Effect of limonene on the tensile properties and chemical changes of natural rubber products

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Abstract

The durability and functionality of medical rubber products made from natural rubber or poly(cis-1,4-isoprene) are essential in medical and healthcare applications. However, natural rubber products are prone to degradation over time, which can compromise their performance. This study investigates the impact of limonene on the degradation of natural rubber, focusing on the material's physical and chemical properties. To achieve this, natural rubber samples were prepared and exposed to different concentrations of limonene oil (20%, 40% 60%). The effect of limonene on the natural rubber was assessed by measuring the changes in tensile strength, physical size of samples, stability and chemical composition over immersion times of 30, 60 and 90 minutes. The findings of this study revealed that the immersion of natural rubber in d-limonene led to a significant reduction of tensile properties due to chain scission and bond breaking as well as cross-linking within the rubber. These mechanical alterations were more distinct with the longer immersion times and the higher limoneone concentrations. Additionally, the samples exhibited noticeable dimensional changes with greater concentrations of d-limonene leading to more substantial swelling and ultimately causing a reduction in tensile strength. FTIR-ATR spectroscopy analysis had also revealed chemical modifications in the rubber's structure, particularly related to carbonyl groups. This study provides valuable insights into the vulnerability of natural rubber to limonene-induced degradation. It highlights the need for further research and formulation to enhance medical-grade rubber products' performance for SDG-3.

Introduction

Natural rubber has superior properties such as elasticity, durability, and flexibility to be applied as a protective barrier for general chemical substances [1]. Natural rubber finds its main use in the tire industry, and its complete replacement by synthetic rubber is not feasible in many application fields. Generally, rubber used in the medical field is based on silicone, natural and polyurethane rubber. Medical rubber products are widely used in various industries, including healthcare due to its unique properties. This is especially true for items containing latex, including gloves and condoms, which are good for providing barrier defense against microbes, such as bacteria and viruses, and infectious fluid [2]. However, these rubber products can degrade due to various factors such as heat and light [3], which can affect their mechanical properties and performance. This degradation may lead to potential health hazards for patients and reduce the effectiveness of the products. Besides excess heat and lighting, natural rubber's long-term stability and reliability may also be affected by exposure to chemical compounds, such as oils and solvents. One such chemical that has been found to impact the stability of medical rubber products is limonene. Limonene is the primary component extracted from the oil of citrus fruit peels such as oranges, mandarin, limes, and lemons [4]. In fact, limonene is naturally a colourless liquid with fragrance. With its unique characteristics, it is widely applied in the pharmaceutical industry, perfume, industrial solvent, household cleaning detergent and cosmetics. Limonene ($C_{10}H_{16}$) is an aliphatic hydrocarbon which categorized as a cyclic monoterpene [5].

To date, limited research exists on the effect of limonene on medical rubber. Earlier informal experiments, such as those exploring the phenomenon of orange peels popping balloons, indicate that limonene deteriorates rubber, resulting in a weakened structural integrity. In order to fill this knowledge gap, this research aims to investigate the effect of limonene on the mechanical properties and chemical decomposition of medical rubber. By applying different concentrations of limonene to medical rubber gloves, both physical and chemical changes in natural rubber can be observed.

The relevance and contributions of the findings of this study is much aligned with the United Nations Sustainable Development Goals (SDGs) 3. The research investigates the stability and performance of medical rubber products, such as surgical gloves, an item essential in ensuring the good health and well-being of many across the globe. Additionally, prolonging the life cycle of medical rubber items through this study helps reduce the overall environmental footprint associated with the production and disposal of rubber products [6]. Hence, this study seeks to enhance the understanding of the interaction between limonene and medical rubber and enable the development of better medical rubber products in the future.

Methodology and experimental setup

Materials

D-limonene 99.5% supplied from Chemsoln, ethanol (R&M), ASTM D412 type c natural rubber samples.

Preparation of d-limonene

Ethanol is used as a solvent for preparing the d-limonene solution. Different concentrations of d-limonene (20%, 40% and 60%) and the sample name is given in Table 1.

Table 1 Preparation of d-limonene solution

Sample Name	Limonene concentration [%]
20% limonene	20
40% limonene	40
60% limonene	60

Effect of limonene concentration on natural rubber tensile properties

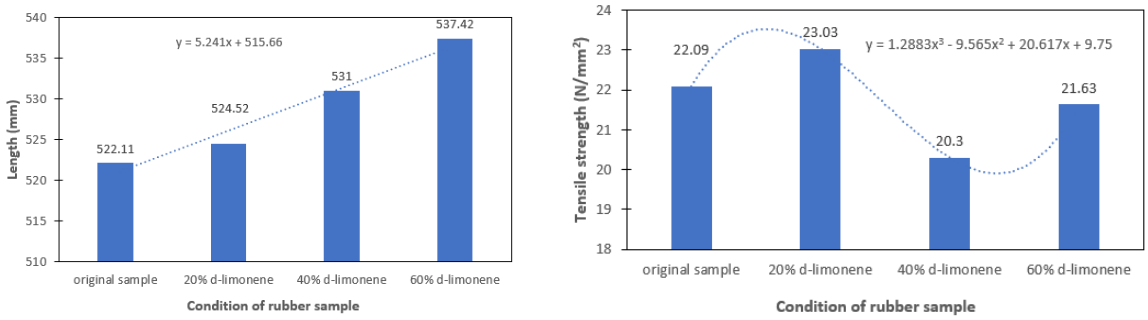
Natural rubber samples were cut according to ASTM D412 type c and were immersed separately in d-limonene solution of different concentrations (20%, 40% and 60%). The samples were left in room temperature for a duration of 24 hours. The rubber specimens were then carefully transferred to an aluminum foil and subjected to room temperature conditions for natural drying. The data obtained from the specimens were presented as part of this study's results as shown in Figures 1 and 3.

Effect of limonene contact time on natural rubber

Natural rubber specimens (ASTM D412 type c) were immersed in different concentration. For every 30 minutes interval, five specimens were removed from the individual samples and left to dry under room temperature condition for 24 hours. The data from the specimens are presented in Figure 2 and 4. FTIR-ATR analysis were performed using Pelkin Elmers Spectrum 2, ATR scan range 650-400 cm^{-1}.

Results and discussion

Physical changes



a) b)

Figure 1 Tensile properties, a) elongation at break and b) tensile strength

Two main reactions occurred during the immersion of rubber specimens in limonene: chain scission and cross-linking [7,8]. Chain scission occurs during rubber degradation, leading to a decrease in cross-link density, causing softening and loss of elastic properties [7]. As the polymer chains break, the material becomes less interconnected, resulting in a decrease in stiffness and flexibility causing the increase in elongation at break and degrading tensile strength properties. Figure 1a depicts a linear rise in the proportion of elongation in rubber samples with the introduction of higher limonene concentration. Cross-linking involves the formation of covalent bonds between polymer chains, resulting in a three-dimensional network structure. It has enhanced the stability and mechanical properties of polymers [9]. This suggests that the influence of chain scissions outweighed that of the cross-linking in the degradation process.

At low concentrations of d-limonene, the swelling effect increased the flexibility and mobility of the polymer chains in natural rubber. This has led to improvement in elongation properties and potentially higher tensile strength. The increased mobility allows the rubber to better absorb and distribute stress. However, as the concentration of d-limonene increases, excessive swelling occurs. This can weaken the intermolecular forces and interactions within the rubber matrix, causing a reduction in tensile strength. The weakened intermolecular forces resulted in lower cohesive strength and a higher propensity for chain scission, which further contributes to a decrease in the tensile strength of natural rubber, as illustrated in Fig 1b.

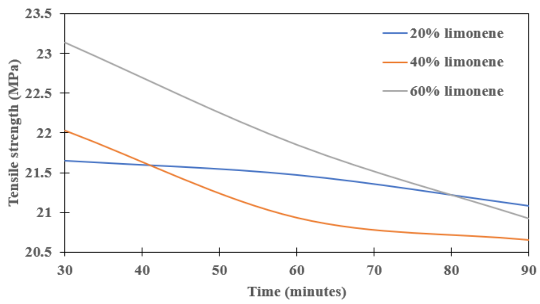
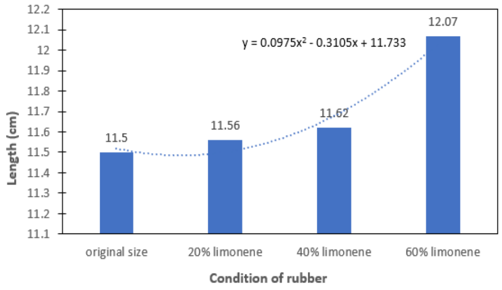
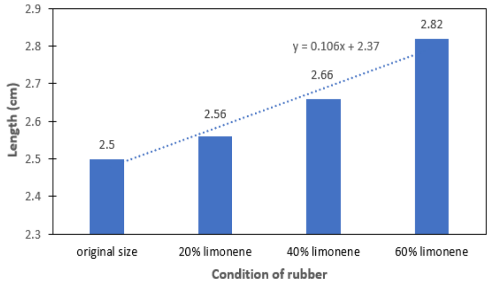


Figure 2 Degradation of rubber in different condition over time

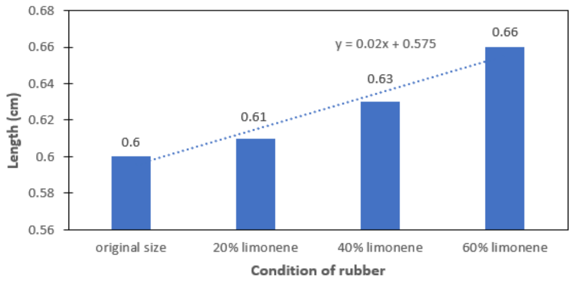
Fig 2 shows the rubber tensile strength under different limonene immersion conditions. The rubber samples in all concentrations show a decreasing trend in tensile strength, indicating the degradation of natural rubber. An initial increase is observed at the 30-minute mark, suggesting a more significant cross-linking effect at shorter durations. Beyond that, higher d-limonene concentrations (40% and 60%) lead to increased cross-linking density, which boosting tensile strength at 30 minutes. In 60% d-limonene condition, the graph exhibits the steepest curve, suggesting the most significant degradation of natural rubber in terms of tensile strength.



a)



b)

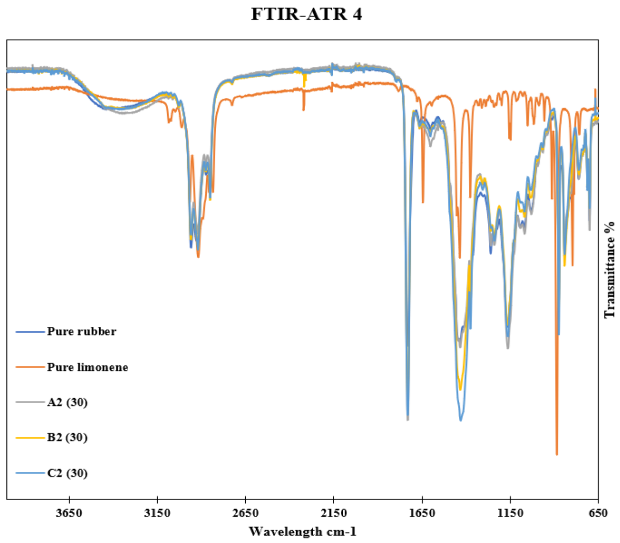


c)

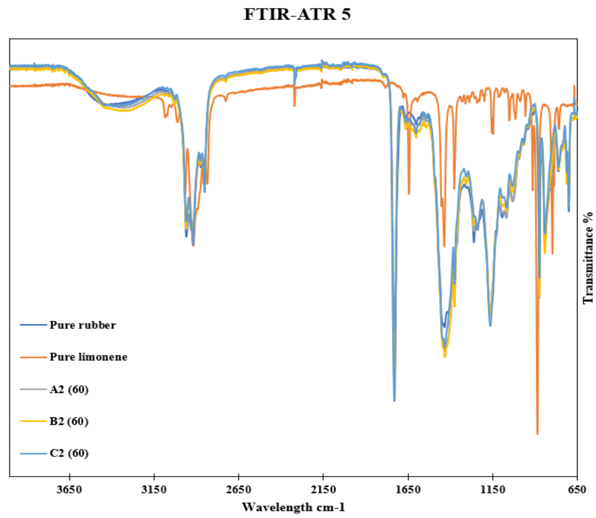
Figure 3 Dimension of natural rubber sample, a) total length, b) head width and c) neck width

From Figure 3, it was observed that as the concentration of d-limonene increased, there was an increase in the total length, head width, and neck width of the dumbbell rubber samples. This phenomenon was attributed to the process of swelling and dissolution. During the swelling process, the liquid molecules of d-limonene penetrate the rubber's polymer matrix, leading to an enlargement in its volume [10]. Long polymer chains, specifically polyisoprene, form the rubber's structure and are held together by various intermolecular forces, such as van der Waals forces and covalent forces [11]. The solvent molecules of d-limonene will cause the polymer chains to split and leave gaps in the rubber matrix by interfering with the intermolecular forces that hold them together. The rubber as a result swells or expands.

Chemical changes



a)



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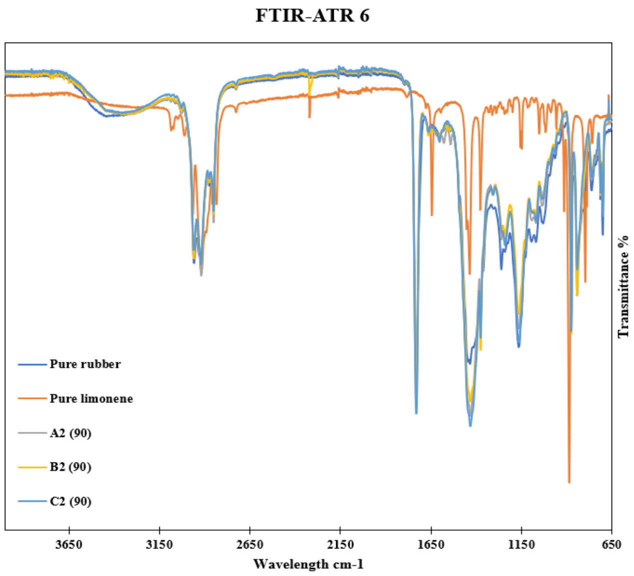

c)

Figure 4 FTIR-ATR spectra of natural rubber samples in 20%, 40% and 60% of d-limonene for a) 30 minutes, b) 60 minutes and c) 90 minutes in a range of 650-4000 cm^{-1}.

Figure 4 shows the FTIR-ATR spectra of the natural rubber samples (grey, yellow, and light blue series) displayed similarities and tended towards the FTIR spectrum of d-limonene (orange series) after immersion with d-limonene. From Figures 4, the peaks observed at 1150 cm^{-1} – 1200 cm^{-1} is typically associated with the presence of C-O groups on the rubber material. The C-O functional group at 30 minutes has a higher intensity. It indicated that the cross-linking effect was higher than chain scission, causing increased tensile strength as discussed in Figure 2. For the immersion of 60 minutes and 90 minutes, the chain scission effect gradually surpassed cross-linking effect as the intensity decreased, indicating the decrease in tensile strength. At 1750 cm^{-1}, this wave number range is associated with the presence of carbonyl (C=O) stretching vibrations in natural rubber [12,13]. The results were almost the same as the C-O group, which increased in intensity at 30 minutes, and decreased at 60 and 90 minutes. The rise of carbonyl peaks indicating the chemical change of rubber upon reacting with natural rubber, as a result of oxidation process taking place.

Summary

The experimental results indicate that the presence of d-limonenehas a significant impact on the physical and chemical properties of natural rubber. As the concentration of d-limonene increases, there is a notable enhancement in both the size and elongation at break of the rubber samples. This is predominantly attributed to the swelling effect induced by d-limonene, which becomes more pronounced at higher concentrations. However, this swelling is accompanied by a detrimental effect on the tensile strength of the natural rubber. The mechanical integrity of the rubber diminishes with the increase of the d-limonene concentration, a result of the combined influences of cross-linking and chain scission within the rubber's molecular structure. The weakening of tensile strength is critical, particularly in applications where mechanical robustness is essential, such as medical-grade latex gloves. FTIR-ATR spectrum of immersed rubber shows the characteristics of d-limonene due to its coating, especially at wavelength 1150 cm^{-1} (C-O) and 1750 cm^{-1} (C=O). The study findings are important for a better understanding of the durability and performance of natural rubber in medical applications, where it may be routinely exposed to limonene-containing substances. It will help advance future developments in medical rubber, particularly in addressing degradation when it comes into contact with limonene.

Acknowledgement

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