## VIRONMENT - FREEN NATURAL RUBBER GLOVES

MALAYSIAN RUBBER BOARD

# **ENVIRONMENT - FRIENDLY NATURAL RUBBER GLOVES**

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### **ENVIRONMENT - FRIENDLY NATURAL RUBBER GLOVES**

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Malaysian Rubber Board (MRB)

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### **Environment - Friendly Natural Rubber Gloves**

#### INTRODUCTION

Biodegradation is the biological breakdown of organic compounds by microorganisms into cell biomass and less complex compounds, and ultimately to water, and either carbon dioxide (aerobically) or methane (anaerobically). The extent and rate of this natural process depend on interactions between the environment, the number and type of microorganisms present and the chemical structure of the compound(s) being degraded. Microorganisms secrete the enzymes that catalyse the degradation of polymers. Oxygen, nutrients and microorganisms are very often the limiting factors in soils. Enhanced bioremediation occurs when the rate of biodegradation is increased by supplying required nutrients to an indigenous microbial population (biostimulation) and by inoculating the site with microorganisms capable of degrading the target pollutant (bioaugmentation).

While microorganisms can degrade most natural compounds, they lack the appropriate enzymes to degrade many synthetics. Compounds having a molecular structure to which microorganisms have not been exposed to (*i.e.* xenobiotic compounds) are usually resistant (recalcitrant) to biodegradation. They pose threats to the ecosystems they contaminate. These may sometimes undergo biotransformation where small structural changes occur that affects the toxicity and mobility of the original compound with no loss of molecular complexity.

Biodegradative activities in natural material and energy cycling constitute one of the most important processes in water, sediment, soil and other ecosystems. An issue of concern for professionals and the public at large is the accumulation of recalcitrant organic compounds in the environment, sufficiently long (persistence) that they have undesirable effects<sup>1</sup>. Persistence can be due to an environment that creates metabolic impotence in an otherwise competent microbial population. The emergence of various elastomeric materials for production of gloves had posed an environmental problem for many years. Their growing use is expected to raise concerns about their environmental impact as a result of their disposal by incineration and landfilling. This monograph provides readily-available knowledge on the biodegradation of natural rubber (NR) and non-NR latex gloves.

#### Degradation of NR by microorganisms

Most commonly-used natural polymers and fibres *e.g.* NR, starches, gelatin, wood and cotton are inherently biodegradable under proper conditions although the extent of degradation decreases with increasing molecular weights of the polymers. Natural rubber (NR) is both a photosynthetically-renewable resource and an environmentally-degradable material. It is an unsaturated high molecular weight polymer, and in nature, is expected to degrade very slowly in comparison with other natural polymers. NR-degrading bacteria are widely distributed in soil, water and sewage and interestingly, with some exceptions, belong to the actinomycetes<sup>2</sup>. As a group, the actinomycetes are characterised by an ability to digest complex materials and to use unusual molecules and are thus significant decomposers in soils<sup>3</sup>. Some early reports on the biodeterioration of NR rubber goods had been reviewed by Cundell & Mulcock<sup>4</sup> and Zyska<sup>5,6</sup>. Different results from the several rubber-degrading microorganisms may be obtained under various test conditions.

Early studies by Shaposnikov *et al.*<sup>7,8</sup> showed that pure strains of some bacteria caused up to a 55% loss in weight of thin rubber sheets in 70 days, and pure cultures of actinomycetes a 43% loss in 45 days. The presence of fungi increased the weight loss due to actinomycetes to 52%. Low *et al.*<sup>9</sup> had used fungi and actinomycetes to degrade diluted latex for six weeks and found reductions of 17 and 24% in molecular weights due to a fungus (*Fusarium* sp.) and an actinomycete, respectively. Heisey and Papadatos<sup>10</sup> isolated 10 actinomycetes from soil that reduced the weight of vulcanised rubber from latex gloves by 10-18% in six weeks. The rubber-metabolising bacteria were species of *Streptomyces, Amycolatopsis and Nocardia*.

Actinomycetes severely degraded the surfaces of rubber pipe-joint sealing rings used for pipelines conveying potable and waste water in the Netherlands<sup>11,12</sup>, New Zealand<sup>13,14</sup>, Germany<sup>15</sup> and the UK<sup>16</sup>. Other microorganisms isolated from deteriorated pipe-joint rings were *Fusarium* sp. and species of the sulphur-oxidising bacteria, *Thiobacillus*.

Exciting evidence began to emerge when Tsuchii *et al.*<sup>17</sup> were able to grow the actinomycete *Nocardia* sp. strain 835A on unvulcanised NR and synthetic isoprene rubber but not on other types of synthetic (chloroprene, butadiene and styrene-butadiene) rubbers. Vulcanised NR

products were also utilised by the organism. Thin films from a latex glove were rapidly degraded and weight losses reached 75% after a two-week cultivation period, producing two fractions of degraded low molecular mass isoprene. They showed that thickness, length and width of the rubber pieces influenced microbial colonisation and degradation of NR products<sup>18</sup>. Following the important contribution of Tsuchii et al.<sup>17</sup>, Kajikawa et al.<sup>19</sup> completely degraded latex glove films after 45 days in batch cultures using laboratory fermenters with Nocardia sp. strain 835A. In semi-continuous culture conditions running over 150 days, uniform colonisation of strain 835A was obtained after five days cultivation and the rubber films degraded within 20 days. Strips cut from truck tyres also degraded quickly when primed by a glove strip with Nocardia<sup>20</sup>. After eight weeks, about 28% of the tyre strip disintegrated into very small particles with a 51% loss of initial weight. Tsuchii and Takeda<sup>21</sup> later found that a crude enzyme from a bacterium, Xanthomonas sp. strain 35Y were also able to biodegrade NR in the latex state to produce two fractions of reaction products. This work was the first evidence for the existence of an extracellular polyisoprenoid oxygenase in a Gram-negative bacteria.

Frequently, the formulation of vulcanised NR influenced its resistance to degradation. In looking at this question, Cundell & Mulcock<sup>13,14</sup> observed that dicumyl peroxide-cured NR was most susceptible and a TMTD sulphurless-cured NR was least susceptible to microbial deterioration. Carbon blacks, non-black fillers and colouring materials are resistant but when in contact with an organic carbon source is very susceptible to fungal growth<sup>6</sup>. In support of this idea, Kwiatkowska *et al.*<sup>22</sup> showed that growth of organisms colonising and degrading vulcanised NR sheets is governed by the carbon black loading rate, *i.e.* the weight loss of unfilled NR was highest while NR with 0.5 and 45 p.p.h.r carbon black were lower. Sulphur as a vulcanising agent is a slightly fungitoxic material, and accelerators are both fungicidal and bactericidal. Anti-oxidants and anti-ozonants have both sensitive or fungitoxic properties. Most plasticisers, softeners and extenders are not fungicidal.

Tsuchii *et al.*<sup>23</sup> further studied NR vulcanisates containing various amounts of sulphur and an accelerator (CBS) to degradation by *Nocardia* 

sp.strain 835A. They found that the higher the sulphur or CBS content, the less was the weight loss of the vulcanisates after microbial attack. Adding carbon black made the vulcanisate more resistant to microbial attack.

#### Non-degradability of synthetic rubbers

Very few synthetic polymers can be degraded microbially. The term synthetic rubber includes the synthetic analogue of NR (namely cis-1,4 polyisoprene) as well as a great variety of other rubbery materials offered by the chemical industry to users.

Synthetic rubber compounds have been reported to be more resistant to microbial attack than NR compounds<sup>12</sup> and the literature show a variety of results depending on the period and mode of tests.

Cundell & Mulcock<sup>13</sup> investigated the microbial resistance of isobutene-isoprene (butyl), chloroprene and acrylonitrile-butadiene (nitrile) vulcanisates in pure culture. After 18 months, the losses in weight of the rubber strips were generally small and they reasoned that such deteriorations may be at the expense of the compounding ingredients in the vulcanisates e.g. 5.3% (NR), 10.8% (chloroprene rubber), 1.6% (butadiene rubber), 2.2% (acrylonitrile-butadiene), 0% (butyl rubbers) and 2.4% (styrene-butadiene vulcanizates). In a review, Zyska<sup>6</sup> wrote that only raw and unvulcanised chloroprene and nitrile may be classified as inert or fungitoxic rubbers. There are however slowlyemerging data about the susceptibility of nitriles to biodegradation in pure cultures. Miller & Gray<sup>24</sup> isolated a species of the bacteria *Rhodococcus* from garden soil that could hydrolyse a number of amides and nitriles (acetonitrile, acrylonitile, propionitrile and n-butyronirile) to ammonia. More recently, simple nitrile compounds were shown to be degraded by an Agrobacterium species<sup>25</sup>, Pseudomonas marginalis<sup>26</sup>, Eschericia coli strain BCN6<sup>27</sup> and the yeast Candida famata<sup>28</sup>.

Additional work of this type demonstrated the influence of polymer size on degradation. Tsuchii *et al.*<sup>29</sup> showed that a soil bacterium (*Acinetobacter* sp.stain 351) degrades 30% of a sample of liquid polybutadiene ( $\overline{M_n}$ =650) in three days but not with the higher oligomers. In another study, they showed that about 40% of a 1,4-type polybutadiene of  $\overline{M_n}$ =2350 was degraded by another bacteria (*Moraxella* sp.) in five days<sup>30</sup>. A polybutadiene sample with  $\overline{M_n}$  of 16,100 was

hardly degraded and they believed that vinyl bondings in the polybutadiene prevented microbial degradation. They also obtained a 60% degradation of a sample of synthetic cis-1,4-polyisoprene ( $\overline{M}_n$ =940) in four days by soil organisms (*Bacillus* sp./coryneform bacteria) but not with synthetic polyisoprene with higher average molecular weights of 2,500<sup>31</sup>.

Polyvinyl chloride (PVC), along with other water-insoluble vinyl polymers (polystyrene, polyethylene and polypropylene) are resistant to biodegradation. However, many of the additives used in PVC, including some plasticizers *e.g.* epoxidised soybean oil, heat stabilisers such as butyl tin laureate and fatty acid lubricants such as zinc stearate, support growth of microorganisms<sup>32</sup>. Plasticizers form a great bulk of plastic formulations and so the microbiology of vinyl is almost always centred on the additive plasticizers. Plasticized PVC exposed to microorganisms became stiff and brittle with an increase in modulus and tensile strength that will break when flexed<sup>32</sup>.

Unlike natural polymers, many synthetic polymers are not biodegraded because they have not been available for a long-enough time in natural evolution for microorganisms to develop degradative enzymes that will utilize the compounds. Microorganisms will have to evolve new genes and genetic functions which encode catabolic enzymes to degrade new chemicals generated by the chemical industry. Gene exchanges among microorganisms can give rise to a particular degradative pathway. Various molecular mechanisms exist to enable microbes to recruit genes from pre-existing genes of related catabolic pathways and to modify the nucleotide sequences in the structural and regulatory genes to enhance expression and to use synthetic compounds as substrates<sup>33</sup>. Thus microbes have occasionally responded to synthetic chemicals by producing degradative enzymes although the pathways may not be optimally regulated.

#### The biodegradability of some glove materials in soil

Tests on the environmental fate of some polymeric materials were made by burying pieces of gloves  $(15 \times 9 \text{ cm}^2)$  in two natural soils in a time-course experiment under laboratory conditions. Residual weight determinations, measurements of microorganism population, film thickness and loss of mechanical strengths were used to compare the extent of biodegradation of the glove materials.

After 12 months of exposure, extensive biodegradation of NR glove pieces occurred with mean weight losses averaging 94% for both soils . Averaged over time, the weight losses in the clayey soils (99%) were significantly greater (P<0.001) than in the sandy soils (88%). Mean weight losses due to neoprene and nitrile were marginal and not significant (neoprene, 2.3%; nitrile, 6.4%; averaged over soils and time), indicating no biodegradation of the polymer proper. The weight loss of vinyl glove pieces averaged 12% for both soils, and occurred during the first month of exposure to soil with little additional change thereafter. This small loss in residual weight was due to plasticizer and other additive loss that also caused stimulation of microbial activity although no significant degradation of the resin occurred.

Significant losses of film thickness were shown by NR and vinyl glove pieces after 12 months incubation (*Table 1, Figure 3*). Microbial enumeration of the pieces revealed a considerable flux in populations, with significantly higher densities of bacteria, fungi and actinomycetes on NR and vinyl than on neoprene and nitrile (*Table 2, Figure 4*). A decline in tensile strength and elongation at break occurred for degrading NR glove pieces but not with the remaining materials (*Table 3*). The lack of significant weight losses by neoprene and nitrile were consistent with their responses in film thickness, lower microbial counts and tensile strength behaviour.

In such tests, degradation is not exclusively microbiological (*i.e.* purely enzymatic process) but include other complex physicochemical actions of the soil environment, usually the autooxidative-progressive ageing effect, that can make the material more amenable to microbial action.

#### NR as an environmentally-superior material to synthetics

In recent years, the waste disposal problem has spurred mounting interest in the biodegradability of polymers, especially when the public is voicing greater concern about protecting human health and preserving the quality of our environment. Plastics, for instance, that became an integral part of contemporary life, already formed a significant part of wastes in municipal landfills. They create a demand for scarce landfill space and some items endanger wildlife and caused considerable aesthetic nuisance. Concerns regarding the environmental impact of solid wastes, recycling and composting options are expected to increase as landfill capacity decreases. Managing waste is thus a challenge facing the global community. Various types of alternative elastomeric materials for gloves are in production worldwide. These non-NR latex gloves include polychloroprene (neoprene), styrene block copolymers, polyurethane, nitrile and plasticized PVC (vinyl) but none of these currently matches NR's physical property profile. The global figure for elastomeric glove consumption was estimated to be as high as 30 billion units<sup>34</sup>. In the dipped glove market, the USA with its flourishing health industry imported 16.8 billion units of rubber gloves in 1994. Synthetic alternatives for latex, especially nitrile and vinyl examination gloves, may grab a larger share of the US dipped glove market, and synthetic rubber glove sales is predicted to be 21% of the estimated 18.67 billion total unit sales of both NR and non-NR latex gloves by the year 2002<sup>35</sup>.

Domestic and contaminated industrial gloves that do not require specific handling are disposed along with other household wastes as non-hazardous municipal solid wastes into domestic landfills. In a landfill, residual chemicals e.g. accelerators, will leach out as the rubber biodegrades. Under standard landfill conditions, vinyl is not biodegradable but the plasticizers (esters of phthalic acid) will leach out from the material when in contact with non-aqueous solvents. Nitrile itself is not biodegradable and the chemical by-products leaching out will be similar to those produced by NR gloves.

Contaminated medical wastes is incinerated to destroy the pathogens within the product. Alternative treatment strategies such as disinfection or autoclaving to render the waste non-infectious followed by burial in a permitted landfill site involve additional costs. Successful waste disposal or the permanent isolation of waste will depend on the scientific understanding of disposal issues, technology development, public acceptance and proper management. Incineration however burdens the environment due to the release of toxic substances into the atmosphere. The generation of wastes in the health industry creates pollutants in just about every category from solid to liquid wastes and gases, and very large amounts of the one-use disposable waste latex or synthetic examination gloves impact onto the environment.

NR latex gloves and other rubber products containing sulphur liberates sulphur dioxide and water when incinerated and the remaining carbon backbone oxidised to carbon dioxide in an aerobic environment. Zinc salts used in latex compounds as accelerators contribute to the ash remaining, which will also contain some sulphur as sulphates. Sulphur

dioxide which dissolves in atmospheric moisture generates corrosive sulphuric acid that contributes to the problem of acid rain. Consequently, incinerator exhaust stacks need to be fitted with wet scrubbing systems to prevent emission of hazardous fumes and acidic components into the atmosphere.

Vinyl gloves have lower tensile strengths and elongation at break compared to NR. Vinyl burnt at high temperatures in an oxygen-rich environment release carbon dioxide and the corrosive hydrochloric acid that contributes to acid rain which is a sensitive issue in Northern Europe. Its monomer (vinyl chloride) is a human carcinogen and may be hazardous during the manufacturing stages and in its disposal. Incinerating PVC also release small quantities of other products including the family of chemicals called dioxins, phosgene, free chlorine and benzene, which are well-known toxins and carcinogens. It was calculated that the medical sector uses up to 450,000 tonnes of disposable PVC products each year, of which vinyl disposable gloves account for about 5% of this<sup>34</sup>. Other synthetics used in lesser quantities, e.g. nitrile rubber, butyl rubber, polychloroprene and thermoplastic elastomers may suffer the same potential restrictions on disposal and incineration releases nitrogen-based reaction products. Nitrile is a copolymer of acrylonitrile, a proven carcinogen and butadiene, a suspected human carcinogen. Commercial grades of nitrile may contain acrylonitrile residues in varying amounts. Neoprene is a polymer of chloroprene which is a toxic substance. Burning neoprene and nitrile is hazardous, with nitrile liberating cyanide and neoprene evolving hydrogen chloride<sup>36</sup>. Styrene-butadiene rubber has inferior physical properties and little is known about their toxicity effects. Polyurethanes are constructed from isocyanates that presents dangers during manufacture and disposal.

The biodegradation of used NR glove wastes in landfills will be influenced by the rubber formulations and the appropriate environmental conditions. The rate of intrinsic biodegradation, because of time limits and sub-optimal conditions, may be very slow from a regulatory standpoint and may require enhanced remediation via bioaugmentation as a treatment technology. The isolation of *Nocardia*<sup>17</sup> and *Xanthomonas*<sup>21</sup> as strong decomposers of rubber in pure culture research indicate such possibilities. The natural process of site remediation

appear theoretically attractive, especially with the appropriate engineering design to utilise the metabolic versatility of microorganisms and of providing a suitable growth environment but data from field demonstrations is presently lacking. There are yet many ecological factors to consider when designing a system for enhanced biodegradation, the important ones being acceptable soil composition and properties, substrate bioavailability, oxygen concentration, temperature, pH, moisture, inorganic nutrients, organic substrates and toxins. In general, bioaugmentation with naturally-occuring or genetically engineered microorganisms (GEMs) has not proved to be consistently effective in any open-surface or subsurface environment.

In contrast, there are many instances in which bioaugmentation of engineered bioreactors and closed environments with selected microbial consortia have enhanced degradation<sup>37</sup>. According to Tsuchii<sup>38</sup>, the ecological study of biodegradation of rubber is still at a primitive stage, and future subjects of research will inevitably be on the waste disposal of used rubber, estimations of their degradation rates in nature, and on the biochemical and physiological studies of rubber-degrading microorganisms.

Composting, the waste treatment alternative for the twenty-first century, is slowly emerging as one of the more desirable biotechnologies for the processing of organic wastes into acceptable products that can be used as soil amendments<sup>39</sup>. Composting is the biological decomposition of organic wastes under controlled conditions. Biodegradable components of municipal garbage could be composted or co-composted for beneficial use as biofertilizers and soil conditioners on agricultural or non-agricultural lands. Composted wastes are commonly animal manures, leaves, municipal biosolids, municipal solid waste and a variety of industrial wastes. In many cases, a bulking agent is added to the material to be composted to facilitate air movement through the pile. In most soil composting operations, care is taken that temperature, moisture and nutrient conditions of the decomposing organic matter is optimised for rapid decomposition and a minimum of odour generation. Research aimed at improving our understanding of composting used NR gloves will help facilitate moves toward environmental responsibility and sustainability.

Traditional NR latex gloves are unsurpassed in their range of properties<sup>40</sup>. Compared to synthetic rubbers, the material has high strength combined with high elasticity and softness and excellent film-forming properties. Moreover, NR latex surgical gloves has proven barrier protective capability, offering barrier protection to humans to guard against contact with blood, blood products, other body fluids or potentially infectious materials. In contrast, the barrier effectiveness of non-NR gloves is not clearly defined under in-use conditions. On the basis of available evidence, it is our opinion that NR is as an environmentally-superior material to synthetic alternatives.

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Figure 1. Mean weight loss of glove materials after burial in two soils. , clayey soil; , sandy soil





Figure 2(a). Glove pieces of NR and neoprene after 24 weeks burial in two soils. Note the degraded pieces of NR compared to the synthetics.





Figure 2(b). Glove pieces of nitrile and vinyl after 24 weeks burial in two soils. Note the degraded pieces of NR compared to the synthetics.



(b)



Figure 3(a).Cut sections of glove pieces of (a) NR, (b) neoprene embedded in wax at 0-time (left) and after 48 weeks of soil burial (right).



Figure 3(b). Cut sections of glove pieces of (c) nitrile, (d) vinyl embedded in wax at 0-time (left) and after 48 weeks of soil burial (right).



Figure 4. Colonies of mircoorganisms associated with buried glove materials growing on nutrient agar; fungi (left), bacteria and actinomycetes (right)

#### TABLE 1. MEAN WIDTH OF NR, NEOPRENE, NITRILE AND VINYL GLOVE PIECES AFTER SOIL BURIAL\*

Glove Material	Width(µm)					
	0-time control	48 weeks				
NR	193.3 a	89.6 e				
Neoprene	168.4 b	167.2 b				
Nitrile	127.8 c	129.6c				
Vinyl	163.0 a	103.4 c				

\*Means of 3 replicate pieces, averaged over 2 soils. For each glove material, values not followed by common letters are significantly different at P < 0.05

## TABLE 2. COMPARISON OF MICROBIAL COLONISATION OF GOVE PIECES OF NR, NEOPRENE, NITRILE AND VINYL AFTER SOIL BURIAL\*

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Glove	Nos/mg glove piece					
Material	Bacteria	Fungi	Actinomycetes			
(a) Clayey soil						
NR	3.2998 X 10 <sup>5</sup> a	4.0968 X 10 <sup>3</sup> de	8.0705 X 10 <sup>3</sup> d			
Neoprene	7.7735 X 10 <sup>3</sup> d	3.5631 X 10 <sup>2</sup> hi	1.9307 X 10 <sup>2</sup> i-k			
Nitrile	$4.4036 \ge 10^3 de$	4.7628 X 10 <sup>2</sup> gh	2.3483 X 10 <sup>2</sup> ij			
Vinyl	1.4249 X 10 <sup>5</sup> b	3.5119 X 10 <sup>3</sup> e	1.0186 X 10 <sup>3</sup> f			
(b) Sandy soil						
NR	9.1774 X 10 <sup>4</sup> b	3.5650 X 10 <sup>3</sup> e	1.7239 X 10 <sup>4</sup> c			
Neoprene	2.3324 X 10 <sup>4</sup> c	$8.0768 \ge 10^2 \text{ fg}$	2.4750 X 10 <sup>3</sup> e			
Nitrile	2.8083 X 10 <sup>3</sup> e	6.0525 X 10 <sup>2</sup> f-h	1.3598 X 10 <sup>2</sup> jk			
Vinyl	1.4891 X 10 <sup>5</sup> b	9.0723 X 10 <sup>2</sup> fg	1.0752 X 10 <sup>2</sup> k			

\*Means of 3 replicate pieces, averaged over 12 samplings. Values not followed by common letters are significantly different at P<0.05

Material	Tensile strength, MPa			Elongation at break, %						
	4 wks	8 wks	12 wks	16 wks	44 wks	4 wks	8 wks	12 wks	16 wks	44 wks
(a) Clayey soil										
NR	-94	-98	-	-	-	-73	-94	-		-
Neoprene	+ 7	+18	+12	+ 7	+11	0	- 5	+ 4	+ 3	- 3
Nitrile	-34	-19	-37	-41	-57	+ 2	+ 5	+ 2	+ 7	+ 9
Vinyl	+72	+64	+48	+32	+79	- 9	- 5	- 1	+ 2	-16
(b) Sandy soil										
NR	- <u>91</u>	- <u>95</u>	- <u>95</u>	- <u>94</u>	-	-65	- <u>91</u>	- <u>90</u>	- <u>93</u>	-
Neoprene	+ 7	+14	+14	+10	-	+ 1	+ 3	- 3	+ 3	-
Nitrile	- 5	+ 1	-20	- <u>28</u>	- <u>70</u>	+ 1	- 1	+ 1	+ 8	+ 8
Vinyl	- 5	0	- 2	+ 7	+23	- 8	- 2	-13	- 2	- 8

# TABLE 3. CHANGES IN TENSILE PROPERTIES OF NR, NEOPRENE, NITRILE AND VINYL GLOVE PIECES AFTER INCUBATION IN TWO SOILS\*

\*Data expressed as % change from 0-time control; means of 3 replicate glove pieces. for each glove material, underlined values are significantly different from the 0-time controls (P<0.05)