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I, RAJESH VENKITACHALAM ,

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Approved by:

IMPROVING THE MECHANICAL PROPERTIES OF POLY HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE FILMS BY A NOVEL ORIENTATION TECHNIQUE

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Rajesh Venkitachalam

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Committee Chair: Dr. James E. Mark

Dr. William R. Heineman

Dr. Allan R. Pinhas

Abstract

Technology advancements bring novel problems as well as innovative products. One of the biggest problems is environmental pollution. A major contributor to solid waste is plastic which cannot be converted into harmless side products by natural means. Efforts are being made however, to develop new polymers and biopolymers that are biodegradable and tough. One such class of polymers, which has shown a lot of potential, is the polyhydroxyalkanoates. The copolymers of this class of polymer possess biodegradability but lack strength, however, one example being poly 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV). Crosslinking such a polymer will result in increases in strength and make the polymer robust for applications in which it could eventually replace conventional plastics. The crosslinked polymer will have better mechanical properties, but possibly at the cost of reduced biodegradability. Although the biodegradability will suffer to some extent it can still largely be converted into harmless products by nature such as carbon dioxide and water.

In the present study, crosslinking was achieved by free radical generation. The pre-crosslinked copolymer sample was prepared using a solvent to facilitate the uniform distribution of the crosslinking agent in the copolymer sample. The resulting crosslinked gel was dried under strain and the resulting film was subjected to stress and its mechanical properties compared with those of the original sample.

Specifically, the study was conducted to test samples which had been dried under uniaxial extension, and to compare their mechanical properties with those of the non-crosslinked copolymer.

Acknowledgments

I want to thank my Advisor Dr. James E. Mark for his guidance and support, without which this research work would not have been possible. I would also like to thank Dr. Frank R. Meeks, my mentor, for giving me encouragement and Dr. Harry B. Mark for his tutelage and advice. I wish to thank Dr. William R. Heineman and Dr. Allan R. Pinhas for their guidance. I would like to thank Dr. Isao Noda of the Corporate Research Division of Procter and Gamble Company for providing the samples and his guidance in making this study possible. It is also a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR-0075198 (Polymers Program, Division of Materials Research). Finally, I would like to thank all the people in the JEM research group for their help.

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Introduction

Synthetic and semi-synthetic polymeric materials were developed originally for their durability and resistance to all forms of degradation including biodegradation. They were designed to have special performance characteristics which were achieved through the control and maintenance of molecular weights and functionalities during their processing and in relevant operating conditions. The wide acceptance of such polymeric materials attributed to their ease of processability and amenability, and ability to provide a large variety of cost-effective items that enhance the comfort and quality of life in modern industrial societies. But these features that make polymeric materials so convenient and useful to human life, have contributed to creating a serious plastic waste burden. It is daunting, but has sometimes been unfairly exaggerated by the media because of the visible spreading of plastic litter in the environment and the heavy contribution to landfill depletion due to the unfavorable weight-to-volume ratio of plastic items (average 1 to 3 weight to volume ratio). As a consequence of increase in consumption of plastics in the developing countries, it is expected that there will be an increase in their production by 2 to 3 folds. Indeed one to two orders of magnitude jumps in plastics consumption with respect to the present annual level of 1-10 kg per capita can be envisaged for those countries, once the living standards of industrialized countries are approached [1].

Polymeric materials being produced have to face all the constraints and regulations that are already in place or to be issued in near future in order to comply with the rules dealing with the management of primary and post-consumer plastic waste. Such

a consideration has to be taken into account in the design, production and consumption of polymeric materials in commodity and specialty plastic items. In this regard, environmentally sound degradable polymeric materials and relevant plastic items will form a key option among those available for management of such waste. At present the methods used for disposing the polymeric materials include burial in landfill sites, incineration with energy recovery and mechanical or chemical recycling. It is expected that such methods will be strengthened, even though one may predict that all of them will coexist with an appreciable decrease of land fill practice. Its also expected that new concepts of prevention will come into play, which will rationalize the production and management of plastic waste. Recycling technologies, including energy recovery by incineration, will be flanked by the increasing option of environmentally degradable plastics, which could replace the conventional commodity plastics, especially in those segments where recycling is difficult or heavily penalized from an economic standpoint. Therefore, an overview on environmentally degradable polymers and plastics cannot therefore be treated outside the framework of the global issues related to waste production and relevant management. The developmental position reached by environmentally biodegradable polymers will be crucial for its acceptance in the future. One of the major aspects that has attracted the manufacturers, polymer scientists, and public officers is represented by the establishment of definitions comprising all the possible categories of environmentally degradable polymers and plastics, together with suitable standards and testing protocols [1].

The utilization of biopolymers, while still in its early stages, is growing in popularity every day. Some biopolymers can directly replace synthetic plastics in

traditional applications, while others possess unique properties that may open new applications. For most biopolymers, it is still too early to determine whether they will be economically feasible on a large, industrial scale.

When you run into a spider's web, the last thing on your mind is, "What a great a material!" But consider that the spider's silk has a tensile strength 16 times greater than nylon! At the same time, silk maintains a very high degree of elasticity. Attempts to manufacture genetically modified silk have thus far been disappointing due to low yields. If they can be improved, however silk can be applied in many applications.

Chitin, a polysaccharide found in the exoskeletons of insects and shellfish, possesses many desirable characteristics. Chitin's most important derivative, chitosan, is nearly a "model" biopolymer with its useful physical and chemical properties, high strength, biodegradability, and non-toxicity. In fact, chitosan brings new meaning to the word "biodegradable" as the human body easily breaks it down into simple carbohydrates, carbon dioxide, and water. This accounts for the extensive research that involves trying to use chitosan in drug delivery systems.

Lactic acid is produced by the microbial fermentation of sugars such as glucose or hexose. Feedstocks can include potato skins and corn. The lactic acid monomer can be used to create low or high molecular weight polylactide polymers. PLA commodity polymers are being developed for use as pulping additives in paper manufacturing and as biodegradable packing materials. PLA's current price level of $5.00/lb (US) will have to be significantly decreased to half or one-third of this amount, however, upon before it gains wide acceptance. Currently, the medical community is the primary user of PLA

with absorbable sutures such as Vicryl™ [made of 90% PLA and 10% polygylcolic acid (PGA)].

During the last half of the twentieth century, plastic products became part our daily life, but there are rising concerns worldwide about the impact that petroleum-based plastics are having on the environment, as well as on the decreasing crude oil resources. In particular, the plastic content in (municipal) waste has increased considerably, and continues to increase steadily. These products have estimated degradation times ranging from 20 years for vending machine cups, to 100 years for PET bottles and 500 years for polystyrene foam cups and dishes. Although recycling is becoming more extensive, about 75% of plastics will still be dumped into landfills, and thus new strategies that can overcome this environmental problem need attention. Plastics are currently used in numerous applications.

Renewable materials such as biodegradable polymers based on agricultural resources (such as potatoes and sugar, etc.) seem to have the potential to offer a viable solution to the problem of environmental pollution. The main advantages of biodegradable polymers are, of course, their ability to degrade under controlled conditions and, when developed further, their ability to compost. These properties would provide the possibility to return them to where they originated, namely, nature. While some mechanical properties of currently available biodegradable polymers are inferior to those of conventional synthetic polymers, in addition to being costlier, extensive efforts are being made to improve the properties and to reduce the cost of these materials. On the other hand, biodegradable polymers can be processed with many of the conventional manufacturing technologies such as injection molding, extrusion, blow molding, etc.

In addition to the products already mentioned, plastics are also used as packaging materials. Plastic packaging can satisfy the high shock absorbing requirements necessary for protecting vulnerable equipment. The mechanical properties of virgin polymers are well known and the design of plastic packaging can be optimized rather well using simulation and optimization techniques. Recycling of plastic packaging materials is, however, often not cost effective because of the difficult separation of the different polymers and the contamination of the plastic packaging.

Non-petrochemical aliphatic polyesters that are thermoplastic and biodegradable are being developed to satisfy environmental imperatives. Derived from the fermentation of carbohydrates and fatty acids, these natural plastics have melting points that range from 60-180° C. Commercial development is based on isomorphous crystalline copolyesters composed of 3-hydroxybutyric and 3-hydroxyvaleric acids. The genes for these microbial polyesters, which are food reserves in bacterial cells, are now being transferred to plants, with the promise of an agrotechnological production method similar to that for starch. The natural copolyesters have molecular weights of about 500,000 g/mol and the product is 100% isotactic [2]. However, chemically synthesized analogues of comparable molecular weight but lower stereoregularity are being made synthetically by catalyzed ring-opening polymerization. Both biosynthetic and chemosynthetic biopolyesters degrade to CO_2 and H_2O in response to naturally occurring depolymerases in soils, oceans, lakes and rivers. The potential for recycling strategy based on the composting of small pieces of plastic, mainly from packaging, is made possible by such materials. The gene responsible for poly(3-hydroxy-butyrate) synthatase has been cloned,

thereby allowing synthesis in vitro of ultrahigh molecular weight bacterial poly(3-hydroxybutyrate) (PHB) using R-3-hydroxybutyryl-CoA monomer.

During the oil crisis in 1973, ICI developed a commercial fermentation process to produce PHB from Alcaligenes eutrophus; an illustration is shown in Fig 1. The polymer has potential as an industrial thermoplastic since it has some solubility and melts at high temperature, similar to isotactic polypropylene. A crucial problem with the development of PHB was its rapid degradation [2] at the melting point, which makes molding and extrusion difficult. Feeding selected bacterial strains with some hydrocarbon or fatty acid with an odd number of carbons solved this problem. The result is a poly-3-hydroxybutyrate-3-hydroxyvalerate copolymer, with a reduced melting point so that it can be molded. Y. Doi has done extensive work on this "bio-copolymerization" [2].

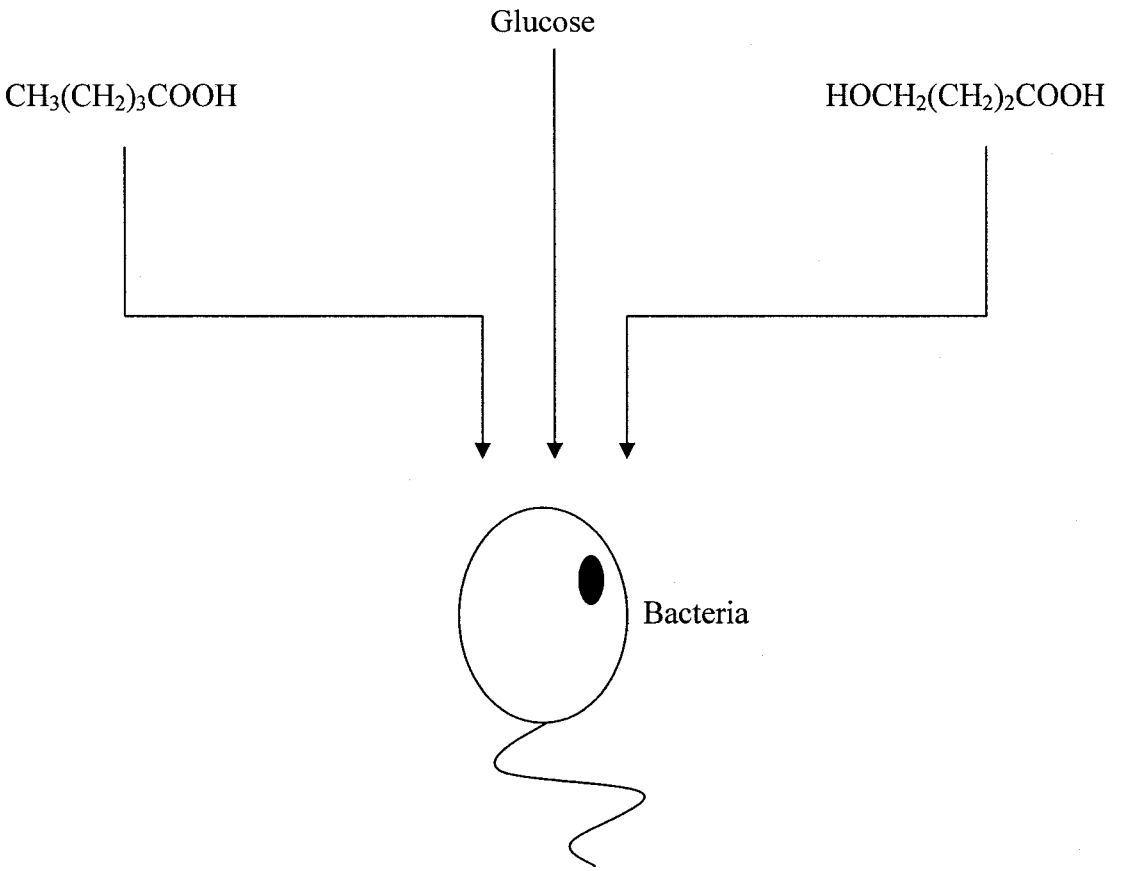
In recent years, controlled drug delivery formulations and the polymers used in these systems have become much more sophisticated, with the ability to do more than simply extend the effective release period for a particular drug. For example, current controlled-release systems can respond to changes in the biological environment and deliver—or cease to deliver—drugs based on these changes. In addition, materials have been developed that should lead to targeted delivery systems, in which a particular formulation can be directed to the specific cell, tissue, or site where the drug it contains is to be delivered. While much of this work is still in its early stages, emerging technologies offer possibilities that scientists have only begun to explore.

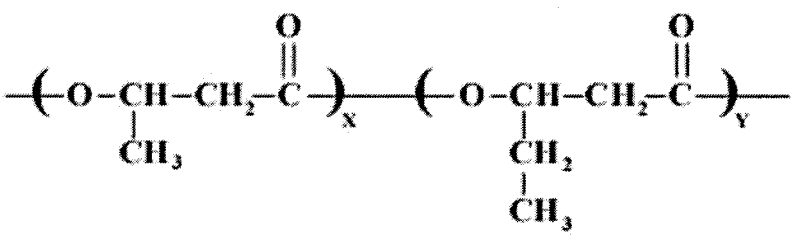
A range of materials has been employed to control the release of drugs and other active agents. The earliest of these polymers were originally intended for other, non-biological uses, and were selected because of their desirable physical properties, for

example: polyurethanes for elasticity, polysiloxanes (silicones) for insulating ability, poly(methyl methacrylate) for hardness and transparency, poly(vinyl alcohol) for

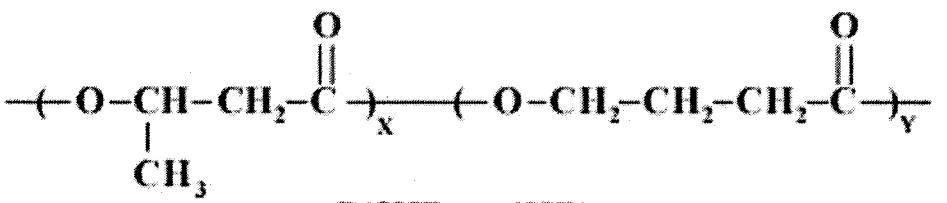
Figure 1.

Modified from Marchessault, R.H., Tender Morsels for Bacteria, Elsevier Trends Journals, vol 4, no 5, 1996.





P(3HB-co-3HV)



P(3HB-co-4HB)

hydrophilicity and strength, polyethylene for toughness and lack of swelling, and poly(vinyl pyrrolidone) for suspension capabilities. To be successfully used in controlled drug delivery formulations, a material must be chemically inert and free of leachable impurities. It must also have an appropriate physical structure, with minimal undesired aging, and be readily processible. Some of the materials that are currently being used or studied for controlled drug delivery include

- Poly(2-hydroxy ethyl methacrylate)
- Poly(N-vinyl pyrrolidone)
- Poly(methyl methacrylate)
- Poly(vinyl alcohol)
- Poly(acrylic acid)
- Polyacrylamide
- Poly(ethylene-co-vinyl acetate)
- Poly(ethylene glycol)
- Poly(methacrylic acid)

However, in recent years additional polymers designed primarily for medical applications have entered the arena of controlled release. Many of these materials are designed to degrade within the body, among them

- Polylactides (PLA)
- Polyglycolides (PGA)
- Poly(lactide-co-glycolides) (PLGA)
- Poly(hydroxybutyrates) (PHB)
- Polyanhydrides

- Polyorthoesters

Originally, polylactides and polyglycolides were used as absorbable suture materials, and it was a natural step to work with these polymers in controlled drug delivery systems. The greatest advantage of these degradable polymers is that they are broken down into biologically acceptable molecules that are metabolized and removed from the body via normal metabolic pathways. However, biodegradable materials do produce degradation by-products that must be tolerated with little or no adverse reactions within the biological environment [3].

These degradation products—both desirable and potentially non-desirable—must be tested thoroughly, since there are a number of factors that will affect the biodegradation of the original materials. The most important of these factors are shown below—a list that is by no means complete, but does provide an indication of the breadth of structural, chemical, and processing properties that can affect biodegradable drug delivery systems [3].

Factors Affecting Biodegradation of Polymers

- Chemical structure
- Chemical composition
- Distribution of repeat units in multimers (consisting of different monomers)
- Presence of ionic groups
- Presence of unexpected units or chain defects
- Molecular weight
- Molecular-weight distribution

- Morphology (amorphous/semicrystalline, microstructures, residual stresses)
- Presence of low-molecular-weight compounds
- Processing conditions
- Annealing
- Capacity for sterilization
- Storage history
- Shape
- Site of implantation
- Adsorbed and absorbed compounds (water, lipids, ions, etc.)
- Physicochemical factors (ion exchange, ionic strength, pH)
- Physical factors (shape and size changes, variations of diffusion coefficients, mechanical stresses, stress- and solvent-induced cracking, etc.)
- Mechanism of hydrolysis (enzymes versus water)

Recently Poly (hydroxbutyrate-co-3-hydroxyvalerate) (PHBV) has been promoted as an environmentally-friendly packaging for cosmetics, which may be the breakthrough to large-scale uses [4].

Polyhydroxyalkanoates (PHA's) are thermoplastic polyesters produced by bacteria as a carbon reserve. Biosynthesis inside the cytoplasm is prompted by conditions of stress such as shortage of an essential nutrient, frequently oxygen, nitrogen or phosphorus. These polyesters, which occur as cytoplasmic granules, are part of the natural biosynthesis-biodegradation cycle; hence, they fit the aspirations of environmentalists for plastics that return to nature through composting [5]. The most

common polyester granules, poly-3-hydroxybutyrate were discovered by Lemoigne of the Pasteur Institute in 1925 [2]. At first he mistook them for lipids but their insolubility in ether led him to their chemical structure, which he accurately described as an aliphatic polyester based on the monomer (R) –3-hydroxybutyric acid, Over the past decade, a wide range of homologous repeat units have been reported, depending on the bacterial species and the substrate used. Steinbuchel and Valentin reported that 91 repeat units are known to occur in PHA's [6]. The rapid development of this subject dates from the 'oil crisis' of the 70's, which prompted polymer R & D on materials from non-petrochemical sources. Since PHB was known to be a crystalline thermoplastic, which resembled isotactic polypropylene in some of its principal properties, it was an obvious research target. Subsequently, the environmental awareness raised by action groups in many nations made biodegradable plastics an important objective. A biodegradable plastic places a small load on the environment because it decomposes into water and carbon dioxide under the influence of microorganisms. Researchers with microbial and chemical interests converged on this timely polymer topic and a series of symposia and an international biennial meeting has resulted [2].

PHA's exist as long side chain (LSC) and short side chain (SSC) materials. These are the two families of polymers that cover a wide range of properties in thermoplastic and elastomeric materials [7]. The changeover from SSC to LSC coincides with a change in properties from those of highly crystalline thermoplastics to those of low crystallinity thermoplastic polyesters.

The driving force for commercial development of the SSC copolyesters is the availability of semicrystalline poly-3-hydroxybutyrate-co-3-hydroxyvalerate, P-3HB-co-

3HV, from Zeneca Inc. (Billingham, UK) [2]. Cast fills and molded objects consisting only of poly-3-hydroxybutyrate, the ubiquitous biopolyester, are brittle and show limited elongation to break. By adding increasing amounts of propionic acid to the glucose substrate of Alcaligences eutrophus, researchers found that a copolymer of increasing valerate content was produced. This copolymeric material had much higher elongation to break and, depending on compostion (0-25% valerate), a reduced melting point ranging from 100 to 180° C. Thus a family of thermoplastic materials with a choice of physical properties was produced [7-8]. Since PHB is thermally unstable, the ability to mold or spin at lower temperatures is a technical advantage. These biopolyesters are produced on a relatively small scale by fermentation technology at Zeneca Inc. at an annual production rate of 320,000 Kg [2].

Understanding the enzymes involved in the biosynthesis of PHB has led to the availability of many different copolymers and homopolymers of PHA. Included among the copolymers are structures where the comonomers are isomeric but there two different linkages, that is, a 1-3 linkage and a 1-4 type, are present thereby eliminating asymmetry in one of the repeating units (see Fig 1.). This type of heterogeneity has a pronounced effect on mechanical properties in the SSC PHA's because of high local mobility of the 1-4 moiety compared with the substituted 1-3 butyrate. Similar effects on other physical properties, such as degree of crystallinity or permeability, can be envisaged.

Important contributions to the development of PHA materials are also being made through the transfer of genes to plants, which may enable the agrotechnological manufacture of PHAs. Canola and tobacco plants are the preferred candidates for large-scale growing of PHAs. However, Arabidopsis thaliana is the favorite laboratory plant for

such studies, which have achieved 15-20% PHB yields (based on dry weight of the plants) through transfer of genes, with subsequent expression of the biosynthetic pathway in the plastid [1]. While there will be a long period before field trials lead to commercial production of PHA's, this approach could be the breakthrough to make 'natural plastics' economically attractive for the selective replacement of non-degradable plastics. This development is expected over the next decade, and should coincide with widespread application of the 'zero emission' concept in industrial chemical synthesis.

Work is in progress to obtain a PHB polymer which has improved properties and this has been a goal of chemosynthesis [9]. Since the chemical properties of PHAs are similar to those of polypropylene, chemosynthesis has been explored as a possible means of production because high-volume production via fermentation technology appears too costly. One of the routes to make crystalline PHA materials is the use of distannoxane catalyst for ring-opening polymerization of lactone monomers [10]. The result of such studies has been promising in terms of the discovery of unexpected physical properties, such as the biodegradability of chemosynthetic PHAs when they have a stereoblock structure [11]. In addition, it has been possible to make mechanically tough PHB by adjusting the level of tacticity, a feature that is never possible in the bacterial synthesis approach. Thus, the high crystallinity and brittleness of PHB can be countered by decreasing the overall tacticity, thereby decreasing the degree of crystallinity. In this way we can obtain a PHB of controlled toughness, which so far has been achieved only by biosynthesizing PHBV copolymers.

The biodegradability of PHAs has been the object of research evaluation, the first challenge being to understand how biodegradability is affected by solid-state properties

such as crystallinity and higher-order organization, such as spherulite formation. More recently there has been an effort to link tacticity to biodegradability. Some important conclusions followed from the research. It was found that the higher the degree of crystallinity, the longer it takes to degrade. It was noticed that a 100% racemic configuration isotactic chain (this is the bacterial product) allows high degradability even when combined with high crystallinity [11-14]. Bacterial (isotactic) PHB and synthetic isotactic (stereoblock) PHB structures have been compared and have been found to be identical [15].

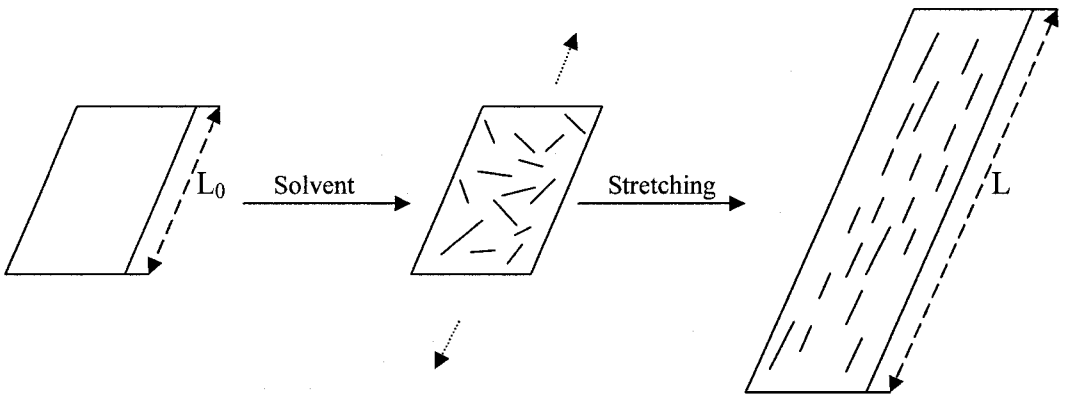
Crosslinked samples can have further improvements in properties by using a novel technique of uniaxial orientation. A technique is described for postponing the formation of anisotropic domains in semiflexible polymers so as to better orient them along a common direction. The primary advantage of this processing route is the improved mechanical properties accompanying the increased orientation [16-23]. This is illustrated by increases in moduli and ultimate properties of such oriented films. There is a sequence of steps required to prepare and orient the samples [4]. The first step is 1) identifying polymer chains of sufficient stiffness to give liquid-crystalline, anisotropic phases (either homopolymers or block copolymers consisting of stiff and flexible sequences); 2) crosslinking the chains, in the presence of solvent, thus conferring sufficient solidity for the polymer to remain in a deformed state for any length of time, with the solvent preventing the premature ordering of the stiff chains or sequences; 3) deforming the swollen network uniaxially or biaxially to induce segmental orientation; and 4) removing the solvent, at constant length or at constant force, possibly causing a first-order transition to a single-phase, homogeneous, and highly ordered material [18,

24-25]. An illustration of drying under uniaxial orientation is shown in Fig. 2. Unusually good mechanical properties can be obtained by this drying of a swollen network of semi rigid chains in a state of strain. This approach describes techniques by which swollen, deformed, and dried networks of semi-rigid chains become materials having very good mechanical properties. In this novel processing method, suitable polymeric chains are identified, with preference for those of sufficient stiffness to give anisotropic, liquid-crystalline phases. The chains are then crosslinked, preferentially in the presence of a solvent. The crosslinkages confer the solidity required to keep the chains in the deformed state during drying and the solvent prevents premature collapse of the chains into domains, not themselves oriented in the direction of deformation. The segmental orientation can be induced by either uniaxial or biaxial deformation of the swollen network, and the solvent can be removed under strain by either evaporation or by diffusion into another solvent miscible with the first, but immiscible with the polymer. The result should be a homogenous and highly ordered material with greatly improved mechanical properties. Naturally occurring polymers are attractive objects for this new orientation technique since many, such as the cellulosics and proteins, consist of semi-rigid chains.

Fig 2.

Modified from Zhao W., Kloczkowski A., Mark J.E., Erman, B. and Bahar, I., Chem. Mater., 10, 794 (1998).

Uniaxial Orientation



Procedures

The Corporate Research Division, Miami Valley Laboratories of Procter and Gamble Company provided pellets of poly-3-hydroxybutyrate-co-3-hydroxyvalerate. The pellets (5g) were dissolved into 10 mL of chloroform, and the crosslinking agent (benzoyl peroxide) was added. The resulting solution, which was clear, was then poured into Petri dishes to obtain thin uniform films. The reason for choosing glass Petri dishes was that the resulting film was easy to remove as it did not stick. These films were kept at room temperature and the solvent was allowed to evaporate for three to four days. The resulting films were white, and were placed into a vacuum oven set between 130-140° C. This was done to remove any residual solvent which may have been present in the sample.

The film was removed and cooled to room temperature and then carefully removed from the mold. Removing a film before it cooled would cause it to stretch resulting in areas of non-uniform thickness. The film thus obtained was cut into 10 mm x 6 mm strips. The thickness was determined by the size of the petri dish and the amount of solution, and ranged from 0.009 to 0.012 mm. For uniaxial orientation the crosslinked sample was swollen in chloroform and then dried in the stretched state. The swollen thin films were stretched using clamps, alongside a ruler for estimating dimensional changes. On the average, the samples were stretched up to three times their initial lengths. The stretched films were then cut into 10 mm x 6 mm strips. Since stretching reduces the thickness and breadth of the samples, films with breadths twice the lengths were swollen and stretched.

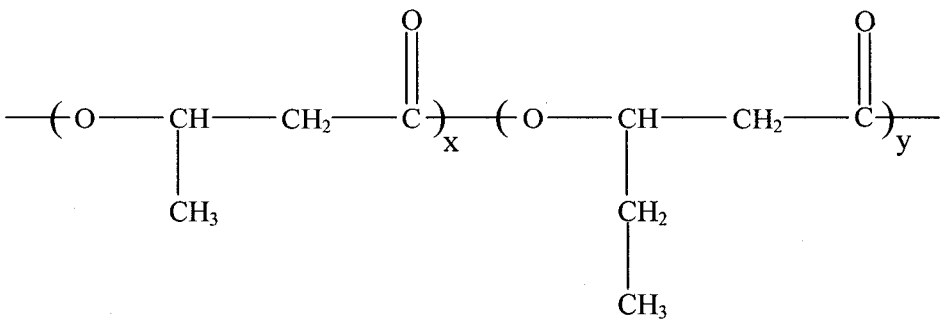
Data Sheet

Modified from Material Safety Data Sheet provided by Dr. Isao Noda of the Corporate Research Division of Procter and Gamble Company.

Acronyms: Poly (3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, Biopol

Class: Polyester

Structure:



Major Applications: Biodegradable bottles, containers, sheets, films, laminates, fibers, medium for drug delivery.

Physical Forms: dense powder, light powder, granules, films

Toxicity: The powders have an acute oral LD50 in male and female rats in excess of 5000 mg/kg. LD stands for "Lethal Dose". LD50 is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. The LD50 is one way to measure the short-term poisoning potential (acute toxicity) of a material [26]. No compound related signs were noted in any animal during the study.

Physical Data:

Melting point 100-180 ° C.

Density: 1.25 g/cm^3

Solubility in Water: insoluble

Specific Gravity: (H_2O = 1) 0.9 – 1.3

Vapor Pressure: Nonvolatile

Odor: No apparent odor

Evolution of the Experimental Procedures

The first goal of the experiments was to form crosslinked samples sufficiently strong to allow tests to be performed on them. The initial route taken to form a crosslinked film was to eliminate the need for a solvent. To achieve this, forming a film of the sample as well as crosslinking it was performed in a single step, using a thermal press. The polymer sample and the crosslinking agent were placed into a mold, which was subjected to a pressure (roughly 10 psi) and elevated temperature (around 130-140° C). The film formed in the mold was found to be brittle and non-uniform and was hard to remove, which rendered the sample unsuitable for crosslinking. The problem was that the copolymer was in the form of pellets and did not mix well with the crosslinking agent. Also the fact that the pellets were very hard resulted in films of non-uniform thickness, which had areas of varying amounts of crosslinking agent. When tested by swelling the film in a solvent it was found that the sample was poorly crosslinked. This led to the need to use solvent in the procedure.

Finding the right solvent:

The ideal solvent for the crosslinking would be one which would dissolve both the copolymer and the crosslinking agent to form a homogenous solution and finally a uniform film. The chosen solvent should be easily removable from the resulting solution, and the solvent should not interfere with the crosslinking reaction. A number of solvents with varying solubility parameter were available for this purpose [12]. The solubility parameter of the copolymer is 19.2 $(MPa)^{1/2}$ [12]. Solvents available for dissolving at room temperature were chloroform 19.0 $(MPa)^{1/2}$, trichloroethylene 18.8 $(MPa)^{1/2}$, and

methylene chloride 19.8 $(MPa)^{1/2}$ [12]. Chloroform was chosen since it was the easiest to remove and allowed both the copolymer as well as the crosslinking agent to react, and its solubility parameter closely matched that of the copolymer. Methylene chloride was also tested. Methylene Chloride has a low boiling point (~40 °C), which meant that the solvent could be easily removed from the solution. The low boiling point of methylene chloride resulted in its evaporation before the free radical generation could be achieved from decomposition of the benzoyl peroxide. Thus crosslinking could not be achieved. To circumvent this problem, the mixture was refluxed so that it could be heated to a higher temperature. This caused some reaction, which lead to a mixture that was odorous and colored, and was assumed to have lead to undesirable chemical reactions. Although the properties of methylene chloride were more suited to the crosslinking reaction, it was discarded as the final result was non-uniform samples, not uniformly crosslinked. The mixture was poured into Petri dishes and the resulting film was tested for extent of crosslinking. The test was to swell the film in methylene chloride and find out how much of the film dissolved. It was found that parts of the film did dissolve in the solvent, which was an indication that the crosslinking was incomplete.

Chloroform with a slightly higher boiling point (~ 61 °C) than methylene chloride was tested next. Using chloroform resulted in production of a uniform film and was easy to remove. To use it, films were made and then subjected to heat in a vacuum oven to give free radical generation. Initially the films were just heated to promote crosslinking but the residual amounts of solvent caused a problem, resulting in incomplete crosslinking. One of the ways in which this problem was minimized was by using a minimum amount of solvent. There was another problem in that the excess solvent

caused the sample to be incompletely crosslinked and resulted in samples with low degree of crosslinking. Removal of the solvent and the crosslinking of the sample were achieved in a vacuum oven. A range of temperatures was used and the optimum temperature was found to be between 130-140° C. A very high temperature resulted in the charring of the sample and a very low temperature resulted in the sample not being crosslinked.

The next step was to compare the samples, which were uniaxially oriented during drying with the non-oriented samples. The samples stretched by hand frequently stuck to the fingers and broke. To overcome this problem clamps were used and the extent of stretching was monitored with a ruler. The samples were dried in the stretched state, which caused the breadth of the sample to decrease. In order to compensate for this decrease in breadth, films with breadths nearly twice of the length were swollen. The stretched samples were subjected to a moderate temperature of 80-100° C in a vacuum oven to remove residual solvent.

Tests were conduced on the sample using an Instron Tester. The samples were subjected to stress using a 2 KN cell. Plots of stress versus strain were obtained for the uncrosslinked sample and crosslinked samples, and compared for improvements in mechanical properties. Samples were tested with an initial length of 10 mm, with a 2 mm/min rate of stretching.

Results

Table I

Comparison of Oriented and Non-Oriented Samples

	Weight Crosslinker (%)	Stress at Max. Load (MPa)	Maximum Strain (%)	Strain at Max Load (mm/mm)	Young's Modulus (MPa)	Toughness (MPa)
Pure Sample	-	13.9	9.7	0.09	304.0	0.87
Crosslinked	7	7.7	25	0.20	135.0	1.45
Uniaxial (2x)	7	4.5	54.5	0.31	59.5	2.06
Uniaxial (3x)	7	5.2	112.5	0.48	61.3	3.56
Crosslinked	8	6.3	36.9	0.23	164.0	1.80
Uniaxial (2x)	8	3.8	54.3	0.20	32.9	1.52
Uniaxial (3x)	8	3.9	242.2	2.10	49.5	6.94
Crosslinked	9	16.2	47.5	0.20	261.0	6.21
Uniaxial (2x)	9	4.6	107.3	0.13	102.0	3.93
Uniaxial (3x)	9	5.6	72.3	0.17	137.0	2.70
Crosslinked	10	13.4	110.1	0.20	249.0	12.10
Uniaxial (2x)	10	6.2	59.2	0.25	157.0	2.86
Uniaxial (3x)	10	8.3	329.1	2.95	62.0	24.50

2x: Represents the samples that had been stretched to twice their initial lengths.

3x: Represents the samples that had been stretched to thrice their initial lengths.

Figure 3. Comparison of Pure and Crosslinked Samples

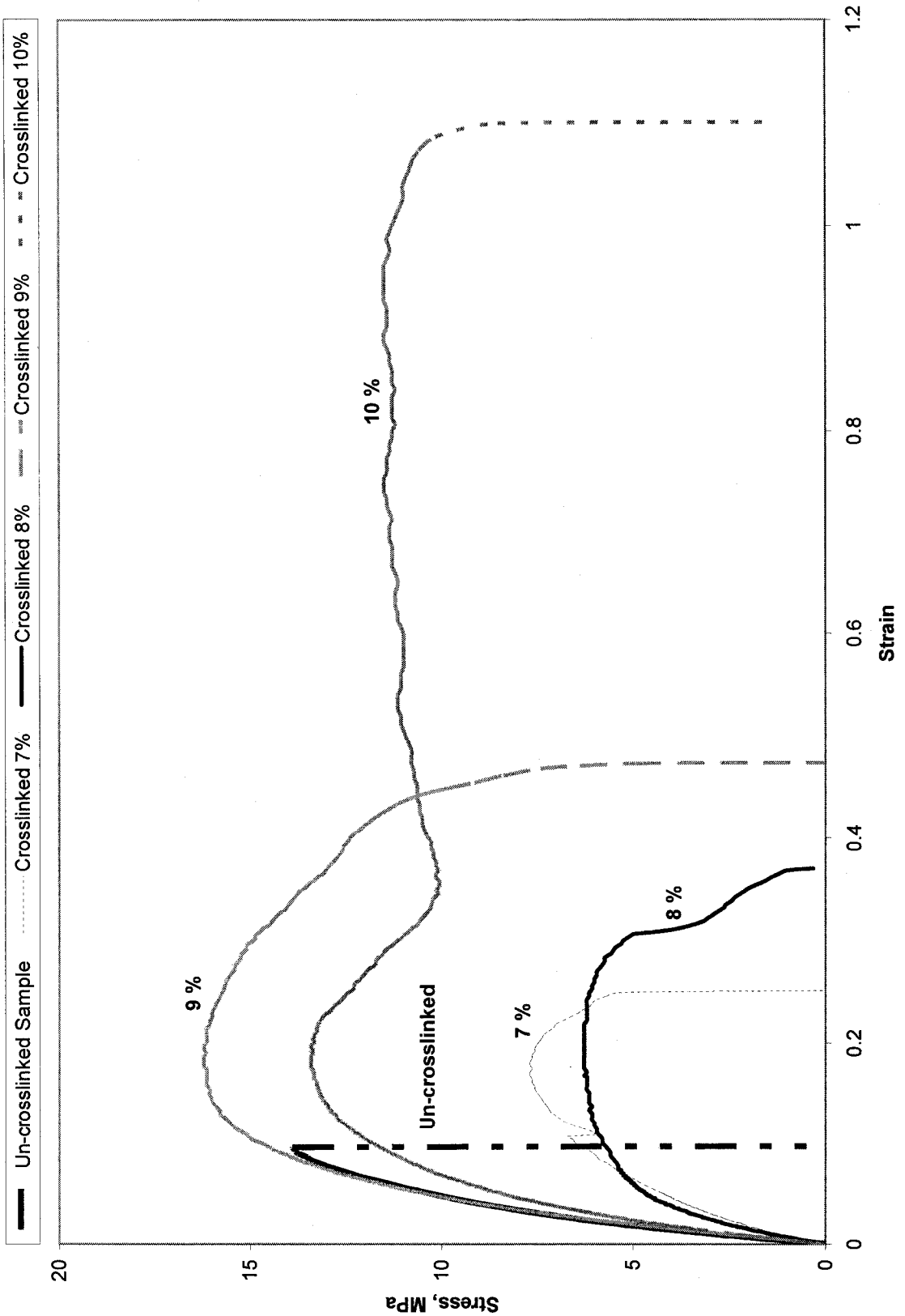


Figure 4. Comparisons Among Uniaxially Oriented Samples Stretched to Twice (2x) their Initial Lengths

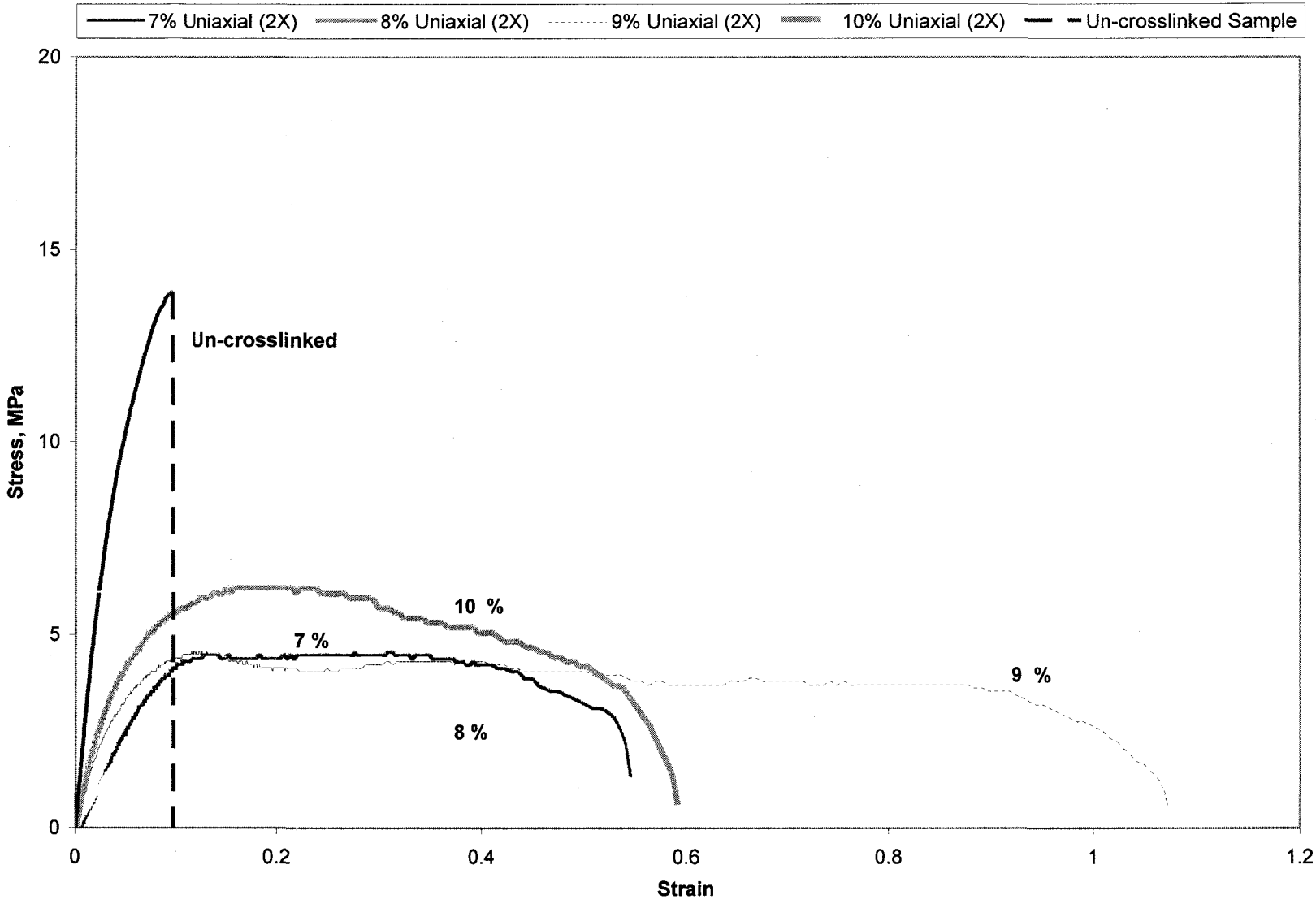


Figure 5. Comparison of Uniaxially Oriented Samples Stretched to Three Times (3x) their Initial Lengths

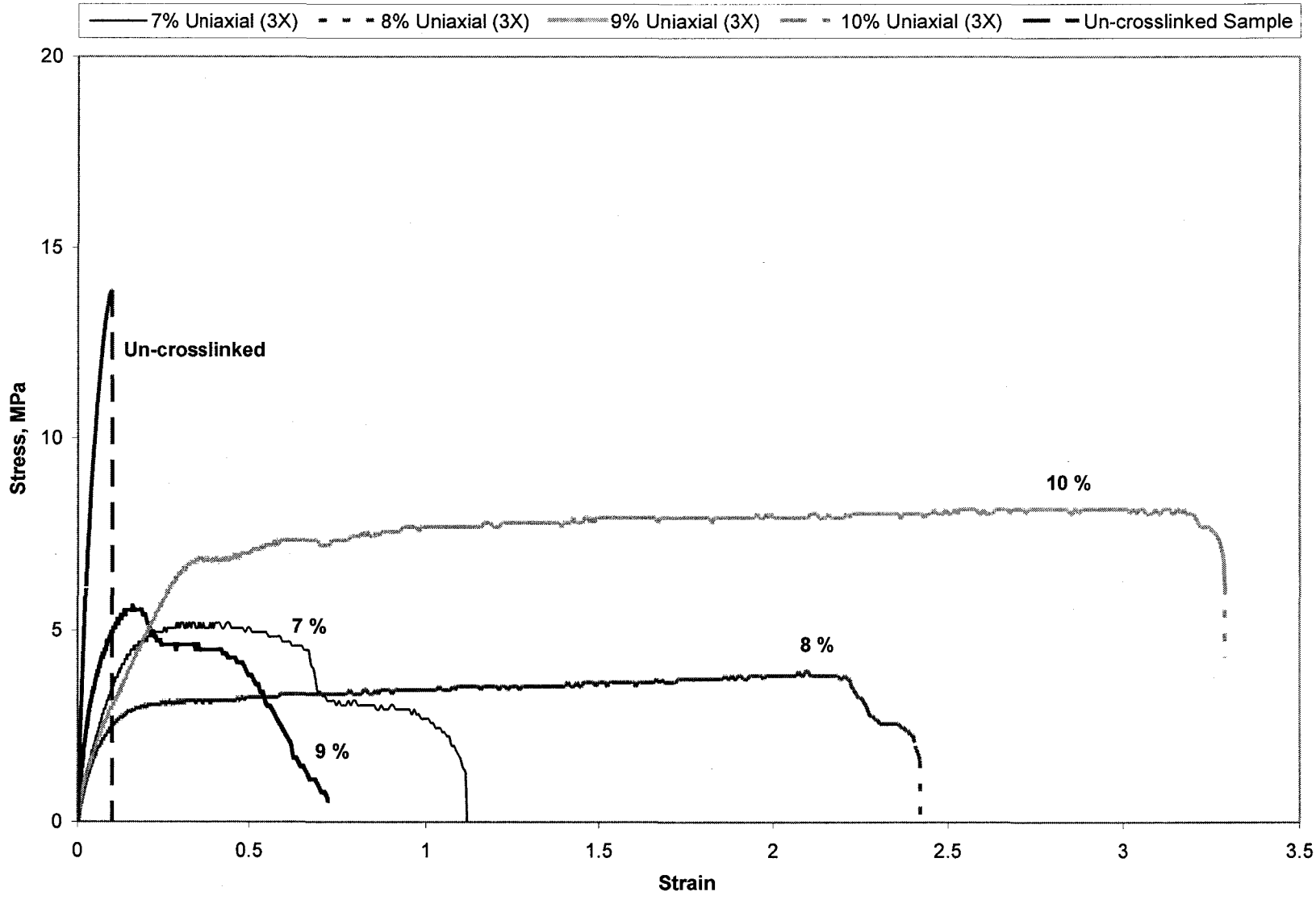


Figure 6. Comparison of Samples Prepared Using 7 % Crosslinking Agent

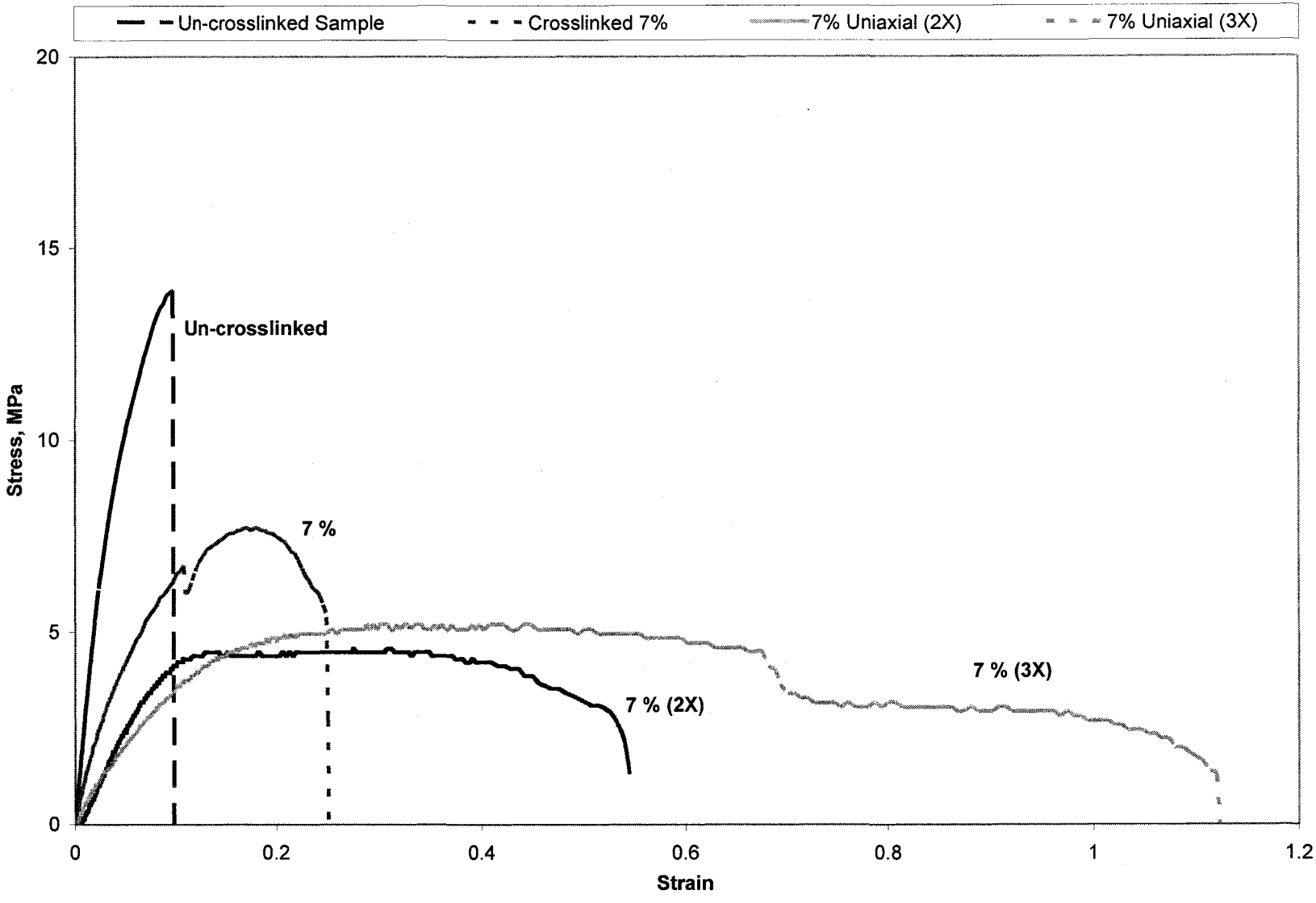


Figure 7. Comparison of Samples Prepared Using 8 % Crosslinking Agent

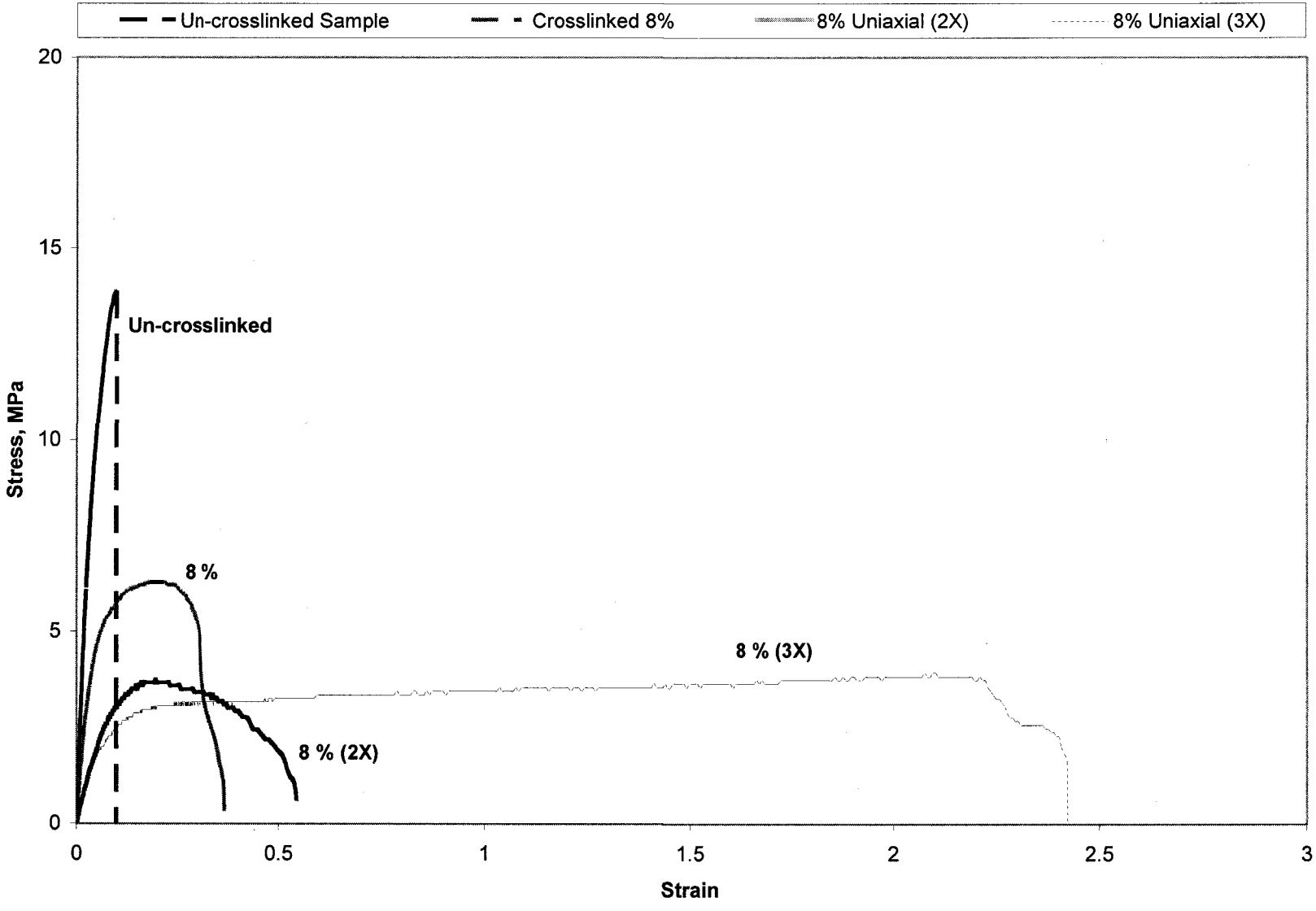


Figure 8. Comparison of Samples Prepared Using 9 % Crosslinking Agent

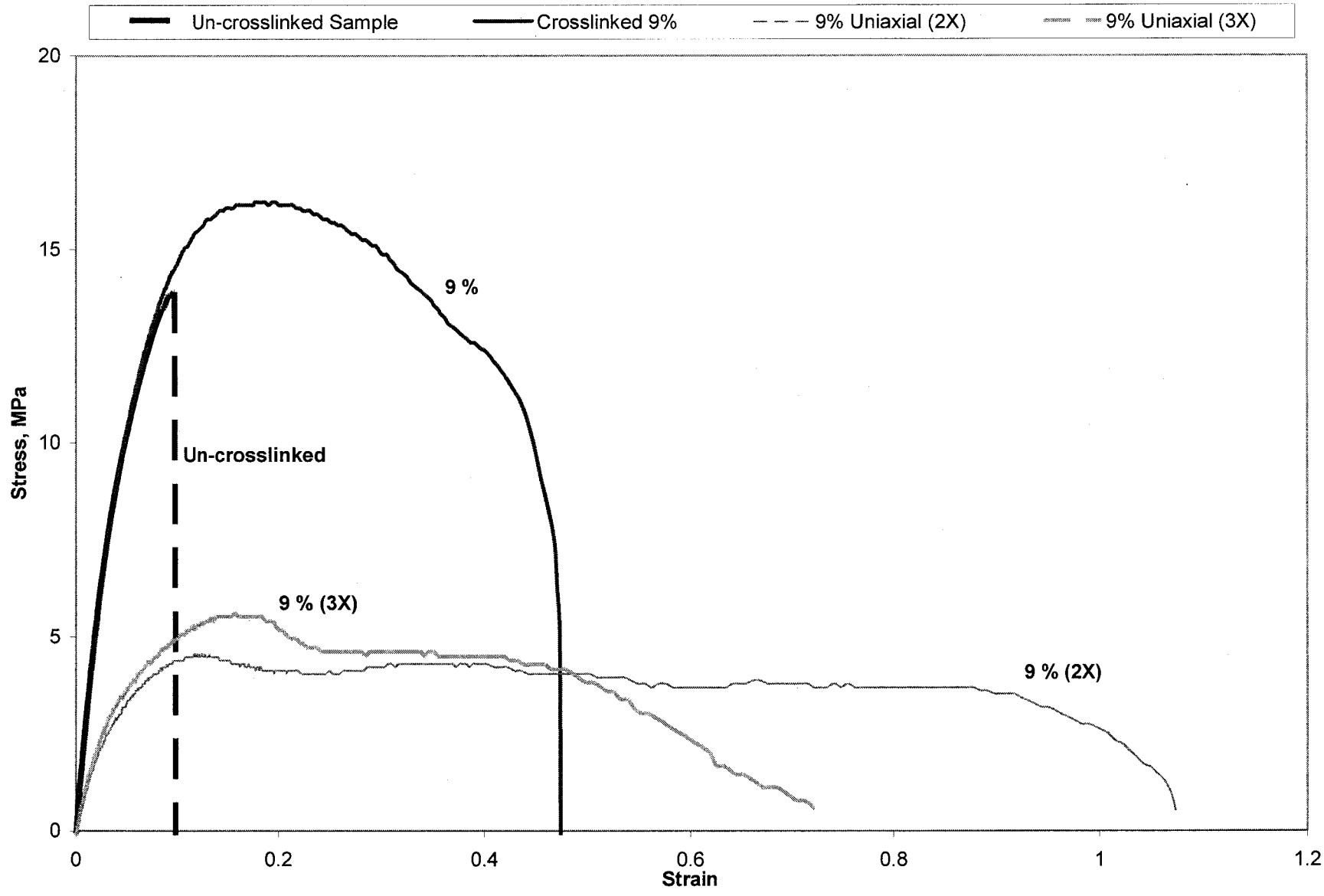
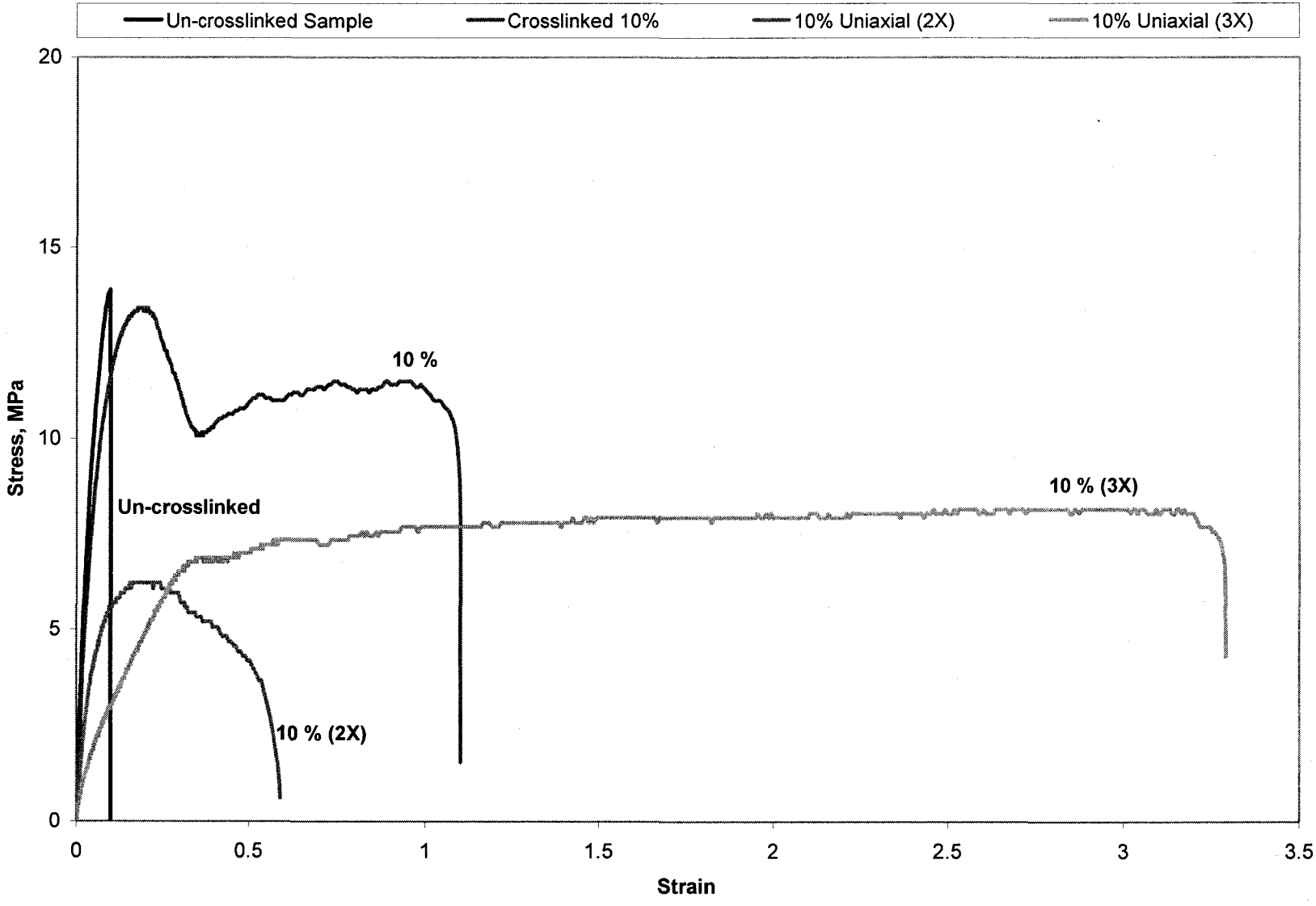


Figure 9. Comparison of Samples Prepared Using 10 % Crosslinking Agent



Discussion

There is a substantial increase in the toughness of the crosslinked sample in comparison to the uncrosslinked sample. This indicates the crosslinked samples are robust and stronger than the pure PHBV and that the crosslinking has improved the toughness of the film. The crosslinked sample showed an increase of 200-1200 % in toughness.

The crosslinked samples dried under uniaxial extension show additional increases in toughness, in comparison to the crosslinked sample dried in the undeformed state. This is true for samples with 7 and 8% crosslinking agents. The samples with higher percentage of crosslinker showed decreases. The 10% crosslinked sample showed an increase of 200% (sample 3x) in comparison to the non-oriented crosslinked sample. From this observation we can draw the conclusion that the orientation of the sample indeed favorably affects the mechanical properties of the film. The samples which had been stretched to three times their original length during drying showed more toughness than the samples that had been stretched to only twice their initial lengths. The higher the strain in the sample during drying the higher the degree of orientation and the larger the improvements in toughness. The ratio to which the samples can be stretched is determined by the brittleness of the crosslinked film and its strength. Obviously care must be taken to stretch the sample so that the film does not rupture.

The crosslinked and uniaxially oriented samples show an increase in toughness as the percentage of crosslinker was increased. As this percentage was increased, there was an increase in the degree of crosslinking and this had direct bearing on the toughness of the sample. The optimum percentage of crosslinker under the conditions of the experiment was found to be in the range 8-10%. The samples with lower percentages showed incomplete

(lower degrees of) crosslinking. The samples with higher percentages of crosslinker were more brittle. They also show regions of varying concentrations of crosslinking agent.

The crosslinked samples in general showed an increase in maximum extensibility, which indicates that the samples were strong and tough. As the percentage of the crosslinker was increased the maximum percentage strain also showed an increase. The uniaxially oriented samples showed an increase in maximum percentage strain as the percentage crosslinker was increased, and were also significantly better than the non-oriented crosslinked sample.

Although the crosslinked and oriented samples showed an increase in toughness, their flexibility had not been affected; in fact the crosslinked samples show higher flexibility than the uncrosslinked sample. The uniaxially oriented samples showed a phenomenal increase in the maximum percentage strain and the samples with higher stretching showed higher maximum percentage strain.

The Young's modulus of the crosslinked samples increased as the percentage crosslinking agent was increased, as expected.

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