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A sustainable novel 3D printing of elastomeric products

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Natural rubber has been in use for generations, from tyres to latex gloves. The mass production of gloves has been done for decades using the traditional dipping process. Similarly to other industrial operations where bulk material processing is taking place, traditional dipping presents challenges on the energy use, wastage of raw materials and customisation. An alternative gloves' manufacturing process should be able to cope with the existing production volume while also opening a completely new approach that will allow a more flexible, energy efficient system with the possibility of manufacturing more complex structures (multifunctional gloves) to cover new market needs. Here, the additive manufacturing approach was used leading to the development of a novel 3D printing technology for rubber materials, capable of generating freestanding thin elastomeric structures, such as gloves. The sustainable aspect of this work comes not only from the use of natural latex raw material, but also from the significant material and energy reduction in the manufacturing itself. The in-house developed 3D Printer for Elastomeric Products (or 3D-PEP) resulted in the manufacturing of the first ever high-performance 3D printed latex glove which is visually almost indistinguishable to one produced on mass scale. The process demonstrates new level of control over the thickness of the product and production flexibility which is extremely valuable for adaption in difficult times of pandemics or other outbreaks that might require a sudden mass access to high performance gloves.

Keywords 3D printing, Additive manufacturing, Rubber gloves, Natural rubber, Multifunctional materials, Sustainable manufacturing.

Natural rubber has been in use for generations in many different applications, from tyres to coatings and latex gloves. It is obtained commercially mainly from the Hevea brasiliensis, also known as the rubber tree, by tapping the bark to release the milky liquid known as latex, a colloidal suspension of rubber particles in an aqueous medium. Natural rubber latex products have superior mechanical properties and provide an excellent barrier against viruses and bacteria[1]. This explains why it is a material still widely used for the manufacturing of medical equipment such as gloves despite the increase in the last few years in the number of people allergic to the naturally occurring proteins present in the rubber[2].

Disposable rubber gloves are extensively used nowadays, especially in the medical sector to provide a barrier against infection[1]. In 2020, the disposable gloves market was valued at USD 10.2 billion globally, 78% of that corresponding to the medical sector. The demand for disposable medical gloves had been constantly increasing in the last few years as a result of the increasing concern for maintaining good hygiene conditions[3]. However, the Coronavirus pandemic has created a major surge in the consumption. Looking at the data provided by the NHS in England, in 2019 on average per month approximately 150 million gloves were delivered. In comparison, as of December 2021, the cumulative average number of gloves delivered in England per month since the beginning of the pandemic is around 508 million, 3 times the value pre-pandemic[4]. Assuming the same consumption worldwide, that means each month around the world 71 billion gloves are being used.

Natural rubber latex gloves have been mass-produced for decades using the traditional dipping process, a complex multistage manufacturing operation well developed for large scale productions. The manufacturing of gloves by dipping revolves around the ceramic hand moulds (also called formers) used as substrate for the rubber film formation. Once the natural rubber latex is extracted from its natural source, the latex is concentrated and compounded with other chemicals into a specific formulation and subsequently transferred into designated baths for the dipping process. The formers go through a meticulous manufacturing process comprising various cleaning stages, several dipping tanks and numerous ovens. Very briefly, the core of the process involves the dipping of the formers in coagulant followed by the dipping in the latex compounded bath. This allows for some of the latex in the tank to adhere to the ceramic mould creating the wet film that after vulcanisation in an oven creates the final glove product[1,5,6].

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However, similarly to other industrial processes where bulk material processing is taking place, the dipping process presents important challenges on the energy use and wastage of raw materials, customisation, control over the deposition of the material or quality monitoring. An alternative gloves' manufacturing process should be able to cope with the existing production volume while also opening a completely new approach that will allow a more flexible system, with significantly improved energy efficiency and the possibility of manufacturing more complex structures (multifunctional gloves) to cover new market needs.

In the medical field for example, many intra-operations require the use of radiation equipment. While surgeons' bodies are usually protected by shielding aprons, the use of X-ray attenuation gloves is not frequent although they are available on the market. These protective gloves, that use different shielding materials, are usually expensive, too thick and they do not provide the dexterity needed for precise surgical operations[7,8]. The main reason for this poor suitability of the product is precisely the limitations of the traditional dipping method for manufacturing complex multifunctional gloves as changes to the formulation of the latex cannot be easily implemented.

To sum up, the large potential market gap for gloves with special capabilities to undertake new demanding tasks combined with the challenges currently faced by gloves' dipping process in terms of energy use, waste of material and lack of production flexibility, raises a great interest in the research for alternative manufacturing methods of rubber gloves.

In this research, we reached out to the 3D printing approach to develop a novel manufacturing process for thin elastomeric films. The term 3D printing is often used non-technically as synonym of additive manufacturing since it simply describes the basic concept of the technology for the general public and it is defined by the standard ISO/ASTM 52900:2021 as the "fabrication of objects through the deposition of a material using a print head, nozzle, or another printer technology"[9]. Among the most interesting characteristics of 3D printing technologies are considerable reduction of material wastage and customisation flexibility, advantages that directly address the current challenges faced by the traditional gloves' dipping industry.

3D printing has become increasingly acceptable by different industry in the last few years, and it is part of a bigger industrial revolution that is taking place towards a new Industry 4.0. Nevertheless, 3D printing of certain materials, such as the elastomers used in rubber gloves, is still challenging. 3D printing of latex has been previously trialled to some extent by inkjet printing with carboxylated styrene-butadiene rubber[10], by a drop-on-demand inkjet process with pure liquid latex[11] and more recently by a direct ink write process with a rubber ink of natural rubber latex and liquid butadiene rubber[12]. Although this research has proven the potential of 3D printing with latex to manufacture small 3D objects, this deposition approach is unsuitable for the manufacturing of the thin elastomeric films needed for products such as gloves. Another method researched for 3D printing with latex is based on vat photopolymerization with photocurable styrene-butadiene rubber latex[13], a technique that has limiting ink formulations and it is not suitable either for thin elastomeric films production.

In this work, we present spray deposition as a new approach for 3D printing thin elastomeric latex films. Spray deposition offers the advantage of generating very thin structures while providing more control than traditional dipping over the location and quantities of the material deposited and the morphology of the rubber film.

The main difference with other available 3D printing technologies is that the temporal substrate, instead of being flat, it is used to provide the shape of the object being manufactured. Spray deposition of silicone onto a non-flat double-curved substrate has been accomplished to manufacture uniform thickness tubular elastomeric membranes[14] yet this specific shape limits the application range. Here we have demonstrated for the first time a latex spraying as the 3D printing deposition method capable of generating not just uniform tubular films but potentially any complex freestanding thin elastomeric product.

Looking closely at this novel spaying deposition approach and studying the ISO/ASTM 52900:2021 standard, there are various key aspects that confirm this novel technology as an actual 3D printing process. The standard definition of 3D printing is quite vague regarding the material deposition technique, any "print head, nozzle or another printer technology"[9] is adequate, what includes therefore our suggested spraying deposition method. However, just by considering this fragment of the definition, potentially any available spray coating process should be considered then 3D printing, but there is a key difference here. The definition states that the deposition of the material is for the "fabrication of objects"[9], free-standing structures where the substrate used as support for manufacturing is only temporary. Traditional spray coating process deposits the material in a similar way, but this is intended to remain attached to the substrate underneath (hence coating) and not removed from it like in our suggested process to create an object on its own, with the example being a glove.

The novel 3D printer developed for manufacturing thin elastomeric films presented in this work (which we refer to as 3D Printer for Elastomeric Products or 3D-PEP) has far more superior and controlled material deposition as compared to traditional dipping, and it is also different from traditional spray coating process as it creates free-standing objects. Those key differences distinctly define this process as a 3D printing technology.

Our 3D elastomeric printer was developed in-house enabling the manufacturing of natural rubber latex gloves as a thin elastomeric example product. The printer uses a spray nozzle to deposit the material onto a ceramic hand former that serves as a temporal substrate for the print. This novel 3D printing latex technology (Fig. 1) is a new avenue as an alternative to current traditional gloves dipping manufacturing, with the ability to create low cost, sustainable elastomeric structures, with distributed production, high efficiency and potentially bespoke complex structures. The sustainable aspect of this work comes not only from the use of natural latex raw material, but also from the significant material and energy reduction in the manufacturing itself.

This work resulted in the manufacturing of the first ever high-performance 3D printed natural rubber latex glove which is visually almost indistinguishable to the one produced commercially on mass scale.

The process demonstrates new decentralised production opportunities, with high level of control over the thickness of the product and customisation capabilities in terms of materials combinations and physical

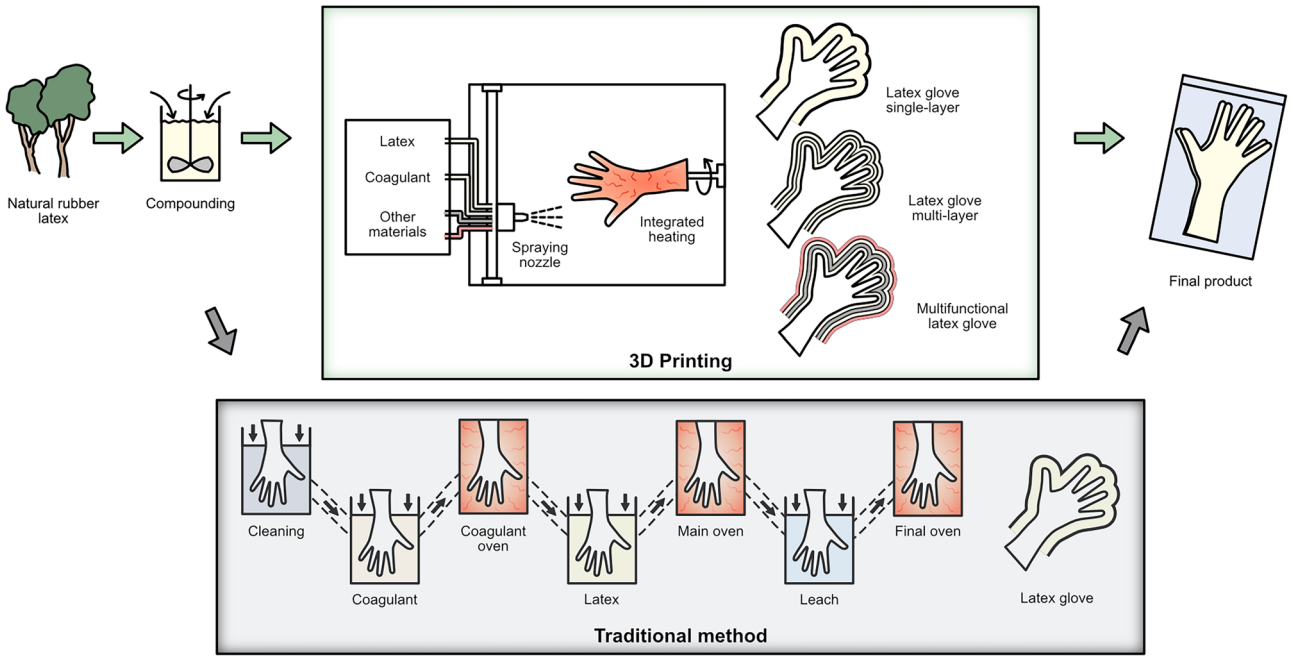


Fig. 1. Concept diagram of the new 3D elastomeric printing technology vs. traditional gloves dipping manufacturing method.

properties enabling future multifunctional gloves; and a production flexibility which is extremely valuable for adaptation in difficult times of pandemics or other outbreaks that might require a sudden mass access to high performance gloves.

3D printer for elastomeric products (3D-PEP)

The 3D elastomeric printer was developed in-house as a modular, self-containing machine at Cranfield University with all the equipment necessary to produce thin elastomeric film products, such as gloves (further details in the publicly available patent WO 2021/198898 A1[15] and video of the glove making process[16]. 3D-PEP has the capability of rubber material deposition, drying and/or vulcanisation of the rubber and removal of the final product from the temporal substrate. Rubber deposition is done by using a spraying nozzle in a 3-axis print head onto a rotating former (represented by the fourth axis) with fully integrated heating as the temporal substrate for the print (Fig. 2a).

For the proof-of-concept of 3D printing of natural rubber gloves, a commercial ceramic hand former for the production of surgical gloves was upgraded with a heating element and used as a temporal substrate for the print. The nozzle, a commercial gravity fed spray gun with a 1.5 mm nozzle, deposits the rubber material at an angle of 45º in relation to its surface at a distance of 60 mm. The integrated heating of the former allows the drying of the latex film to start even when the deposition of the material is still undergoing, with secondary heating accelerating the drying and/or vulcanisation process, all taking place directly inside the deposition chamber. A stripper mechanism at the back of the printer (Fig. 2b) removes the final glove product from the temporal substrate once the drying/vulcanisation step is finished.

3D printing of gloves

3D-PEP uses a custom G-code, developed specifically for the 3D printing of surgical gloves. This G-code was manually programmed without the use of an automatic generation tool. The 3D printed thickness values were used as feedback to optimise the G-code of the 3D printer to achieve uniform rubber film on the former. Although one of the advantages of this novel process is the possibility of controlling the thickness by areas, the focus here was in proving that the system could manufacture uniform gloves, similar to the commercially dipped products.

The printing sequence started with the rubber latex deposition to cover the whole surface of the former with a thin layer of the material. In the commercial spray gun, compressed air at 3.5 bar separates the latex material into droplets for the spray deposition, while at the same time partially evaporating the water present in the latex before even reaching the substrate. The former was pre-heated to 50 °C from the inside with an integrated temperature system, that continued to maintain the temperature of the former during the whole deposition process. The heat accelerated the water evaporation from the latex, even when the deposition sequence was not yet completed. Both the partially air-dried material from the spraying deposition and the heated former helped in reducing the total manufacturing time needed while also helping to avoid dripping of the material from the former. This prevented formation of defects and material waste. Since the latex compound was already pre-vulcanised, further post-vulcanisation of the film was not performed. Once the drying of the rubber was finished, the glove was removed from the former either manually or using the automated stripper mechanism

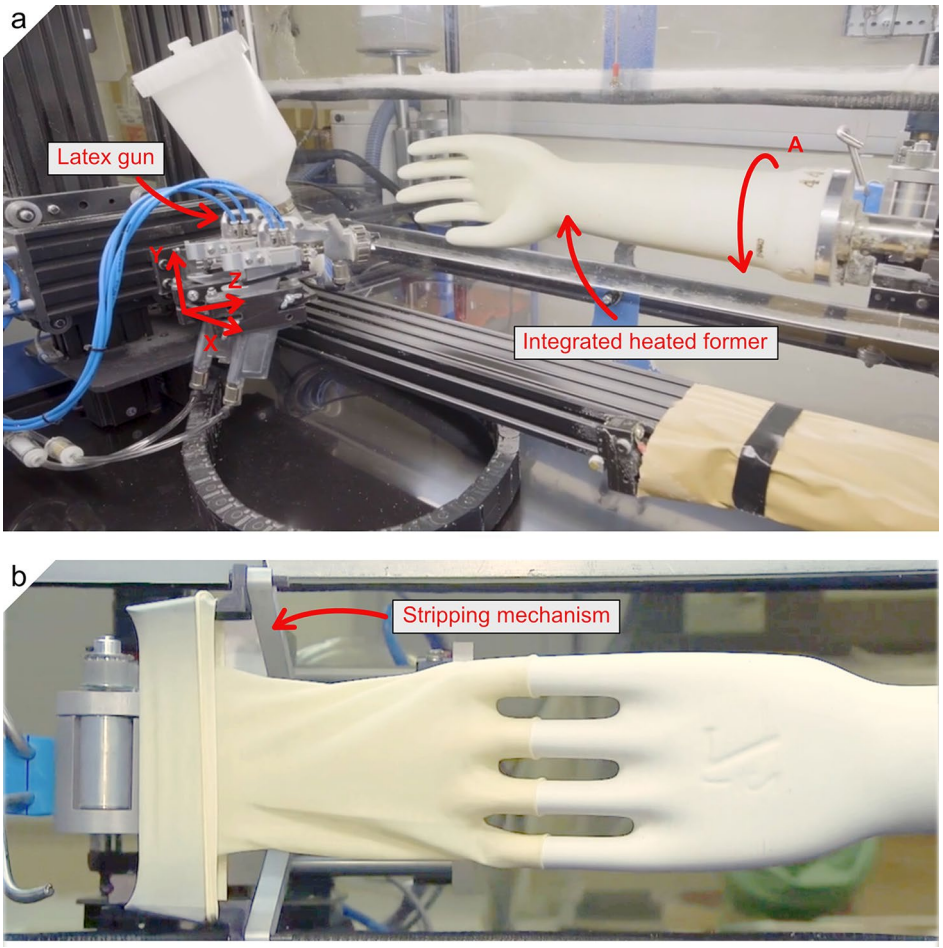


Fig. 2. In-house developed modular 3D printer for elastomeric products or 3D-PEP. (**a**) Deposition chamber of the 3D-PEP. (**b**) Close-up of the stripping mechanism behind the deposition chamber.

integrated at the back of the machine. Corn-starch was used to powder the surface of the final gloves to remove the inherent stickiness of the natural latex material.

Optimisation of the 3D-PEP

The initial latex deposition trials using the in-house 3D elastomeric printer presented numerous problems around the clogging issues of the latex spraying nozzle due to the high total solid content (TSC) of the commercial, pre-vulcanised latex, as supplied by the manufacturer. A diluted solution with deionized water and ammonium hydroxide solution ACS reagent, was found to be more suitable for a continuous deposition process at the earlier stages of these developments. The successful deposition of this material resulted in the manufacturing of the first ever high-performance 3D printed natural rubber latex glove.

Excessive dilution of the latex can also create problems with the rubber film formation increasing dripping of the material from the former after deposition, leading to non-uniformities and added wastage. More dilution of the latex also demands further energy to evaporate the water content, increasing the CO_2 emissions from the manufacturing. Calculations show that savings of 2% on the total energy consumption in a rubber gloves' factory could be achieved by changing to a concentrated latex. The 2% savings, if using electricity, would account to the reduction of approximately 1400 tons of CO_2 emissions per year. The addition of ammonia for the material dilution is not optimal either in terms of sustainability of the process, safety in the handling of the latex material and equipment degradation. For these reasons, the use of the latex material as concentrated as possible is preferable for a more efficient and sustainable production.

Further optimisation of the 3D-PEP with larger and better-quality nozzles and refined printer parameters allowed the deposition of commercial pre-vulcanised natural rubber latex directly without dilution in the next generation of our printer. The custom G-code used for the deposition of the material onto the temporal hand substrate was also developed and polished for better glove uniformity for this research. The resulting 3D printed glove is visually almost indistinguishable to one produced industrially on mass scale (Fig. 3).

Thickness measurements

The data of the thickness of 4 different 3D printed gloves specimens, A to D, and two commercial benchmark gloves, surgical and examination, has been represented in Fig. 4 and in Table 1.

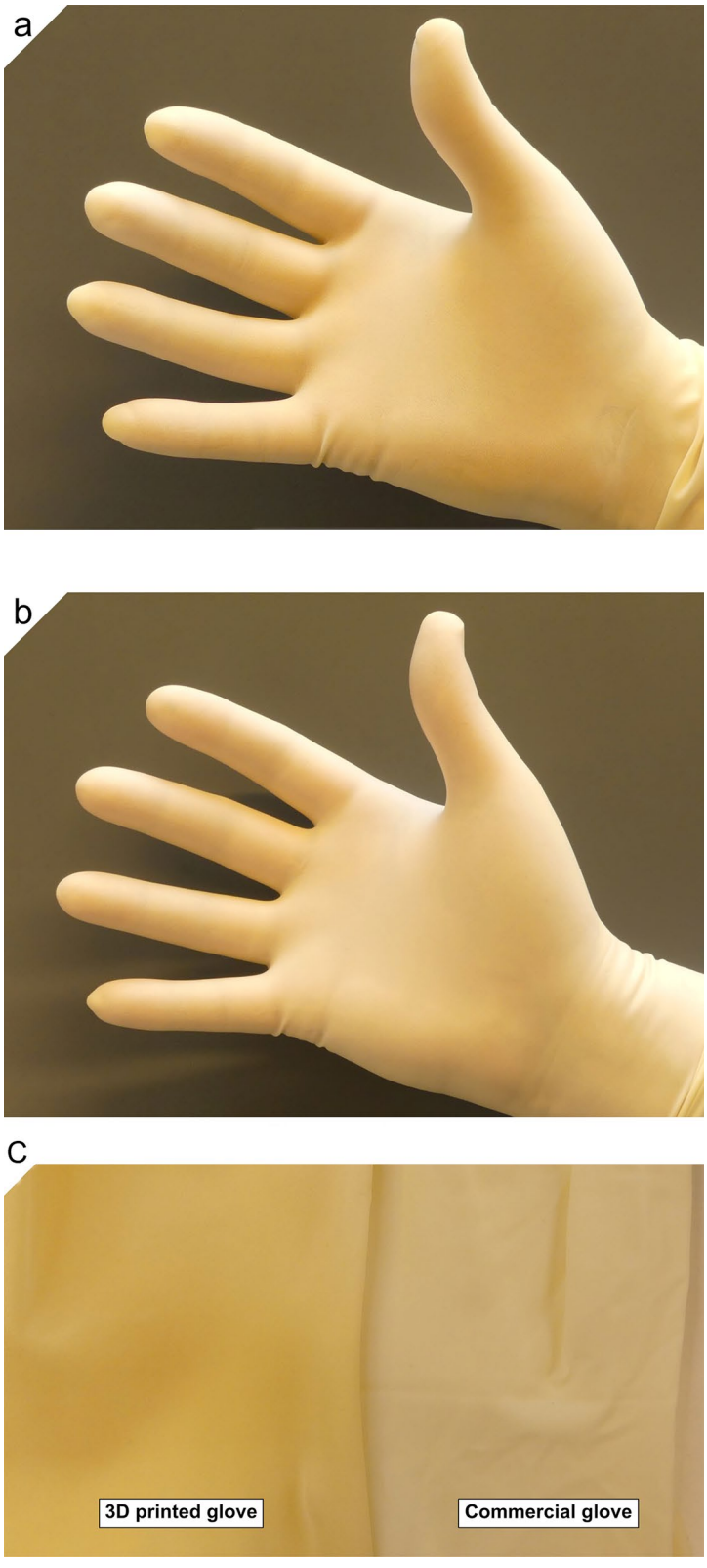


Fig. 3. Comparison of 3D printed and commercial gloves. (**a**) 3D printed glove. (**b**) Commercial surgical glove. (**c**) Comparison of film surface finish of 3D printed glove (left) and commercial surgical glove (right).

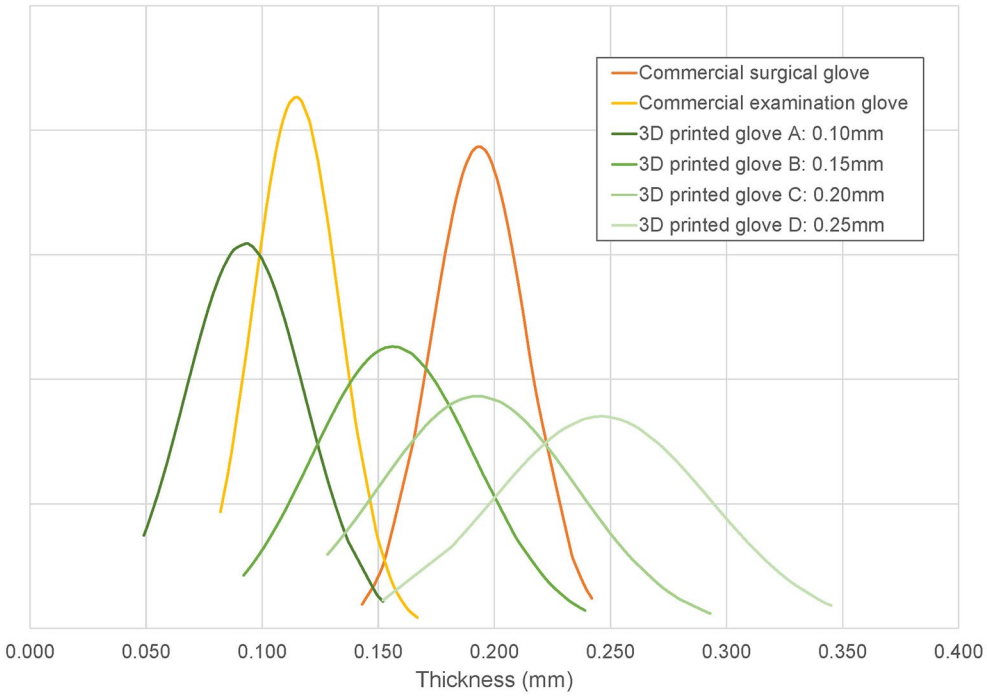


Fig. 4. Thickness distribution measurements of natural rubber latex gloves.

	3D printed glove A	3D printed glove B	3D printed glove C	3D printed glove D	Commercial surgical glove	Commercial examination glove
Mean (mm)	0.093	0.156	0.193	0.246	0.193	0.115
Standard deviation	0.0258	0.0352	0.0428	0.0469	0.0206	0.0187

Table 1. Thickness measurement mean values of natural rubber latex gloves.

There is a clear tendency in these values obtained: the thicker the 3D printed gloves are (greater thickness mean), the higher their standard deviation within each glove and therefore slightly worse the thickness uniformity of the samples. This could be the effect of the manufacturing method with a G-code only partially optimised during this research for the 3D elastomeric printer, with irregularities that gradually add up with increased amount of material deposited. Nevertheless, the standard deviation of commercial and our 3D printed gloves appeared quite similar even now, although no statistical comparison was conducted. Further development of the G-code towards industrial implementation should exceed the uniformity values.

Comparing the benchmark to the 3D printed gloves, on one side sample A with a thickness closer to a commercial examination glove is the best in terms of uniformity, with a standard deviation within the glove of 0.0258, a value just slightly higher to the standard deviation of commercial gloves. On the other side, sample C has a mean thickness similar to commercial surgical gloves but a value of standard deviation within-glove double the commercial ones. The main difference between commercial and 3D printed gloves is that the commercial samples have a uniform change in thickness from the cuff (thinner) to the fingertips (thicker) as a result most likely of their manufacturing process by dipping (in which the formers are dipped vertically and the latex excess drips to the fingertips); while our 3D printed gloves can be controlled with the optimised G-code.

The current thickness control using our 3D-PEP system underline the great potential of the technology as shown by the wide range covered by samples A to D. Because of the characteristics and limitations of the manufacturing traditional dipping process, having such precise control over the mean thickness of the whole glove is already challenging but being able to even control that thickness by areas is virtually impossible. That difficulty in controlling the thickness accurately in the dipping process becomes evident in the small differences detected in thickness measurements of mass-produced benchmark samples. 3D printing allows that superior control by modifying the number of layers being printed or the amount of material being deposited, either in targeted areas or in the entire glove, what provides an immense flexibility to produce the next generation of better quality and more complex multifunctional gloves.

Tensile testing

Tensile testing was performed on 6 specimens of each of the 3 different glove samples: 3D printed gloves, and commercial surgical and examination gloves as benchmark.

	Tensile strength		Maximum strain	
	Mean (MPa)	Standard deviation	Mean (%)	Standard deviation
3D printed gloves	19.2	3.0	767.0	37.7
Commercial examination gloves	22.7	1.2	707.6	24.0
Commercial surgical gloves	25.9	2.3	782.7	27.2

Table 2. Mechanical properties values of natural latex glove samples.

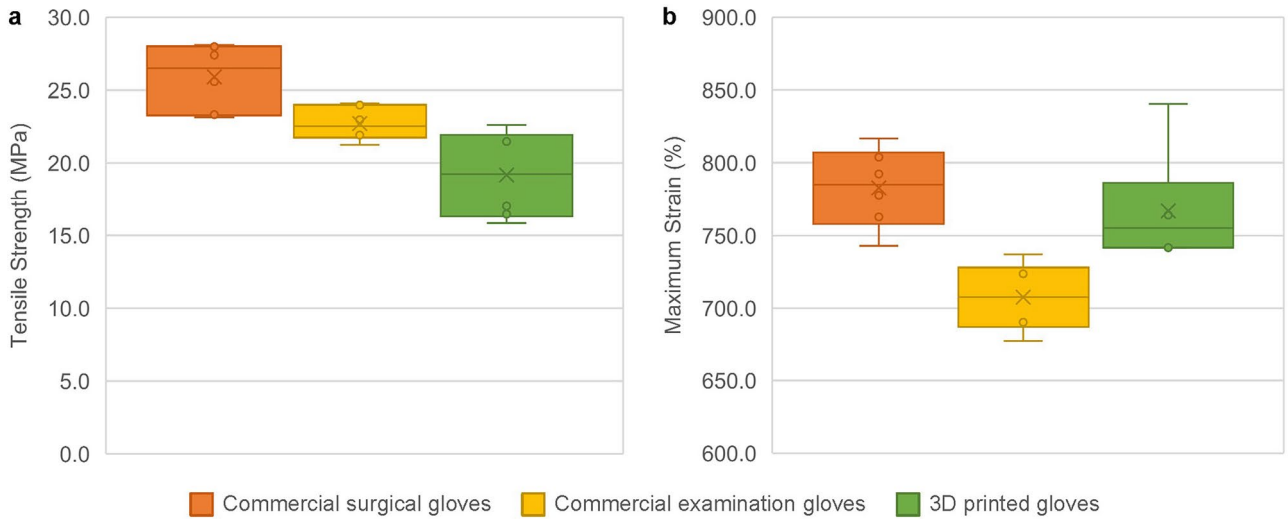


Fig. 5. Mechanical properties of natural rubber latex gloves. (**a**) Tensile strength. (**b**) Maximum strain.

The results presented in Table 2; Fig. 5 show values for tensile strength and maximum strain of the 3D printed gloves are in the range of the commercial benchmark. These are promising results considering that the material used for this work was off-the-shelf pre-vulcanised latex not optimised for gloves' manufacturing or for our unique 3D elastomeric printer.

Manufacturing analysis

To demonstrate the potential productivity of this novel technology and suitability for industrial implementation, a simplified manufacturing analysis estimation was conducted. Actual production data for natural rubber surgical and examination gloves using traditional dipping method was provided by Meditech Gloves. The estimation of the 3D-PEP was done considering a reasonable development in the near future of the current prototype for industrial implementation, with an estimated 90% material efficiency, using 55% TSC natural rubber latex as achieved in the proof-of-concept and with 2 nozzles depositing simultaneously an estimated 250 g/h of natural rubber (mass of the actual rubber deposited once water is evaporated). It was also assumed that the deposition of the material would be done continuously, with the wet formers moving onto another section of the modular 3D printer for drying and/or vulcanisation and stripping of the final product. An average mass per surgical glove of 10.5 g and per examination glove of 6.1 g were used for the calculations.

The results of this manufacturing analysis estimation are shown in Table 3. The novel modular compact 3D elastomeric printer could theoretically produce per day approximately 1000 surgical gloves, 2 orders of magnitude less than a traditional dipping line. Nevertheless, taking into account the large volume difference of these two manufacturing processes, the 3D-PEP actually could be able to manufacture theoretically 10 times the amount of gloves for the same factory volume, or what is the same, the current production of gloves could be manufactured in factories ten times smaller what would impact the factory footprint and the energy being used.

Additionally, it is important also to consider other advantages derived from the use of these modular 3D elastomeric printers. Firstly, the production of gloves could be decentralised, deploying these units closer to the end user and providing more flexibility and resilience to the industry, what is extremely valuable for adaption in difficult times as the Coronavirus pandemic has shown.

Secondly, the great production flexibility and reduced influence of breakdowns and maintenance. Traditional dipping lines have large outputs of a single product, and changes on the set-up are limited and cause considerable production shutdowns and significant waste. These novel modular 3D elastomeric printers could be manufacturing different products at the same time, and production changes would be quicker and more efficient with much less waste product. Moreover, the breakdown of one of these systems or scheduled maintenance would only affect a small proportion of the total output of the factory compared to similar downtimes in large traditional dipping lines.

	Traditional dipping (industrial data)		New 3D-PEP (3D printer for elastomeric products)	
	Surgical	Examination	Surgical	Examination
Output	130,000 gloves/day	250,000 gloves/day	1008 gloves/day	1752 gloves/day
Volume occupied by the machinery	1430 m^3	2420 m^3	1.2 m^3	1.2 m^3
Production rate	3–4 gloves/h· m^3		35 gloves/h m^3	60 gloves/h m^3

Table 3. Comparison of actual traditional dipping glove production vs. estimated 3D printing per hour and volume.

Conclusions

We have demonstrated for the first time that high performance elastomeric products can be 3D printed using latex and our specially designed novel printer, 3D-PEP. This research produced the first 3D printed natural rubber latex glove, visually almost indistinguishable to one produced on mass scale.

The results obtained with commercial off-the-shelf pre-vulcanised latex yielded adequate mechanical properties and superior thickness control. The properties of those gloves are promising and already rivalling with those mass-produced.

The impact of this new manufacturing technology will reach many other industrial sectors. The work has been focused on 3D printing of natural rubber latex gloves, but the 3D-PEP has the potential of manufacturing many other complex freestanding thin elastomeric structures for products such as condoms; balloons; seals and gaskets; countless medical equipment including catheters, bladders, squeeze bulbs, wound dressings or tubing; and even toys, bellows and footwear.

The results of the manufacturing analysis estimations conducted here show great potential of the technology for its future implementation in industry, being suitable not just for manufacturing small batches of rubber gloves but for a sustainable full-scale production, decentralised, more flexible and resilient for adaptation in difficult times, such as the Coronavirus pandemic.

Further research though is still required to enable industrial implementation. Optimisation of the printing parameters and the development of a fully customised latex ink for 3D printing are still needed, for which a better understanding of the spraying deposition mechanism and droplet-size effect on properties is necessary. Likewise, a larger number of samples tested for statistical analysis and more detailed manufacturing estimations will provide stronger evidence for industrial deployment. This successful proof-of-concept demonstrates the potential for the 3D-PEP technology, and opens these promising avenues for further research towards successful industrial adoption.

Methods

Materials

Compounded and pre-vulcanised commercial natural rubber latex (Polycraft Liquid Latex) was purchased from MBFibreglass. It is preserved with low ammonia and has a total content of solid (TSC) rubber particles range between 52.7% and 56.7%. This natural rubber latex was used diluted and as received. The dilution was done with deionized water and ammonium hydroxide solution ACS reagent 28.0–30.0% NH_3 basis from Sigma Aldrich (80v% of commercial latex plus ammonium hydroxide (with a total of 6v% of ammonia content) and 20v% of deionized water). Prior to their use in the 3D printer both compounds were filtered to remove any large rubber agglomerates that could potentially cause blocking issues during the deposition process.

Thickness measurement procedures

Thickness measurements were performed on several glove samples with a digital micrometre to obtain thickness homogeneity values, both for 3D printed samples and commercial benchmark. The thickness of each sample was measured in 60 points distributed throughout the whole surface of the glove. Commercial natural rubber latex surgical (ExcellSurgical) and examination gloves (PolyCareExamination) were provided by Meditech Gloves as benchmark. The results of the thickness measurements were later compared statistically by probability theory using a normal distribution function.

Tensile testing

Tensile testing of the glove samples was performed using an Instron 5500R tensile test machine fitted with a 100 N cell at a crosshead speed of 500 mm/min. The specimens were cut using a dumbbell shape die C defined in the ASTM D412 standard[17]. Commercial natural rubber latex surgical (ExcellSurgical) and examination gloves (PolyCareExamination) were provided by Meditech Gloves as benchmark. Interquartile ranges for the box plot representations were calculated excluding the median.

Data availability

All data generated or analysed during this study are included in this published article.

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Author contributions

E.P.Á. participated in the conceptual part of the project, carried out the experimental work, data analysis and wrote major part of the manuscript. K.K.K. contributed to the formation of the project and conceptual part of the work, supported the data analysis and helped with the manuscript writing.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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