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Mechanism of Cryogenic Shredding Process of Scrap Tire

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There are about 41% (by weight) of scrap tires were pulverized to produce rubber powder and granules in the tire recycling industry of Taiwan. However, the reuse of the by-products, steel and fiber, of the scrap tires still needs to be improved. It is difficult to remove the remaining rubber on the surface of steel or fiber. This problem reduce the availability for further reuse of steel and fiber. In addition to the improvement of magnetic, gravity separation techniques or carbonization process, using cryogenic shredding process to separate rubber and fiber (or steel) had been used as another alternative. Cryogenic shredding process for scrap tires showed many advantages, the objective of this paper is to explore the mechanisms for the cryogenic shredding process of scrap tires.
Cryo-SEM is used to investigate the topographic information, in-situ, from room temperature to -195℃. One square inch shredded tire chips are prepared for SEM study. The percentage of the shrinkage of rubber is also estimated, ca. 6.7%. Mechanisms of cryogenic shredding effects on the tire chips are discussed. The proper practice of cryogenic shredding process for scrap tires is also suggested.

Keywords: tire recycle, scrap tire, cryogenic, cryo-SEM

Introduction

The policy of tire recycle in Taiwan embryos since 1989. The "Resource Recycling Fundation" was established by the Environment Protection Administration in 1998 in order to prevent fire or hygiene problems resulted from waste tires or to solve the problems related with tire recycle. Currently, there are about 110 thousands tons of waste tires produced each year in Taiwan. The alternatives to maximize the reuse or recover of scrap tires rather than landfill include direct reuse, retread, dedicated incineration, tire derived fuel, press, pyrolysis, cryogenic mills and ambient grinding.[1] All these methods are used for the present in Taiwan.
According to the study by Ton et al,[2] there are about 41% (by weight) of scrap tires were used to produce rubber powder and granules for further reuse, such as playground, highway pavement, or highway barriers. However, the efficiency of shredding process of scrap tires is still needed to be improved. This situation leads to piles of fibers and steels with adhered rubber stocked in many tire recycle factories which are unable for further reuse of steel or fiber.
As the bonding of rubber/fiber or rubber/steel within the car tires is inherently expected to be strong to insure the durability and driving safety while tires hitting on the road. During the production of car tires, adhesive layers are used to enhance the bonding between rubber and steel (or fibers). There are many literatures reported the adhesion of the rubber with other materials and using SEM, TEM et al to investigate the interfaces.[3-18] A cross section of rubber, adhesive layer and the steel of a car tire is illustrated in Figure 1. The width of the interface between adhesive layor and the steel is estimated as ~ 70 nm.[3,4,10] The grain size (Cu_xS/ZnS) and the grain homogeniety determine the bonding strength of the interface and the durability of the adhesion. Other factors which have effects on the adhesion of rubber and steel (or fiber) include the efficiency of the adhesion promotors or stabilizers, the length of molecular chains, surface structure and the thickness of interface.[13-15]

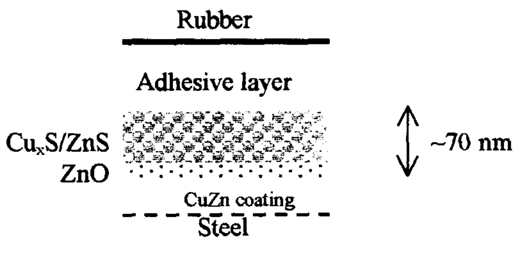

Figure 1 A cross section of rubber/steel of a car tire.

After breaking two different materials which adhered together, there exists two kinds of failure modes--cohesive failure and interfacial failure.[3,4] If cohesive failure happens, the rubber is still adhered on the surface of the steel or fiber after shredding car tires. Otherwise, if a smooth steel surface is obtained, it is called as a interfacial failure. Normally, a mixture of cohesive and interfacial failure modes were found on the shredded tire pieces. As a result of cohesive failure, the remaining rubber would reduce the availability for the further recycle of steel and fiber. Once the rubber still adhered with fiber or steel , actually, they are accounted as "wastes" if not being utilized. To solve this problem, carbonization had been tested to remove the remaining rubber studied by M.-H. Lee in our research group.[2] After carbonization, most of the remaining rubber adhered on the steel surface can be removed and the steels can be reused by a Steelmaking Corporation.

Cryogenic shredding process seems to be the other alternative to remove the remaining rubber after shedding process. It is known that as the temperature of rubber lower than its glass transition temperature, it becomes brittle and eases for broken into smaller pieces. However, the high cost of freezing energy to lower down and maintain the low temperature of scrap tires while shredding is another task to be tackled. Unless alternatives of freezing energy at low cost can be provided such as high speed cold air studied by Liang et al[19] or a cold environment produced by liquifying petroleum gas.

The objective of this paper focuses on the surface investigation of tire chips at different temperature using cryo-Scanning Electronic Microscopy (cryo-SEM). And the mechanisms of cryogenic shredding effects on the rubber are also discussed.

This study is part of a project entitled "Reinforcement on the efficiency of scrap tires shredding process" which attempted to evaluate the cryo-shredding process.

Experiment

Recovery of temperature

In order to realize how fast the rubber will recover its elasticity after immersed in liquid nitrogen, the surface temperature of a frozen tire chip is immediately measured right after the sample exposed to ambient atmosphere. The surface temperatures of a tire chip varied with time were recorded.

Sample preparation for Cryo-SEM

5*5 mm^2 samples with thickness of ~800μm were prepared to meet the required size of the sample for the surface investigation using cryo-SEM. Samples are collected directly from the shredding unit of the tire recycle factories. The bottom of sample is polished to reduce the thickness. The original surface of tire chip is reserved for surface investigation. Before mounted on the observation stage of SEM, the tire sample was coated using Au with a depth of ~20 nm to improve image quality.

Cryo-SEM

Cryo-SEM TOPCON ABT-150S is used to investigate the surface of the tire sample. Low accelerating voltage of 5 kV is used for better topographic information. The coating technique, vacuum condition, freezing step and the adhesive material used to fix the sample on the stage are important to obtain clear SEM images.

The temperature of the sample can be lowered down by cooling the stage using liquid nitrogen which will not releases to the observation cell. The thin sample located on the cold stage was assumed to be at the same low temperature as the stage. The temperature variations of the stage can be recorded. Once the temperature of the stage rapidly reached -195℃ (within 15 minutes), SEM pictures were taken after 10 minutes to insure the temperature stability of the thin tire sample. So it is possible to compare the surface variation of the tire sample in-situ at different temperatures (from room temperature to -195℃).

Results

The surface temperatures of a frozen rubber (at −130 ℃) varied with time after taken out to ambient environment were measured and plotted in Figure 2. The surface temperature is immediately recorded right after the sample exposed to ambient atmosphere. After approximately 2 minutes the surface temperature elevated over its glass transition temperature; after 10 minutes the surface temperature of rubber recovered to room temperature.

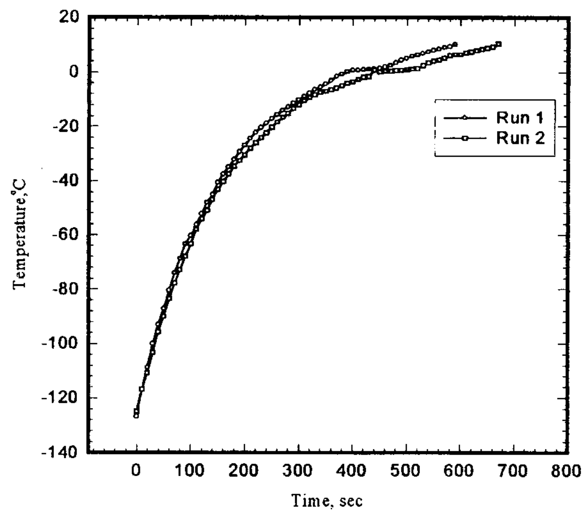

Figure 2 Recovery of surface temperature of a tire chip in ambient atmosphere after immersed in liquid nitrogen.

Figure 3 shows the surface of the cross section of a tire sample at room temperature with fibers on the top and the bottom sides of the picture, and rubber was in the middle part. This tire surface is an originally torn surface without scratching or polishing traces. There are irregular white lines appeared on the surface of the rubber where the structures are deformed to some extent. After cool down the temperature to −195 ℃, the image was illustrated as Figure 4. It can be recognized that there are changes in height along those "white lines". These topographic changes due to freezing effect made them look like "ladders". Many other sample pictures taken in this study had the same changes as the temperature lowered to −195 ℃.

Figure 5 shows the image of the same sample after the temperature of the sample recovered to room temperature for a period of time. The surface of rubber appeared no difference as compared to Figure 3.

By measuring the width of the rubber from the original SEM pictures, it is found that there was a shrinkage of ~6.7% in width. This value is close to former estimation ~7.0% which the shrinkage is mainly due to freezing effect.[20]

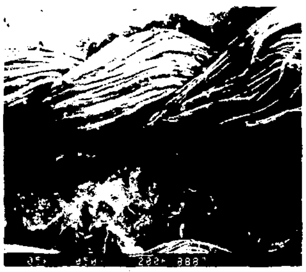

Figure 3 The surface image (50×) of a tire sample at room temperature.

Figure 4 The surface image (50×) of the same tire sample at -195℃.

Figure 5 The surface image (50×) of the same tire sample recovered to room temperature.

Discussion

Mechanisms of failure of shredded tires

There are 41% by weight of the scrap tires are pulverized to make rubber granules or powder in Taiwan. Up to date, piles of fibers and steels with adhered rubber are stocked in many tire recycle factories which are waiting for solutions, besides landfill. However, tire-making process is "irreversible". Sulfer and carbon inside rubber were bounded within matrix and the adhesive layers are expected to be durable after dramatic progress. Also as mentioned before, adhesion promotors, stabilzers and many other methods were used to enhance the adhesion between rubber and steel (or fiber). All this realities make it difficult to maximize the reuse each component of scrap tires.

The shredding process of scrap tires to make powders include crump, first shredding step, second shredding step, first grinding step and second grinding step, subsequently. Pieces of tire chips with smaller sizes are produced after each step. After the second shredding step, tire chips with size of 1 square inch were produced and the fibers and steels are by-products. Ideally, the expected final products are fiber, steel, and rubber granuals with homogeneous size. However, the fiber and steel still have rubber adhered on them after shredding.

After magnifying the surface of the rubber (an originally torn surface without polishing), white lines shown in Figure 3 are found after shredding. So it is believed that the structure alone the irregular white lines are deformed. That means the surface structure of rubber was destroyed to some extent after several shredding steps. And the white lines (deformed regions) will be the preferred positions for the initiation of fracture during following shredding process.

The other preferential region for fracture are the interfaces between different materials, i.e. the boundaries of rubber/steel and rubber/fiber. By examining the interfaces of rubber/fiber or rubber/steel after shredding, there are mixed modes of failure: cohesive failure and interfacial failure, mostly are cohesive failure mode. As figure 1 shows the thickness of the adhesive layer and bonding layer is within a range much less than 1 mm. And eventhough the bonding or adhesion were expected to be strong, fractures occurred along interfaces between rubber and fiber (or steel) after shredding.

Conclusively, the failure modes of shredded tire chips include structural deformation failure of rubber and the interfacial failure or cohesive failure near rubber/fiber or rubber/steel interfaces.

It is proposed that if cryogenic shredding process introduced after the second shredding step, we can expect to obtain more homogeneous rubber granules, more interfacial failure and less remaining rubber adhered on steel or fiber as mentioned below.

Cryo-Shredding Process

Besides carbonization, cryo-shredding process seems to be the other alternative to remove the remaining rubber from steel or fiber. As cryo-shredding process should be proceeded under cold environment at least near the glass transition temperature of rubber near –70 ~ –80 ℃, suggested for a cryogenic grinding process by Liang, too.[19] At this temperature range, rubber is characterized in brittleness and easy to be broken into pieces. In this study, it was tested that the surface temperature of a frozen tire sample elevated over –70 ℃ around 2 miniutes after taken out from liquid nitrogen as indicated in Figure 2. And the thermal energy produced from friction during shredding process will increase the temperature of the tire chips. Thus, it is necessary to provide freezing energy continuously while shredding to maintain a low temperature environment.

As there is a shrinkage of 6.7% in width and creating "ladders" on the surface after freezing the rubber, as shown in Figure 4. These ladders which were deformed regions are preferential for failure if cryo-shredding or cryo-crashing step applied at this moment. That means deformed region is split off after further shredding under cold environment, and smaller pieces of rubber granules with homogeneous size can be obtained. As the deformed regions of rubber presented on most tire chips after the first and the second shredding steps of car tires. So the proper practice of cryogenic shredding process for scrap tires after the second shredding step is then suggested.

Actually, cryo-crashing of tire chips had been tested by Dr. Shu in our research group. More homogeneous rubber granules, more interfacial failure and less remaining rubber adhered on steel or fiber were obtained as compared to ambient-crashing.[2]

However, the major problem of cryo-shredding process is to provide the freezing energy to lower down or maintain the low temperature at ~ –70 ℃. If the surrounding temperature failed to be lower than the glass transition temperature of rubber during cryo-shredding, the "brittleness" of rubber will disappear and recover its flexibility. At this moment, homogeneous size of the granules can not be obtained.

Conclusion

There are about 41% (by weight) of scrap tires were pulverized to produce rubber powder and granules in the tire recycling industry of Taiwan. However, the reuse of the by-products after the second shredding step (steel and fiber) of the scrap tires still needs to be improved. Following are conclusions and suggestions for this study:

1. The failure modes of shredded tire chips include structural deformation failure of rubber, interfacial failure and cohesive failure near interface.
2. From the cryo-SEM investigation, surface deformed regions of rubber are preferential regions for initiation of fracture.
3. The temperature for cryogenic shredding process is better below the glass transition temperature of rubber near –70 ~ –80 ℃.
4. Introducing cryogenic shredding process of scrap tires after the second shredding step is suggested, because deformed regions of rubber induced by shredding are preferential for fracture, i.e. to pulverize tire chips with a size of 1 square inch. However, the cost-benefit for freezing energy should be further evaluated.

NOMENCLATURE

Cryo-SEM: Cryogenic Scanning Electron Microscopy

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