Elasticity Studies on Leather Retanned with Various Types of Acrylic Polymers

by

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Abstract

Different acrylic polymer retanning agents were synthesized with acrylic acid as the primary monomer and eight other acrylate monomers (MAA-methyl acrylic acid, EA-ethyl acrylate, BA- butyl acrylate, VAc-vinyl acetate, MA-methyl acrylate, AM-acrylamide, IA-Itaconic acid, HEA-2-Hydroxyethyl acrylate) as commoners. The eight copolymers were applied in the retanning process separately and the elasticity of the resultant leather was discussed. The results showed that the leather elasticity could be tested by calculating Young's modulus of the elastic deformation, which was a variable region on the load-displacement curve, and Young's modulus of the elastic deformation could serve as an independent parameter in characterizing leather's physical properties. The relation between the elasticity and the dosage of copolymer was discussed, and it revealed that every comonomer had a proper dosage at which level the resultant leather showed the lowest Young's modulus. Then the effects of the eight comonomers on leather elasticity were compared under the same condition. It showed that the soft comonomers, BA and EA, contributed more in leather elasticity than other selected comonomers.

Resumen

Diferentes agentes recurtientes poliméricos fueron sintetizados basados en ácido acrílico como el monómero principal y ocho distintos acrilatos monoméricos ("MAA"- ácido metil acrílico, "EA"-etíl acrilato, "BA"-butil acrilato, "VAc"-acetato vinílico, "MA"-metil acrilato, "AM"-acril amida, "IA"-acido itacónico, "HEA"-2hidróxietil acrilato, como co-monómeros. Los ocho co-polímeros se utilizaron separadamente en procesos de recurtición y la elasticidad resultante en los cueros se discutió. Los resultados demostraron que la elasticidad se podría comprobar por cálculo el módulo de Young de la deformación elástica, el cual es una región variable en la curva de carga contra el desplazamiento, y el módulo de Young en la deformación elástica, podría servir como un parámetro independiente para la caracterización de las propiedades físicas del cuero. La relación entre la elasticidad y la oferta del co-polímero fue discutida, y reveló que cada co-monómero tendría una oferta adecuada a la cual este nivel resultó en un mínimo valor del módulo de Young. Los efectos de los ocho co-polímeros entonces sobre la elasticidad del cuero fueron comparados bajo la misma condición. Se demostró que los co-monómeros más blandos, BA y EA, contribuyeron más a la elasticidad del cuero que otros co-monómeros seleccionados.

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INTRODUCTION

Retanning is critical to attain the required physical properties for leather products, during which acrylic polymers are commonly used. Acrylic polymer retanning agents have proliferated worldwide because they are products with low cost but high performance[1]. Research about acrylic polymer products has also been carried out world wide during the past decades, and some of the researchers, for example, Anton[2] from Rohm and Haas Company and Jianzhong Ma[3] from China, have contributed a lot.

Elasticity is a precious property of leather products, and leather with good elasticity gives a comfortable and soft feeling when touched. There is a lack of information, however, regarding performance of acrylic polymer retanning agents in terms of elasticity of the resultant leather. Nor is much known regarding effective methods to measure the elasticity. Such information would help leather manufacturers select the right acrylic polymers to provide leather with the desired qualities. We therefore conducted research to identify a practical method to measure leather elasticity by calculating Young's modulus of the elasticity deformation, i.e., the initial linear curve in the load-displace curve when it was pulled under a certain condition. Additionally, we selected eight comonomers, which were used to copolymerize with acrylic acid and obtained the proper dosage of each comonomer by comparing the elasticity of the products produced. The effect of different comonomers on leather elasticity was examined. In this way, we identified the most effective comonomers for producing elastic properties in retanned leather.

EXPERIMENTAL

Synthsis of Copolymers

First, 50ml of water was fed into a flask; the temperature of the water bath was controlled at 75°C. Then ammonium persulfate was dissolved in 20ml of water. According to the compositions of every comonomer in table I, AA and the comonomer were mixed together thoroughly. As the temperature of the flask approached 75°C, the ammonium persulfate and the monomer mixture were drip fed to finish in 60min. After the feeding, the temperature was raised to 80°C and it was kept for 120min. Then the system was cooled to room temperature and 40% sodium hydroxide solution was added to control the pH value at 5.0.

Application of the Copolymers

Wet blue goat sides with a thickness of about 0.9 mm were obtained from a tannery in Hebei Province. To minimize the experimental errors, the leather samples of every group were taken from the adjacent place in the same piece. After obtaining the proper dosage of every copolymer in every group, there was a comparison between the eight selected copolymers, and the eight samples were also taken from the same but larger piece.

Measurement of the Leather Properties

Leather properties, including tensile strength, constant load elongation, breaking elongation, tear strength, were determined on a tensile testing machine, according to the standard[4]. The pulling speed was 100 mm/min and the samples tested were 50 mm in length and 10 mm in width.

Young's modulus of the elastic deformation (not exactly Young's modulus in material science), which is used to characterize leather elasticity in this paper, is also determined under the same condition. The original curve we obtained is a load-displacement curve, and it is converted into a stress-strain connection as follows:

$$\text{Young's modulus} = \frac{stress}{strain} = \frac{\dfrac{load}{width \times thickness}}{\dfrac{displacement}{length}} \quad (1)$$

As to the reason why we take this method, there will be a detailed explanation in the results and discussions part.

RESULTS AND DISCUSSIONS

Why we take Young's Modulus to Characterize Leather Elaticity

It is noticed that there was a regular phenomenon when leather samples are pulled under a certain condition, i.e., there is a platform in the initial part on the load-displacement curve (see figure 1). The curve is linear before the platform and the platform is different when the sample is changed. As we know, leather is a macromolecule and it obeys the general principles which also apply to macromolecules. Take curve no.1 in figure 1 for example, the pulled sample undergoes a linear elastic deformation O-A, at which stage the deformation is reversible when the strength outside is removed. Then it passes through the inflection point A and comes to a platform A-B, which is called forced high elastic deformation, and in this stage the sample stretches quickly even under little additional strength. As the pulling goes on, the load increased more rapidly than the displacement does, which stage is called strain hardening[5]. Finally, it breaks at point E.

As to the initial stage O-A, we can see more clearly in figure 2. There is a linear relation between the load and the displacement at the initial stage and all the curves shows the same. The deformation at the initial linear stage, which is defined as leather elasticity, meets Hook's law according to the knowledge of polymeric material. The deformation is reversible when the load outside is taken off, with no plastic deformation left.

TABLE I
Compositions of every comonomer (mol %)

comonomers	MAA	VAc	MA	EA	BA	AM	IA	HEA
Dosage of comonomer (comonomer/total monomers, mol %)	0%	0%	0%	0%	0%	0%	0%	0%
	10%	10%	2.5%	2.5%	5%	10%	2.5%	2.5%
	20%	20%	5.0%	5.0%	10%	20%	5.0%	5.0%
	30%	30%	7.5%	7.5%	15%	30%	7.5%	7.5%
	40%	40%	10%	10%	20%	40%	10%	10%

TABLE II
Retanning procedures

Operations	Products	Quantity (%)	Time (min)	Control
Washing	water	400%		35 °C
	NPS-1	0.5	40	
Neutralizing	water	200		35 °C
	$NaHCO_3$	0.6	60	pH=5.5
Washing				
Retanning	water	150		35 °C
	copolymer	5(based on solid)	120	
	HCOOH	0.6	20	pH =4.5
Dyeing and fatliquoring	water	150		50 °C
	ammonia	1.2	10	
	SE	5		
	SC	5		
	SG940	3	60	
	HCOOH	1.5	30	pH =3.8
Washing				
Drying				

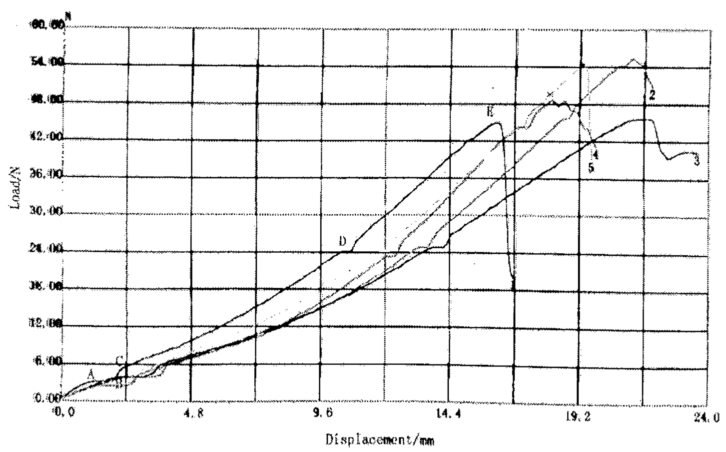

Figure 1: Load-displacement curves

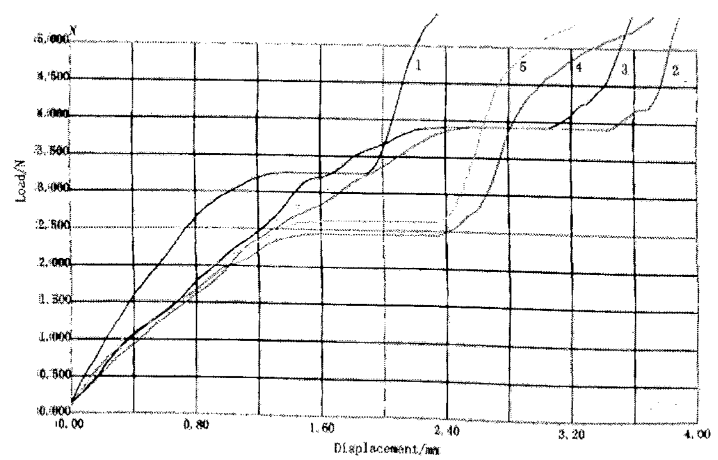

Figure 2: Load-displacement curves of the initial stage

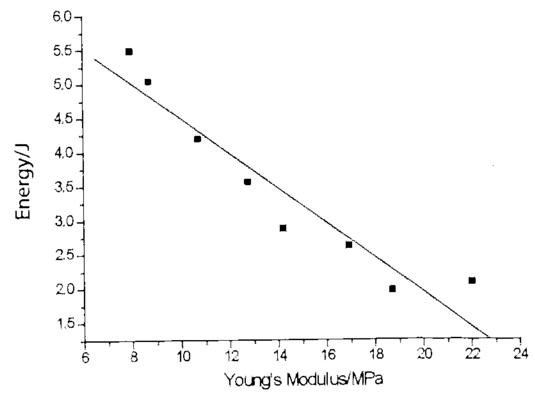

Figure 3: Correlation between Young's modulus and energy method

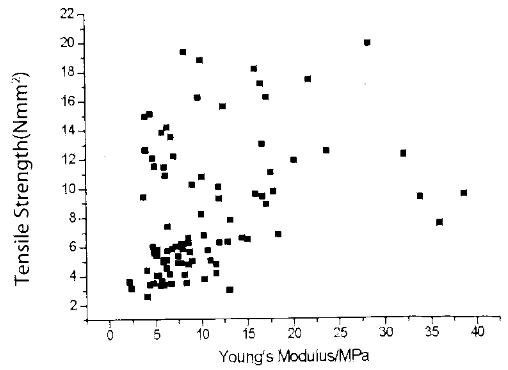

Figure 4: Scattergram between Young's modulus and tensile strength

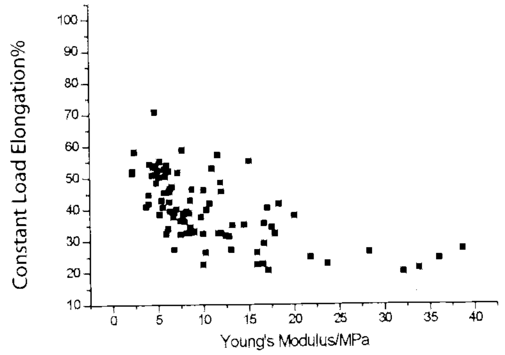

Figure 5: Scattergram between Young's modulus and constant load elongation

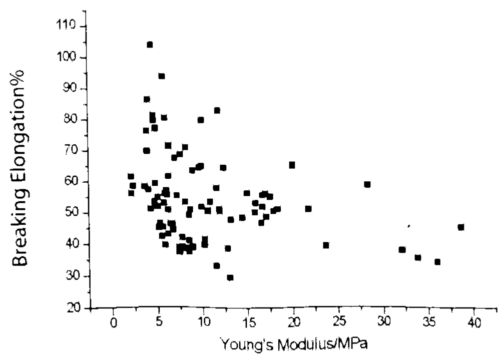

Figure 6: Scattergram between Young's modulus and breaking

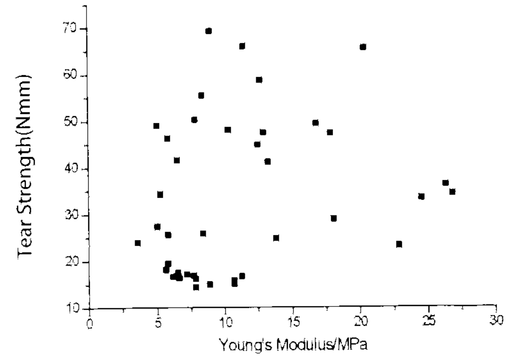

Figure 7: Scattergram between Young's modulus and tear strength

Young's modulus can easily be obtained from formula (1). The lower Young's modulus a leather owns, the more elastic it will be, as elastic leather with a lower Young's modulus needs less strength to achieve the same reversible deformation than those with higher Young's modulus. Actually Young's modulus we adopt in the paper is not the exactly Young's modulus in material science, as the elongation of the elastic deformation may differ greatly when leather of different kinds or even different location in the same piece is used. Any deformation range appointed before[6], for example 10%, is not exactly enough to totally express the leather elasticity. So, our method, taking the full reversible deformation range into account, is more objective.

Energy approach is an important and scientific method in property testing,[7,8] and it is also taken into account in the paper by calculating the integral. The integral area is the one from zero to the inflection point under the curve. Figure 3 shows that the correlation coefficient between Young's modulus and integral is -0.95. This means these two methods can achieve the same result, and we can take the simple method, i.e., to measure Young's modulus of the linear curve, to characterize leather elasticity.

Relation Between Young's Modulus and some other Physical Properties

The four physical properties, tensile strength, constant load elongation, breaking elongation, tear strength, are absolutely necessary to leather. A relation was wished to find between the four independent property and Young's modulus. So we designed a great deal of tests and got a great deal of experimental data, see details in figure 4, figure 5, figure 6 and figure 7. Six regression methods were introduced, i.e., linear regression, logarithm regression, polynomial regression, exponentiation regression, exponential regression, moving average regression, to explore their correlations. The result showed that there might be a linear relation between Young's modulus and constant load elongation, but the correlation coefficient turned out to be –0.62. The analysis approved that there is no coherence between Young's modulus and the four properties, i.e., Young's modulus can serve as an independent parameter in describing leather physical properties.

The Relationship between the Elasticity and the Dosage of Copolymer

Acrylic polymer is bounded through carbon-carbon bond, and it shows some chain flexibility. The effects of the dosage of copolymers to acrylic acid and different side group on leather elasticity are discussed.

Methyl Acrylic Acid

There is an obvious trend that Young's modulus becomes lower with the introduction of MAA, and it differs according to the dosage change of MAA. The lowest Young's modulus occurs when the dosage of MAA is 30% (see details in fig.8). On the one hand, the second copolymer breaks the relatively better regularity of molecular chain which originally exists, and the molecular chain becomes more flexible; on the other hand, there are two different substituents in the same carbon in MAA molecule, and it makes the symmetry better than that of AA, so the chain flexibility of AA-MAA copolymer is better than that of polyacrylic acid. Copolymer with more flexibility will produce leather with more elasticity, as the copolymer itself shows some elasticity and it also makes the fibers slip over one another easier. Obviously the copolymer with 30% MAA better meets the demands of elastic leather.

Vinyl Acetate

It helps to lower Young's modulus when VAc of a small amount is added, but Young's modulus becomes higher as the dosage of VAc increases gradually. The substituent of VAc is a ester group, so there is only carboxyl in the AA-VAc molecular chain to combine with leather fibers, which makes the long polymer chain more flexible and the resultant leather more elastic than that of polyacrylic acid. But the flexibility becomes worse as the ester group increases, because the substituent tends to hydrolyze when pH value is changed in retanning process. The result is more hydroxyl group, which has a strong chemical bonding with many polar groups, is generated in side chain. This makes the long main chain less flexible and the crystallinity of the polymer higher with the dosage of VAc increases. Leather fibers will tend to stick together because of more bindings when treated with polymer of this kind. So, Young's modulus of the resultant leather becomes higher.

Methyl Acrylate

It is obvious that the introduction of MA makes the resultant leather less elastic and Young's modulus remains a high level when the dosage of MA is more than 10%. A space baffle effect is formed because of methyl pendant in the molecular chain and results in a decrease in the flexibility of polymer and an increase in Young's modulus of the resultant leather.

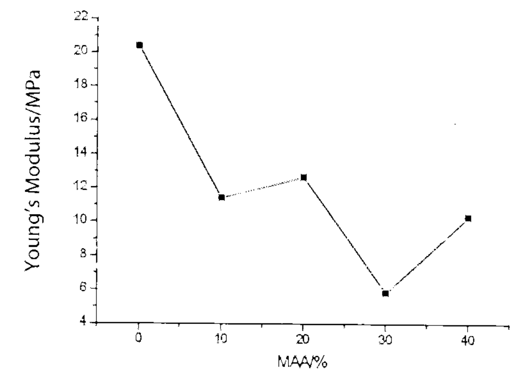

Figure 8: Effect of MAA dosage on Young's modulus of resultant leather

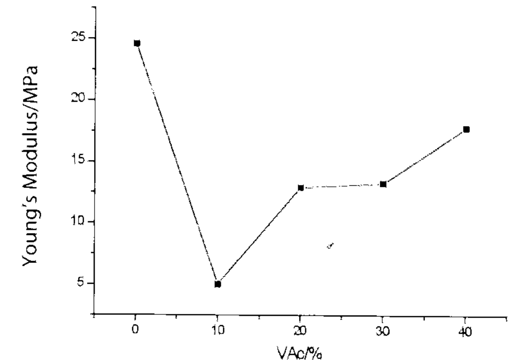

Figure 9: Effect of VAc dosage on Young's modulus of resultant leather

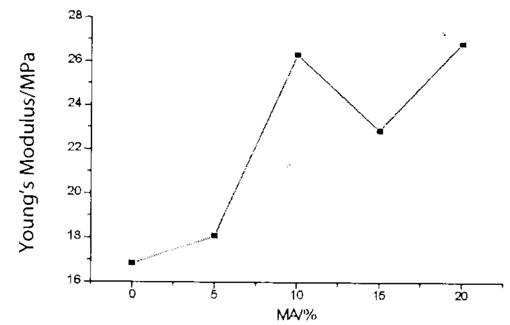

Figure 10: Effect of MA dosage on Young's modulus of resultant leather

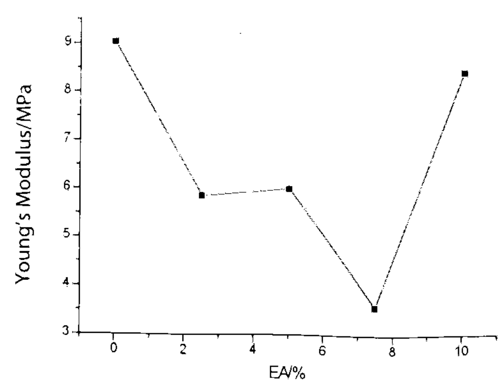

Figure 11: Effect of dosage of EA on Young's modulus of resultant leather

Ethyl Acrylate

There is a decrease of Young's modulus when EA is added, and it shows the best elasticity when the dosage of EA is 7.5%, though the trend reverses as the dosage of EA reaches 10%, as shown in figure 11. It is commonly known that EA is constantly used as a soft copolymer in polymerization, and its side group has little combination with polar groups, this makes leather fibers treated with AA-EA copolymer easier to slide over each other, i.e., the polymer shows some lubricating property. Actually, there is a balance between the space baffle effect and the lubricating property of the side group and the balance occurs when the dosage of EA is 7.5%.

Butyl Acrylate

It can be obtained from figure 12 that small amount of BA helps to keep Young's modulus at a relatively low level, especially when the dosage of BA is lower than 10%. The side group is long enough to minimize the combination between long chains and the polymer shows some lubricating property. There is also a balance between the space baffle effect and the lubricating property of the side group, and it occurs only when the dosage of BA is low.

Acrylamide

The introduction of AM breaks the relatively better regularity of molecular chain originally exists. Its introduction resulted in the decrease of Young's modulus when the amount of AM is small (see details in figure 13). Amide bonds begin to show its effect as the dosage of AM increases, as the polar group has a strong combination with other polar groups, including groups in leather fibers. More AM makes the molecular chain less flexible and the polymer state closer to glass state, at which state the polymer is hard and the resultant leather show less elasticity.

Hydroxyethyl Acrylate

There is a similarity between figure 13 and figure 14 on the curve, as AM and HEA both have a strong polar side group. The reason why HEA makes Young's modulus higher is similar to that of AM

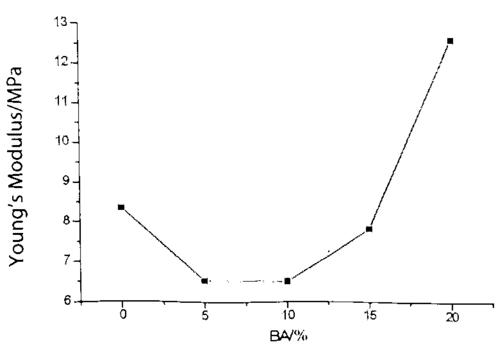

Figure 12: Effect of dosage of BA on Young's modulus of resultant leather

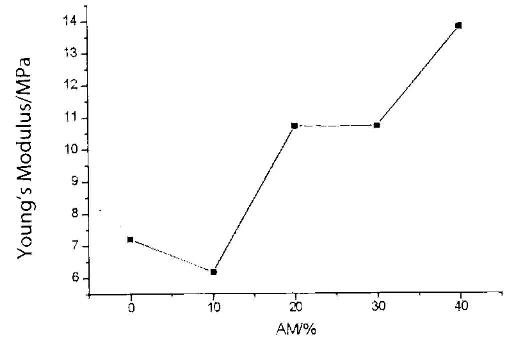

Figure 13: Effect of dosage of AM on Young's modulus of resultant leather

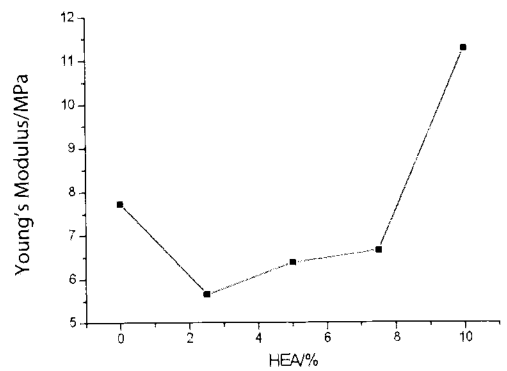

Figure 14: Effect of dosage of HEA on Young's modulus of resultant leather

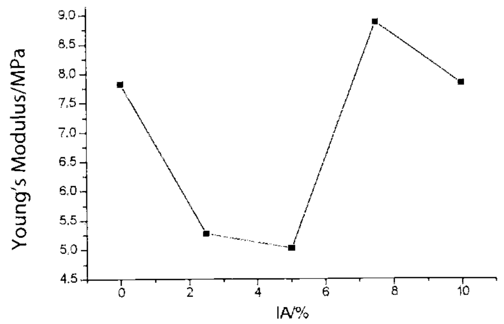

Figure 15: Effect of dosage of IA on Young's modulus of resultant leather

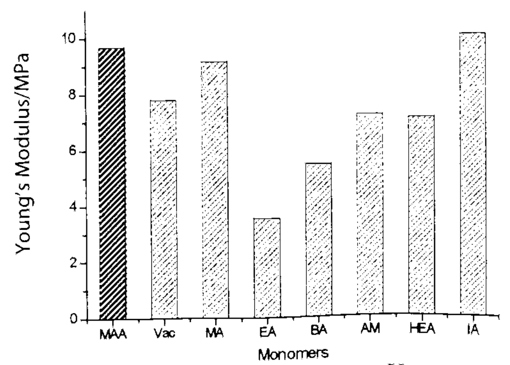

Figure 16: Effect of different comonomers on Young's modulus of resultant leather

Itaconic Acid

It can be obtained from figure 15 that a second comonomer in the long molecular chain produces better leather elasticity, just as the introduction of most of the comonomers mentioned above. The relatively low dosage of IA shows lower Young's modulus than higher ones. The space baffle effect of substituents is counteracted as there are two carboxyls in the same carbon in IA molecule, which makes the molecular chain more flexible when the dosage of IA is low. There is also a balance dosage at which level the space baffle effect and the combination of carboxyl work together to produce a lowest Young's modulus. But as we all know, carboxyl is a strong polar group and it has a strong crosslinking with other polar groups. The combination plays a more important role as the dosage increases, and Young's modulus of resultant leather becomes higher.

The Relationship Between the Elasticity and Comonomers

Eight copolymers with the comonomers in their best dosage were selected and they were applied in retanning under the same condition. Figure 16 shows that the copolymers contains MMA, MA or IA produces leather with the highest Young's modulus, while copolymers contains EA or BA produces leather with the lowest Young's modulus. This provides a guide for those who want to get leather with more elasticity.

CONCLUSIONS

Our study showed that Young's modulus of the elastic deformation on the load-displacement curve can serve as an independent parameter to characterize leather elasticity. Furthermore, the study investigated the relation between the dosages of comonomers and Young's modulus of the resultant leather. The results revealed that every comonomer had a proper dosage at which level the resultant leather showed the best elasticity. The kind of comonomers also influenced Young's modulus; the soft comonomers, EA and BA, showed the best results.

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This year is the 200th anniversary after Thomas Yang brought forward the significant conception of Young's modulus. We'd like to express our respect for the great scientist and the article can't be completed without his theory.

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