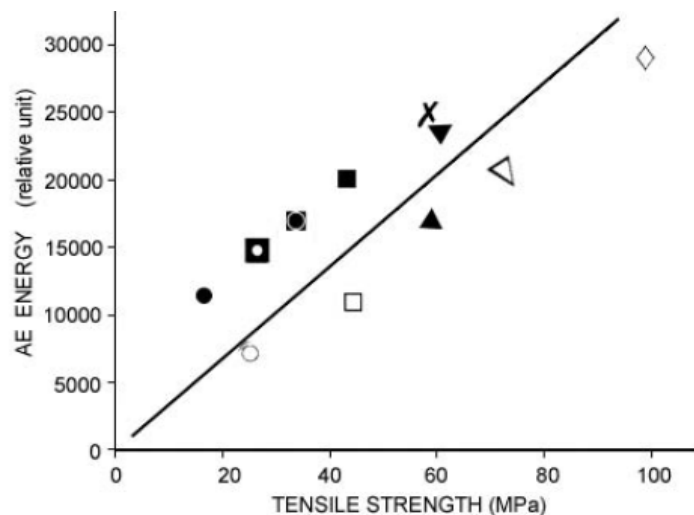


Figure 2. Acoustic energy versus tensile strength of various pectin/protein films: pectin (closed circle), pectin-gt (X), FSG (open triangle), SFG-gt (diamond), pectin-FSG (0.1) (open square); pectin-SFP (0.1) (open circle), pectin-SFP (0.1)-gt (closed circle in a square); pectin-FSG (0.2) (up closed triangle); pectin-FSG (0.2)-gt (closed down triangle); pectin-SFP (0.2) (open circle in square); pectin-SFP (0.2)-gt (closed square).

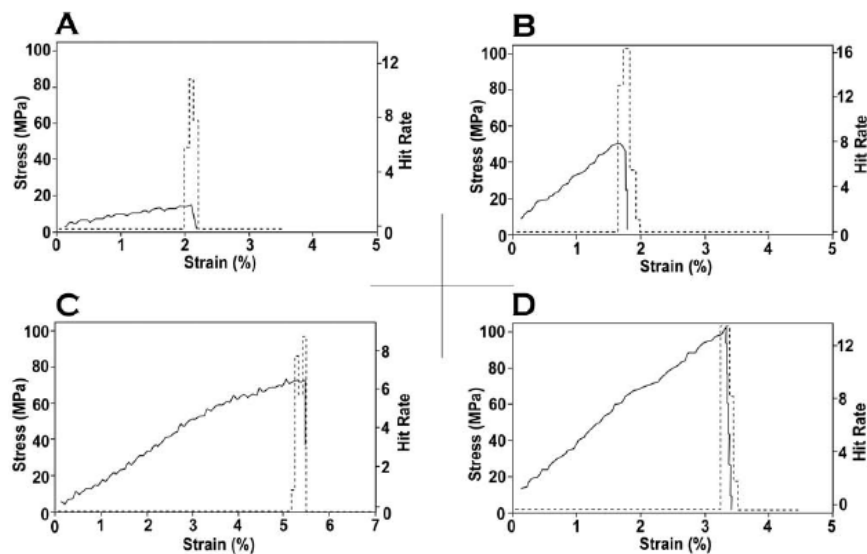


Figure 3. Relationship of strain-stress curve (solid line) with the acoustic emission hits (dotted line): pectin (A) and FSG (C) films; glutaraldehyde/methanol-treated pectin (B) and FSG (D) films.

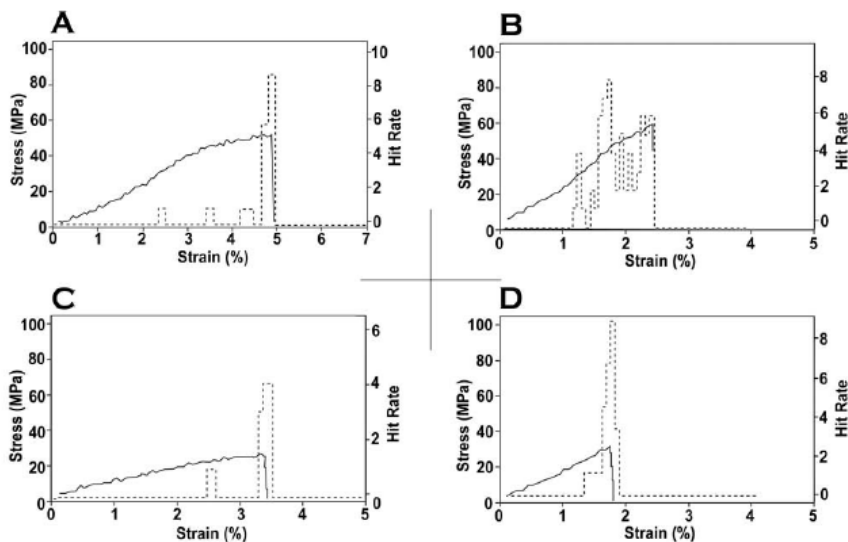


Figure 4. Relationship of strain-stress curve (solid line) with the acoustic emission hits (dotted line): pectin-FSG (A) and pectin-SFP (C) films; glutaraldehyde/methanol-treated pectin-FSG (B) and pectin-SFP (D) films.

AE hits occurred at the peak stress. Furthermore, AE hits are more frequent and are more evident for cross-linked films than for those not cross-linked. The cross-linked composite films produced a wide band of acoustic waves at a much earlier strain (figure 4 B and D). This behavior may be ascribable to structural defects such as crevices found between fibers in cross-linked blend films (figure 1). If the direction of those crevices and the direction of film elongation coincide, AE events would be further enhanced.

In conclusions, the results presented in this study indicate that inclusion of proteins into pectin films improved both mechanical strength and flexibility. The treatments of resultant composite films with glutaraldehyde/methanol further enhanced film strength and reduced water vapor permeability, while retaining the flexibility of the original pectin films to some degree. However, it appears that only chemical cross-linking can suppress the films' solubility in water, because methanol treatment is a dehydration process that reduces only the interstitial spaces between macromolecular chains and is reversible. The results suggest the potential of pectin and protein composite films in the applications of wrapping or packaging materials compared to other commercial films, which requires moderate mechanical strength and low water vapor transmission.

#### 4. PECTIN/PVA FILMS

PVA is constructed from nonrenewable resources and is not as environmentally friendly as pectin. It would be advantageous to replace PVA with pectin, because PVA films are widely used in industries. Examples include water-soluble pouches for packaging detergents and insecticides, flushable liners and laundry bags for contaminated linens, coating for paper and a temporary protective coating for metal finishes. Since the utility of a material as a coating is closely related to its film forming properties, pectin might replace PVA in these applications.

It is of interest to note that pectin/PVA films for the most part appear transparent to the naked eye. Optically dense phases appeared to be interconnected through lucent phases. The existence of two distinct phases in pectin/PVA films was confirmed by phase-contrast optical microscope. Pure pectin film was uneven and consisted of small ridges and crevices, which were oriented parallel to the film plane (data not shown). Pure PVA film appears smooth except for a few small linear ridges (data not shown). For composite films, the fracture plane becomes increasingly smoother with increasingly lower weight ratios of pectin to PVA. This may indicate the coating of pectin with PVA at higher PVA content. Pectin/PVA films form compatible biphasic composites over a wide range of compositions.

These films undergo brittle to ductile transitions with increasing concentrations of PVA. Addition of glycerol to pectin/PVA films significantly increased the ductility of these films when relatively brittle. The solubility of pectin/PVA films were temperature and composition dependent. At 30, 50 and 70°C respectively, films containing 30% or less PVA were more soluble than pure PVA films measured at the same temperature. At 70°C all compositions of films containing pectin/PVA are more soluble than pure PVA films. In general, addition of PVA to pectin films resulted in films with more PVA-like properties, and addition of pectin to PVA films gave more pectin-like properties to PVA films. Increasing the amount of PVA in the blends reduced the storage and loss modulus of the films above the glass transition temperature. The values of glass transition temperature observed decreased as the amount of PVA in the blend increased. Addition of glycerol depressed the glass transition temperature of PVA and merged it into the glass transition temperature of the pectin/glycerol blend. Changes in the molecular weight and degree of ester hydrolysis of PVA exerted a rather small effect on the blends.

Because PVA has good tensile strength and high elongation to break, the inclusion of PVA to pectin blends had good impact on the toughness of the resultant composites. The water solubility of the two polymers facilitates blending and processing.

## 5. PECTIN/PEO FILMS

Poly(ethylene oxide), PEO, is a food hydrocolloids. Pectin and PEO composite films were prepared for food packaging purpose. Microscopic analysis revealed the composite films with well-mixed integrated structures made of evenly distributed synthetic hydrocolloids in the biopolymers (figure 5).

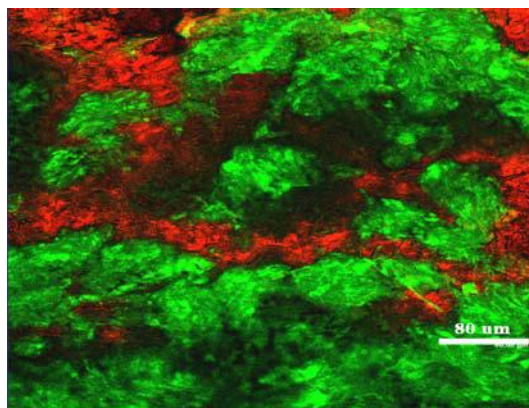


Figure 5. Confocal laser scanning microimages of pectin/PEO composite film. The organization of the biopolymers were resolved by confocal fluorescence (excitation 484 nm, emission 520-580 nm), the PEO was defined by confocal reflection (633 nm). The micrograph was collected in stereo projection in extended focus images of 20-30 micrometer-thick slabs of the film. Field width, 470  $\mu\text{m}$ .

In a variety of end uses, packaging and wrapping materials are often subjected to a force during tensile strain. The materials must be able to resist considerable stress without failing to a fracture at a designed stress. Furthermore, as edible food wrapping materials, the materials may be taken with foods together either for convenient purpose or to enhance or alter the food texture. In these cases, their mechanical properties directly relate to the mouth feel, which is an important measurement of food quality. Table 3 shows the mechanical properties of selected samples of compression and blown films. In general, the composite films have mechanical properties, such as Young's modulus and tensile strength that are similar to cast films from most natural hydrocolloids that are consumed in our ordinary life. The changes in PEO content dramatically enhanced the mechanical properties of the composite films. The results of the stress-strain cyclic tests are shown in figure 6. For the PEO-free samples, the loop created by the first cycle is bigger than those created by following cycles. Among the following cycles, the difference in loop size is not significant. For samples containing PEO, the size of loop decreased gradually as cycled, then, became constant in the last two cycles. At the end of the cyclic test, the PEO containing sample expressed a much higher stress than the PEO-free sample. Although the PEO free samples are more resistant to mechanical force

and less permanent deformation occurred than with the PEO-containing sample; the inclusion of PEO strengthens the composite films.

**Table 3. Mechanical properties of pectin/PEO composite films**

Samples	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (J/cm <sup>3</sup> )
I, (10:90)	2.35 ± 0.09	6.14 ± 0.6	77.2 ± 4.49	0.16 ± 0.08
II (30:70)	8.8 ± 0.3	13.1 ± 2.0	353.4 ± 26.9	0.90 ± 0.12
III (50:50)	3.1 ± 0.8	7.3 ± 1.5	125.2 ± 25.3	0.20 ± 0.07
IV (70:30)	2.3 ± 0.3	2.8 ± 0.3	151.2 ± 20.8	0.03 ± 0.01

Ratio in parenthesis: pectin/PEO, w/w.

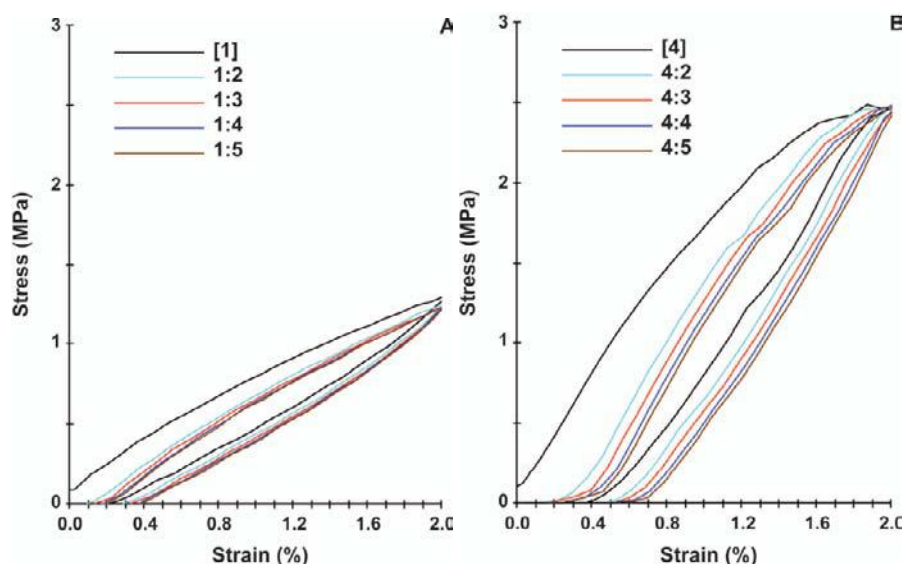


Figure 6. Stress-strain curves obtained from cyclic tensile tests for samples of pectin without PEO (A) and with PEO (B). For the PEO free films, the loop created in the first cycle is larger than following cycles. For the PEO-containing films, the size of loops gradually decreased as cycled, then became constant in the last two cycles.

The addition of PEO has an influence on film destruction caused by an external destructive force. Without PEO, the external force created a clear-cut fracture surface (data not shown), indicating the good adhesion between the two biopolymers. With the inclusion of PEO, the deformation created a fibrous surface (data not shown). This can be seen clearly from SEM and fluorescent microscopy. As shown in figure 7 A and B, fibers were pulled out, extended, and then, broken, but still embedded in the matrix phase. We examine the fibers with confocal reflection and confocal fluorescence in two channels. It confirms that the main component of the fibers is PEO; however, the biopolymers were either inserted or encapsulated within the fibers (figure 7C).

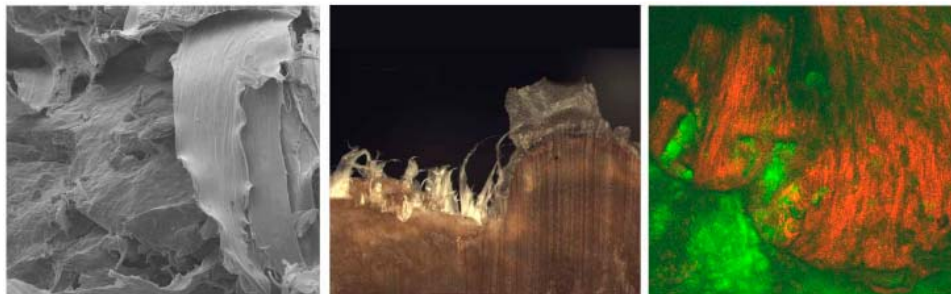


Figure 7. Microscopic images of the fractural surfaces of pectin/PEO composite films obtained by scanning electron microscope (left), laser microscope (middle), and confocal laser scanning microscope in confocal fluorescence and confocal reflection two channels (right). Field width: 520  $\mu\text{m}$  (left) and 480  $\mu\text{m}$  (middle and right).

In the spectrum of food packaging and wrapping materials, antimicrobial film is a new member. Besides providing a physical barrier, the films function by prohibition, protection and suppression of microbial migration to or growth in the packages by creating antimicrobial surfaces or releasing antimicrobial substances. The use of antimicrobial materials in food packaging improves food safety and is more convenient to the consumers; therefore, the market for antimicrobial food packaging is projected to grow rapidly [19, 20]. In the present study, we incorporated an antimicrobial polypeptide, nisin, into the film formulation. The antimicrobial activity of resultant films is shown in figure 8. Without nisin incorporation, films were not active at all (diamond). In contrast, the nisin incorporated composite films inhibited bacterial growth.

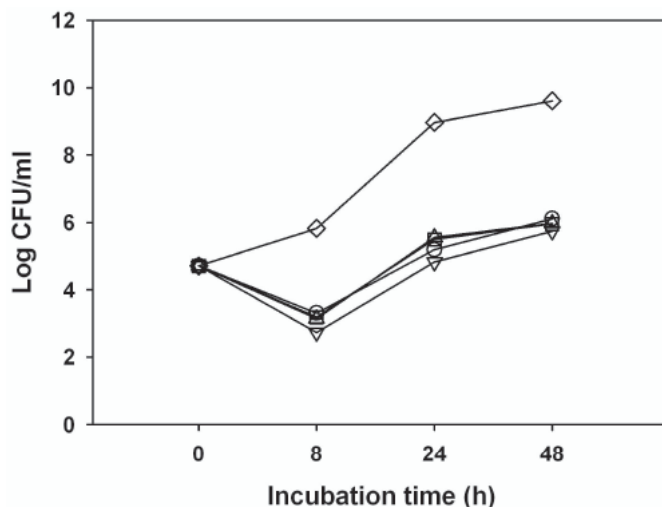


Figure 8. Growth of *Listeria monocytogenes* in BHI broth at 24 °C. Control (diamond), Nisaplin® prior to loading (square), Nisaplin® post loading (circle), Nisaplin® in composite film I (up triangle), and Nisaplin® in composite film II (down triangle).

## 6. SUMMARY

Pectin is used as food ingredients, although pectin is not a energy contributor to the body and only digested by colonic microflora. Pectin is water soluble and readily to associate with other polysaccharides, proteins, polyelectrolytes, and synthetic hydrocolloids to form networks. New uses for pectin derived products are needed to better utilize abundant crop processing residues. Edible and/or antimicrobial packaging materials were developed from pectin and starch, pectin and proteins, or pectin and food-grade synthetic hydrocolloids. The composite films possess the mechanical properties similar to those of petroleum-derived thermoplastics that are currently used for food packaging, and can absorb antimicrobial agents and control their release, serving as an active barrier for the inhibition of bacterial migration and growth. The edible films provide a barrier to moisture, lipids, and aromas, and can be used to alter or retain the food texture, based on the ratio of pectin and other film components. These new packaging materials are green biobased products that can replace petroleum-based products.

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