DETERMINATION OF FATIGUE BEHAVIOUR AND CRACK PROPAGATION OF FILLED VULCANIZED RUBBER

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Abstract

The technical rubber is high filled and cross-linked polymeric material. It can be applied in many applications in the industry because of its unique and variable elastic and damping behaviours. The rubber is set the high requirements about efficiency and stability for the characteristic value of material due to the typical dynamic loading of the rubber. The long durability could be generally reduced through damage of materials and wear mechanism, which are nearly always the cause of crack creation and propagation.

The most important technical rubber is often based on natural rubber (NR) and styrene butadiene rubber (SBR). The matrix of rubber could be reinforced with the active fillers. The most important active fillers are carbon black and silicic acid. The specific quantity addition of this filler combined with the vulcanization gives various possibilities for the setting of mechanical behaviors of rubber.

The review describes recent research about crack propagation of vulcanized rubber filled with waste rubber powder where the main intention is to gain insight into relationship between concentration of rubber powder in vulcanized rubber on critical stress by crack propagation.

Key words

Crack propagation; Fatigue analysis; Fracture mechanics, Vulcanized rubber; Rubber powder; Waste rubber, Revulcanization

WASTE RUBBER POTENTIAL AND REUSE OF WASTE RUBBER

Disposal of discarded rubber products, mainly tires, is an important because of environmental problem. These materials cannot return to the ecological environment through natural biological degradation, hydrolyzation or decomposition, like plants or animals, because they degrade very slowly. They belong to the class of non environmentally friendly materials. Among various methods for treatment of waste rubber products, reclaiming or recycling is the most desirable approach to solve the problem.

Around 14,000,000 t scrap tires are amassed in the World annually. This offers great recycling potential. The processing of scrap tires with regard to other possible application is steadily growing in importance.

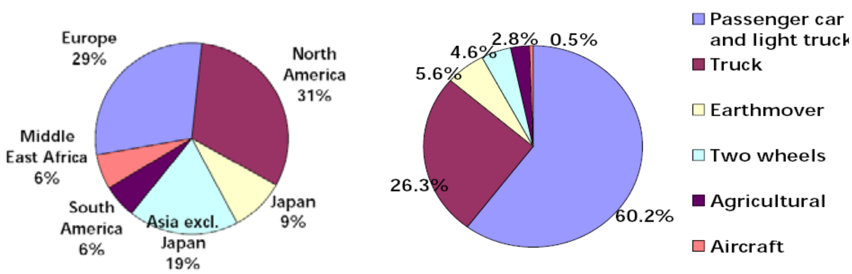

Fig. 1. *Scrap tire statistic in the world*

New opportunities are opening up for the recycling of non-retreadable end-of life tires, involving recovery as energy or as material.

Tires can be used as fuel either in shredded form or whole, depending on the type of combustion furnace. In considering the value of tires as fuel, it is interesting to compare the typical composition of tires with coal. Compared to coal, the tire had less moisture, significantly more combustible matter, and less fixed carbon. Tires contain more than 90% organic materials and have a heat value of about 32.6 mJ/kg compared to that of 18.6–27.9 mJ/kg of coal [1]. Therefore, one ton of tires yields the same energy as 0.7 ton of oil. The low level of sulfur (1%) contained in tires compared with certain types of coal (5%) make them a substitute fuel with less impact on the environment.

Whole tires can be retreaded. Retreading is the best environmental solution. It consists in a new tread moulding on a used tire carcass. The quality got is comparable to new tire as for road behaviour and security. However, it is not possible for poor quality tires. Otherwise whole tires can be used as filling material for roads, retaining structures, noise-abatement walls and as shock absorbers along jetties and quaysides.

Landfill is one of the early ways for disposal of discarded rubber products. With the decreasing scope of available sites and due to the corresponding cost explosion, this process of waste rubber disposal is no longer feasible. Landfill with waste tire is, also the most unwanted approach due to environmental problems and has no future possibility [2]. When tires are ground into granulate or powder, ground tires can be used to make moulded objects such as refuse containers and golf cart wheels. The powdered form could also be used to make surfaces of sport ground, play ground etc.

Fig. 2. *Reuse of waste tire rubber*

RUBBER POWDER-RUBBER POLYMER-BLEND-SYSTEM

Natural and synthetic rubbers such as latex, nitrile, millable polyurethane, silicone, butyl, and neoprene, which attain their properties through a process known as vulcanization, are thermoset polymers. Thermosets are plastics that undergo chemical change during processing to become permanently insoluble and infusible. The most important rubbers used in the tire industry are SBR (passenger car tires) and NR/SBR (truck tires).

The reactive process for cross-link is vulcanization. Vulcanization refers to a specific curing process of rubber involving high heat and the addition of sulfur. It's a chemical process in which polymer molecules are linked to other polymer molecules by atomic bridges composed of sulfur atoms. Along the rubber molecule, there are a number of sites which are attractive to sulfur atoms. These are called cure sites, and are generally sites with an unsaturated carbon-carbon bond, like in polyisoprene, the basic material of natural rubber, and in styrenebutadiene rubber (SBR), the basic material for passenger car tires. The active sites are acrylic hydrogen atoms, that mean they are hydrogen atoms connected to the first saturated carbon atom connected to the carbon-carbon double bond. During vulcanization, the eight-membered ring of sulfur breaks down in smaller parts with one to eight sulfur atoms. These small sulfur chains are quite reactive. At each cure site on the rubber molecule, such short sulfur chain can attach itself, and eventually reacts with a cure site of another rubber molecule, and so forming a bond between two chains. This is named a creation of cross-link elastomeric matrix.

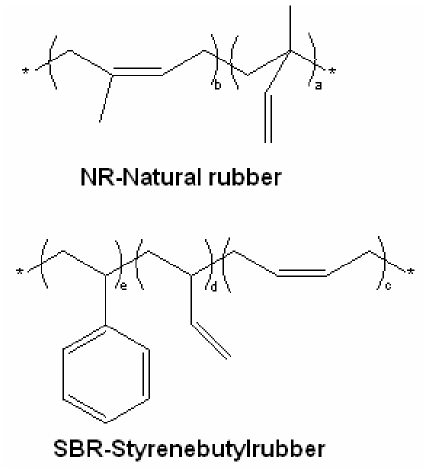

Fig. 3. *NR and SBR*

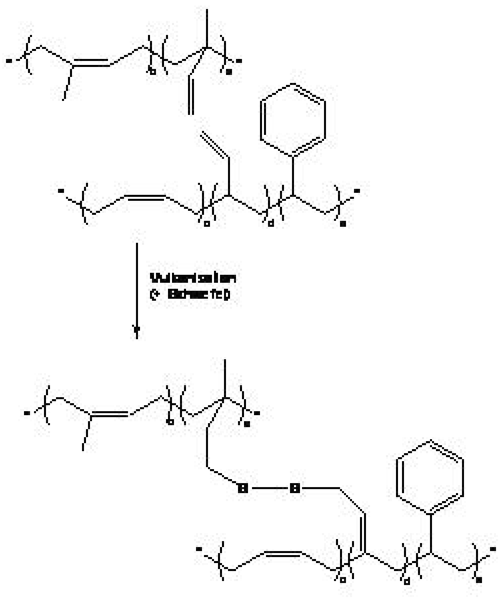
Fig. 4. *Vulcanization of NR and SBR*

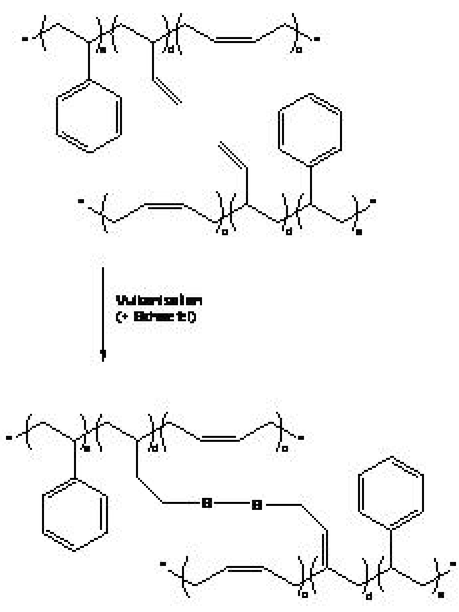
Fig. 5. *Vulcanization of to moleculs of SBR*

The use of filler, carbon black, together with sulfur vulcanization, has remained the Fundamentals technique for achieving the incredible range of mechanical properties required for great variety of rubber products. Increased reinforcement of the rubber material has been defined as increased stiffness, modulus, tearing strength, crack, fatigue and abrasion resistance [3]. A practical definition of reinforcement is the improvement in the service life of rubber articles that fail in a variety of walls, one of the most important being rupture failure accelerated by fatigue processes, such as occurs during the wear of a tire trend [4]. It is possible to use waste rubber powder as active filler. This material could actively improve dynamical and mechanical properties of elastomer matrix.

The next diagram shows a comparison of mechanical properties of raw rubber and revulcanized waste rubber. The big difference is due to elastic matrix of NR and their mechanical behaviour. The positive mechanical behaviour of rubber increase with increasing quantity of NR. The different between SBR and SBR/NR new rubber material is stress 30,2%, strain 57,8 % and E-Modul 4,7 %.

The phenomenon of positive increasing of thoughness with quantity of NR is able to influence the behaviour of the material made from raw rubber with filled waste rubber powder. In this work, it will be mixed the different concentration of waste rubber powder in raw rubber in the rubber powder-rubber polymer-blend-system and revulcanized for determining the influence of the concentration of waste rubber powder on the mechanical properties of new reactive material.

In the fig.7 and 8, it can be seen the expected dependence of this phenomenon. For truck tire rubber, it is expected the decreasing tendency of mechanical properties with higher concentration of waste rubber powder because the new rubber will be filled with the same material but the filled material will have a degenerate mechanical properties. For the car tire rubber, it is expected the increasing tendency for 50 % of old rubber and with higher quantity of old rubber decrease.

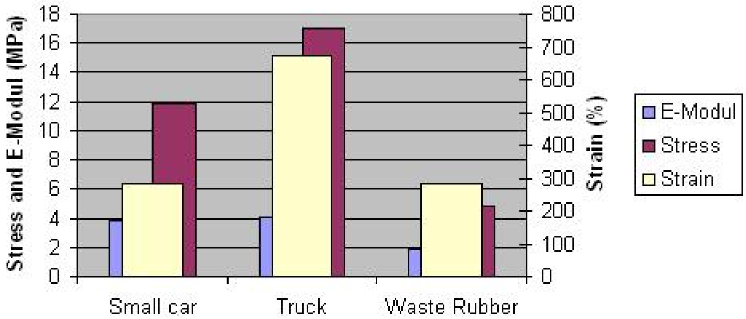

***Fig. 6.** Mechanical properties of raw rubber and revulcanized waste rubber powder*

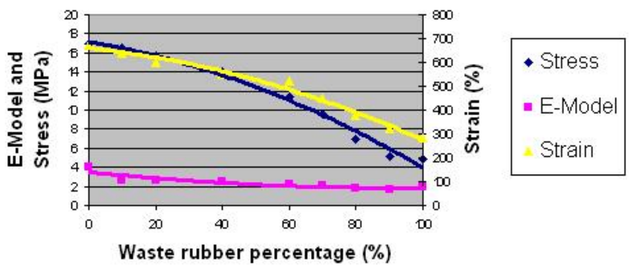

***Fig. 7.** Expected mechanical properties of truck rubber powder-rubber polymer-blend-system*

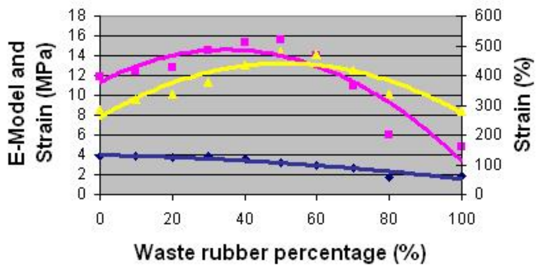

***Fig. 8.** Expected mechanical properties of car rubber powder-rubber polymer-blend-system*

REVULCANIZATION OF WASTE RUBBER POWDER

The process of rubber powder revulcanization is a similar curing process like vulcanization of rubber. With the different that the useful material must be reactivate before the process of revulcanization starts. Reactivation is the mechanical, chemical or physical reclaiming process that breaks down three-dimensional network of crosslinked rubber in presence of different energy source. Due to the breaking of network structure, macromolecular rubber chain is transformed into small molecular weight fragments so that it can be easily miscible with the virgin rubber during compounding.

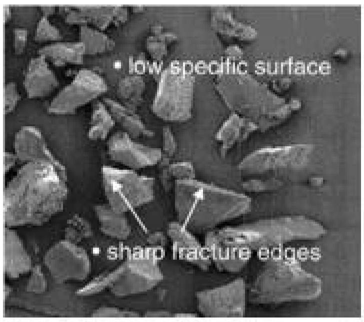

Fig. 9. Rubber powder following

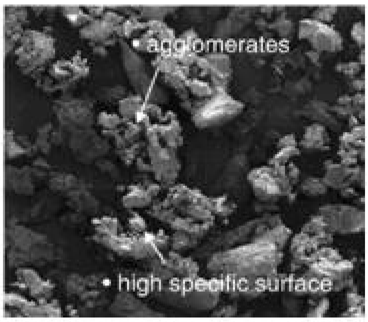

Fig. 10. Rubber powder following ambient

The mechanical reactivation is the most important method. The recycling of scrap tires comprises of the production of rubber powder and rubber granulate with different particle size distribution. The aim of comminution is to liberate and separate of tires. The scrap tires are ground by one of three reactivation methods: ambient, cryogen or SSSP (Solis State Shear Process) grinding. In the cryogen grinding, the scrap rubber is cooled down to temperature around -150°C in the nitrogen atmosphere. The particle size of the rubber powder is ≤ 1 mm and the specific surface area of particles is 0.05 m^2/g. In the opposite of cryogen grinding, the scrap tires are ground by the warm grinding method at ambient temperature. This method is generally cheaper because nitrogen is not required. The ambient grinding is more important and more used for grinding of tires. The rubber powder ground by ambient grinding has specific surface area of particles 0.25 m^2/g and the particles size of 100 – 500 µm. The SSSP method is the ambient grinding method that can produce the rubber powder with particle size of 50 – 600 µm. The microscopic observation of ambient and cryogen grounded rubber powder is shown in the Fig. 9 and 10.

The process of revulcanization consist in breaks down of crosslinked rubber, double carbon-carbon bond and free sulfur atoms from the process of vulcanization. Process of revulcanization is shown in the Fig.11.

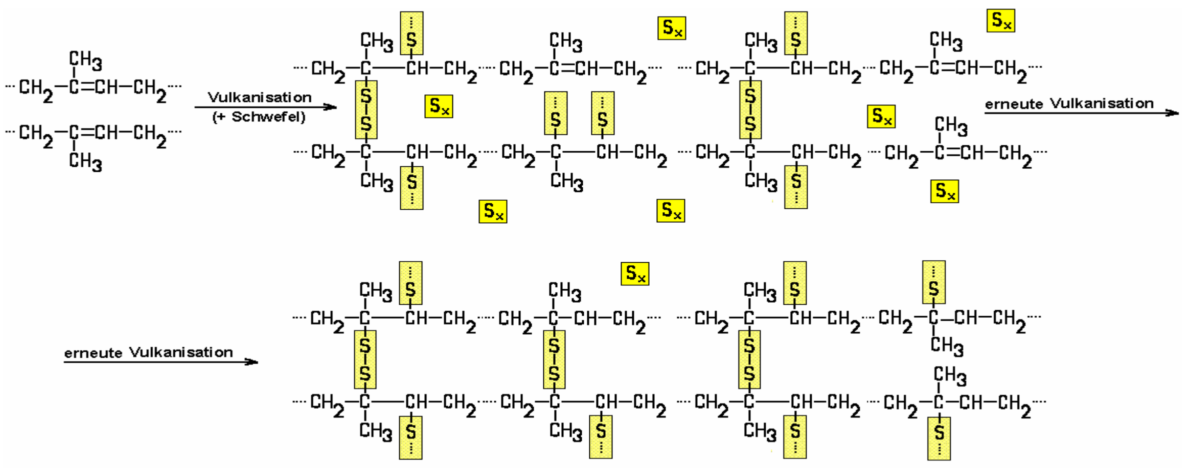

Fig. 11. *Revulcanization of waste rubber powder*

CRACK PROPAGATION OF FILLED VULCANIZED RUBBER

Crack growth is very important in materials such as metal and glass, attempts to find a theoretical description were made early on. A fundamental theoretical concept applicable to both metals and different types of glass, and also very effectively to rubber, was developed by Griffith.

His point of departure could hardly be simpler: crack growth always represents an enlargement of the surface. Hence a crack can only grow if the mechanical energy W_M input is greater than the free surface energy W_S generated by the crack´s enlargement. In rubber, the applied mechanical energy is almost completely stored elastically [5].

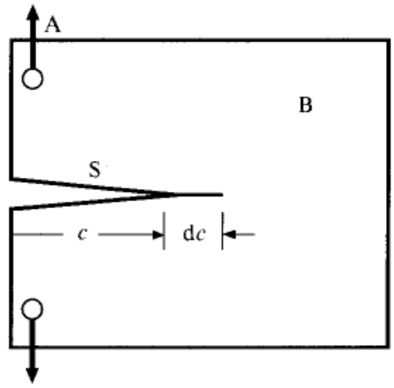

Fig. 12. *Crack propagation*

Surface energy has a constant value per unit area (or unit length for a unit thickness of body) and is therefore a linear function of (crack length), while the stored strain energy released in crack growth is a function of (crack length)^2, and is hence parabolic. These changes are indicated in the fig. 13. Therefore Griffith´s energy criterion can be formulated in the case of elastomers as follows: An infinitesimal enlargement of the crack surface by dA as the cut lenght increases by dc entails a reduction of the elastically stored energy by dW:

$$-\frac{dW}{dc} \geq W_S \frac{dA}{dc} \text{, where} \qquad (1)$$

$$W = W_M + W_S = W_E + W_A + W_S \text{,} \qquad (2)$$

$$W_M = \frac{\pi \cdot c^2 \cdot \sigma_A^2}{E'} \text{,} \qquad (3)$$

$$W_S = 4 \cdot c \cdot \gamma \text{,} \qquad (4)$$

When fracture occurs can be defined G_{crit} as the critical value of strain energy release. Hence G_{crit} represents the fracture toughness of the material. In plane stress the Griffith equation is:

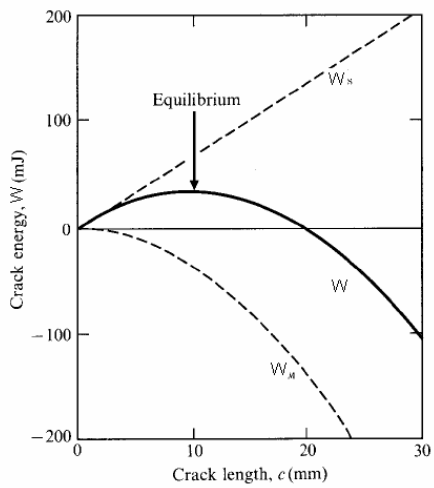

Fig. 13. *Griffith-Criterion*

$$\sigma_F = \left(\frac{2 \cdot E' \cdot \gamma}{\pi \cdot c_0} \right)^{\frac{1}{2}} \qquad (5)$$

A small crack would be initiated in the specimens of rubber powder-rubber polymer-blend-system for the observation of crack propagation and determination of critical stress value by crack growth. The tests specimens would be made with different concentration of waste rubber powder and then would be measured. The different specimens with the notch would be stretched in the tensile machine under constant crosshead speed.

A Camera system observed the crack propagation. The whole test station is shown in the fig.14.

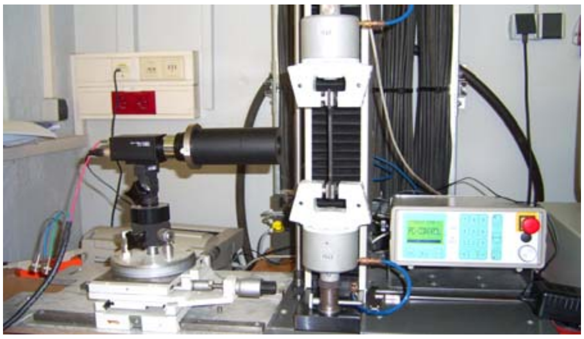

Fig. 14. *Testing station*

CONCLUSION

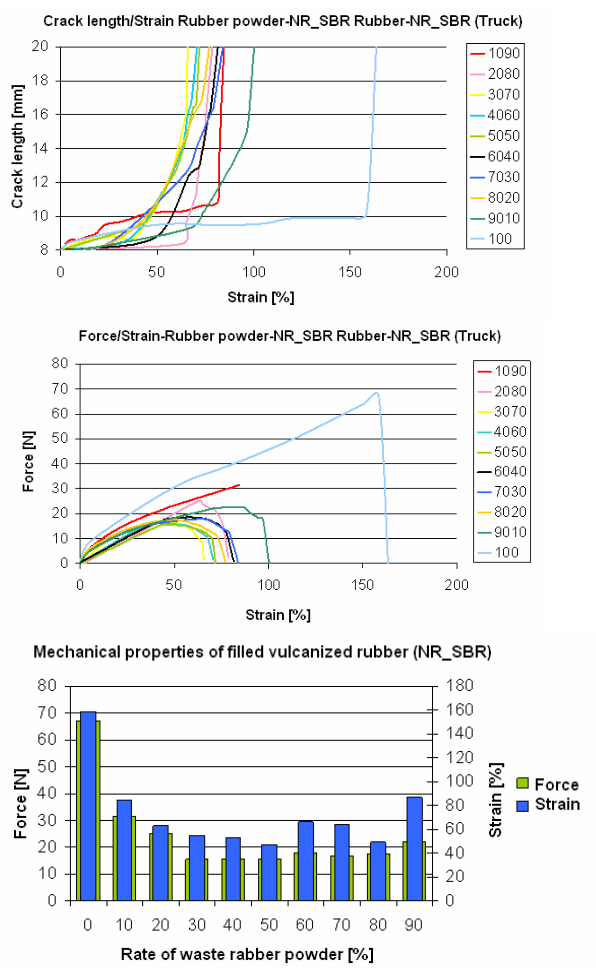

Fig. 15. *Crack propagation in NR_SBR - NR_SBR rubber powder-rubber polymer-blend-system*

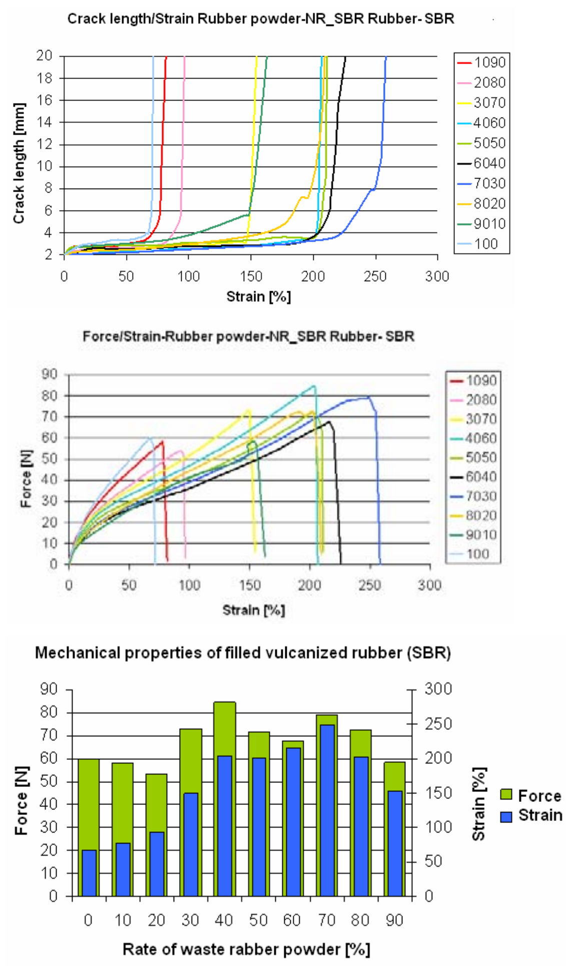

Fig. 16. *Crack propagation in NR_SBR - SBR rubber powder-rubber polymer-blend-system*

The paper shows the influence of the waste rubber powder concentration in the pure rubber on the critical stress ratio by crack initiation and crack propagation. Two different rubbers would be researched and compounded with the most important waste rubber powder made from truck tires. The results showed the positive influence of the waste rubber powder as filler in pure rubber on the fracture mechanic of polymer-blend-system. The increase of the critical stress by crack initiation is clearly documented. With the increase of the waste rubber powder concentration in the pure rubber would be improved the mechanical properties of polymer-blend-matrix.

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