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Sustainable Alternative Material for PPE Kit – A Molecular Dynamics Simulation Approach at Nano Level

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Abstract

Personal protective equipment (PPE) kits vividly used for safeguarding-groups, especially the medical fraternity that are vulnerable to pathogen transfer from infected patients. Due to the current pandemic outbreak, PPE kits have gained canter-stage to avoid viral transmission. Presently, most economical PPE kits made using polypropylene and high-density polyethylene. However, it observed that for maintaining acceptable levels of fluid permeability through the fabric, the garment possesses several layers of the same material. The multi-layered fabric gains greater physical strength as the density of the fabric increases; however, the multiple layers hinder ergonomics and elevate the temperature in the vicinity of the wearer's body, making it uncomfortable. To address this issue, we performed a random copolymer molecular dynamics simulation on blends of poly(methyl 2-methylpropanoate), poly(propanoic acid), poly(2-hydroxypropanoic acid), and poly(ethane-1,2-diol). The predicted properties of the copolymer suggest new strategies for the design of protective gear.

Keywords

Personal protective kit, Poly(lactic acid), Poly(methyl methacrylate), Material studio, Molecular dynamics

Introduction

Health and safety are vital for every individual, especially to those working in the healthcare industry. The healthcare workers treating the patients with highly contiguous diseases must protect from a variety of air and blood-borne contaminants. Therefore, the safety of the individuals at risk addressed by donning of gloves, masks, coverall, etc. which are collectively known as PPE. Material is the crucial component in assuring the prevention of contamination of any high infection diseases through the PPE so that it provides the required safety to the individual. This material must adhere to all the standards set by the governing body. Alongside this, it should be cost-effective and durable to fulfil the vast requirements of the pandemic.

Currently, available PPE kits manufactured using polypropylene, polyester, polyethylene, cotton, or blend of these materials varying in fiber type, bonding process, fabric finish based on specific requirements. These are non-woven multi-layered chemically bonded fabrics. One such multi-layered fabric made from polypropylene is spun bond melt blown spun bond, which protects against dust particles and liquid. Likewise, the laminated fabric materials tend to provide better resistance to particle penetration and lighter compared to the prior [1].

Further, these fabrics undergo several treatments to enhance their resilience against particle and static. PPE of conventional fabric is prone to discomfort to the user upon donning for an extended period. The primary cause of the trouble is skin irritation and humidity caused inside the PPE due to a rise in temperature, which might increase pathogens' growth [2]. This article discusses four such material instead of above mentioned commonly used material to make the PPE to produce a breathable, hydrophobic, lightweight.

Literature study of possible alternative materials

Poly(lactic acid) (PLA) is a polyester material derived from renewable sources. The various properties like mechanical, physical, microstructural, and chemical tuned for the required needs, which makes PLA one of the required materials for the present research [3]. It is a thermoplastic polyester derived mostly from corn starch, roots, chips, and sugarcane. PLA has excellent moisture absorbing property which draws moisture away from the body by spreading the moisture quickly, making it a superb wicking fabric [4]. Its bioplastic nature has made it popular in food packaging industries and to make disposable tableware and garments. Biocompatibility and non-toxic property make it suitable for biomedical applications [5, 6].

Poly (methyl methacrylate) (PMMA), commonly known as acrylic or acrylic glass, is a transparent and rigid thermoplastic petroleum-based polyester. Its excellent light transmission, toughness, and durability make it better than the other polymers. Its density ranges between 1.17 - 1.20 g/cm^3. PMMA is a highly versatile, sustainable material with high biocompatibility, which makes it ideal for dental and orthodontic use. It has a high glass transition temperature. PMMA is used in automobiles to make the vehicles lighter, which reduces their energy consumption [6]. Some of its disadvantages are weak heat resistance, limited chemical resistance, and reduced wear and tear.

Poly(ethylene glycol) (PEG) is a synthetic polyester commonly referred to as poly(ethylene oxide), PEO. If the molecular weight is above 100,000, it is considered to as PEO, if the molecular weight is lower, then its known PEG. The polymers have both hydrophilic and hydrophobic parts, in general, known as amphiphilic. PEG is a non-toxic material popular in biomedical research and used in many different pharmaceutical formulations. It often used in the food and cosmetic industries.

Polyacrylic acid (PAA), at the necessary form, consists of acrylic acid monomers combined at the double bond to form a carbon chain with a carboxylic acid attachment on every other carbon. PAA is hygroscopic, brittle, and colourless in nature with a glass temperature of (Tg) at nearly 106 °C. It can be used as a glue in the medical field due to its good bonding strength. PAA films are used in orthopedic implants to prevent them from corrosion and to manufacture detergent and diapers.

Polymer blending is one of the methods used to customize the physical properties of the polymers. By blending one or more individual monomers, there are chances of acquiring better results for the polymer. It can conclude from thermodynamics that two or more components are miscible, provided the Gibbs energy or the free energy resulting from the mixture is less compared to the sum of the component's Gibbs (or free) energy. This change in energy is due to the change in total free energy, (ΔGm), The entropy of mixing (ΔSm) and enthalpy of mixing (ΔHm) expressed through Gibbs equation [7].

Blending of these alternative materials

Blend of PLA-PMMA

PLA is blended with other thermoplastic polymers to alter its mechanical, thermal barrier, and degradation behavior. Several researchers have focused their study on the blends of PLA with PMMA since they possess excellent chemical and physical properties. Biomaterial products like scaffolds and load-bearing implants are some of the areas trying to use these blends [8]. The presence of PMMA hinders the crystallization of PLA during the blending phase. The crystallization process just for PLA is relatively slower in a practical situation. Therefore, this blend can be considered a stable combination of amorphous type [7].

Blend of PLA-PEG

The blends of PLA and PEG have been a choice for biomaterial products because of their various biological favorable properties, which include biodegradability and mainly the non-immunogenicity property of this blend. Its degradation rate and hydrophilic nature adjust by altering the composition of the resulting copolymer of the mixture. In the study made by Xiang et al. to conclude that in a copolymer structure, the existence probability of alternating chain combination is relatively lesser when compared to the random chain combination copolymer based on simulations of molecular dynamics. The values of the glass temperature of PLA and PLA-PEG from simulation agree with differential scanning calorimetry results [9].

Blends of PAA-PEG

PAA when mixed with poly(oxyethylene) (POE) viz PEG forms an in-solution hydrogen-bonded interpolymer complex. The miscibility between the two monomers is due to the hydrogen bonding between the acidic groups in PAA and the ether group present in PEG. PAA has carboxylic acids in which there is hydrogen bonding between the acids and low crystalline energy in POE, making PAA and POE compatible. At a high PEG ratio, there was better compatibility, but when there was an increase in PEG molecular weight, the compatibility decreased [10].

In this article, the individual material monomers are constructed and then blended using material studio 4.0 software to check for their compatibility and the energy expenditure to carry out the polymerization process. These carried out using the SYNTHIA and BLEND modules available in the material studio software. The final blended material must be tested for virus penetration, air permeability, water permeability, mechanical, and moisture sorption.

Methodology

Three pairs of random copolymers analyzed for their mutual compatibility. Initially, repeating units of each constituent monomer constructed. Each repeating unit was blended with the other three monomer repeating units, first as the base material and then as the screening material. The combination revealed four blends. Each blend was assessed based on their chi-parameter (Flory-Huggins parameter χ) and their mixing energy. The Flory-Huggins parameter suggests, if the parameter is negative, the compatibility of both monomers is excellent. That is, the two monomers have favourable interactions. However, suppose the parameter has a significant positive value. In that case, it indicates that the molecule prefers to be surrounded by similar units at that temperature. Hence it is less compatible with the other monomer (Chi-parameter is temperature dependent).

The importance of the blends analysis illustrated in the journal article - A molecular dynamics study on the miscibility of polyglycolide with different polymers discuss on the chi parameter. The polymerization process of mixtures happens between polyglycolide, polylactide, and polyacrylonitrile. The outcome of the study under molecular dynamics simulation using both the forcite and blends modules reported. The model studied based on the Flory-Huggins theory. The polymerization process performed at 238 K and 378 K; the article describes the miscibility criteria as the result of the analysis (Figure 1).

The monomers, once constructed, are analyzed for their compatibility. The most critical parameters include the Flory-Huggins setting, mixing energy, and van der Waals's power from the available results of blend analysis. These parameters provide a glimpse of whether such a copolymer is possible and the probability of its occurrence because of such a polymerization reaction—the blend analysis performed with varying mole-fractions of the screening monomer's repeating unit. These blends become a prerequisite or as input parameters for SYNTHIA analysis. After confirmation of a specific combination of two monomers being possible, the copolymer alternatives analyzed for glass-transition temperature, modulus of elasticity, shear modulus, bulk modulus, density, the permeability of various gases such as nitrogen, carbon dioxide, and oxygen. The results from the analysis were compared with the benchmark material used for making protective garments - i.e., poly(propylene).

A simulation study using materials studio

The results were available from the materials modeling software assessed with a prior assumption that the manufacturing process of non-woven fabric from each of the alternative copolymers is like the fabric made using poly(propylene). Figure 2 discuss the process flow using material studio software. To better against poly(propylene) - the alternatives must have: (a) Higher molecular density in a cubic lattice structure as the size of constituent atoms increases void space - is reduced due to which permeability of surrounding gases also reduces. Due to lesser permeability, the number of layers in a protective garment decreased, easing ergonomics. (b) Low

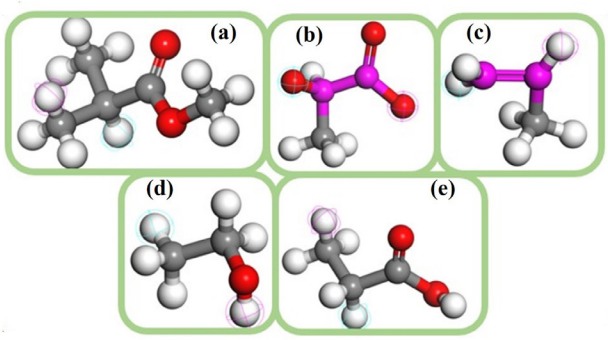

Figure 1: (a) Methyl methacrylate, **(b)** 2-hydroxy propanoic acid, **(c)** Propylene, **(d)** Ethylene glycol, and **(e)** Acrylic acid modeled in materials studio software.

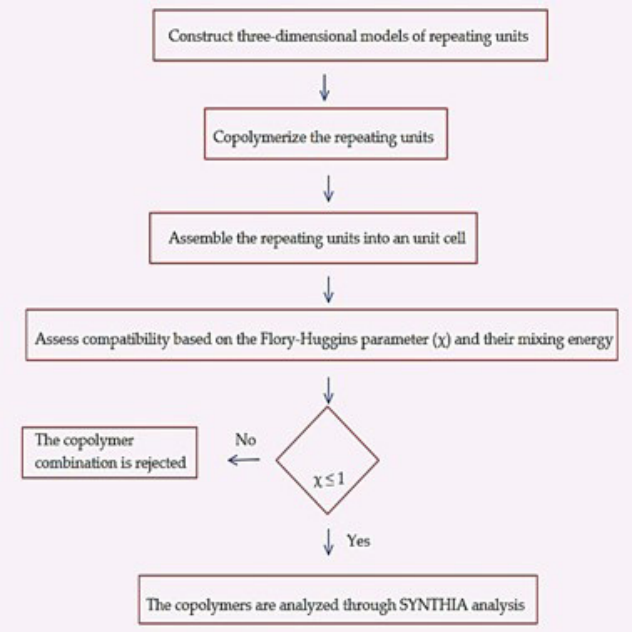

Figure 2: Process flow diagram of copolymer analysis using the materials modeling software.

mixing energy if the monomers are compatible with each other - the production rate of these alternate copolymers increases. Thus, a significant reduction in the cost of production.

Results and Discussion

By the blend analysis of the monomer units shows the critical characteristic of miscibility as a relation of interaction parameter and mixing energy with the variation in temperature. The Flory-Huggins parameter considered to estimate the miscibility behavior of the binary mixtures. Thus, it could also describe the miscibility of components in a mix. According to the Flory-Huggins theory, a negative value, or a value less than 1 of c indicates that at this temperature, the two molecules have better miscibility and a favorable interaction. The details were as shown in figure 3 and figure 4.

From the interaction parameter plot, we note that all the mixtures are miscible from the temperature range of 200 K. And from the mixing energy plot, we can see the mixtures are

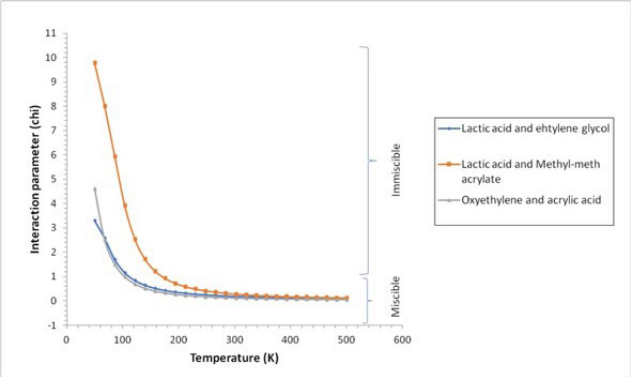

Figure 3: Interaction parameter and temperature plot.

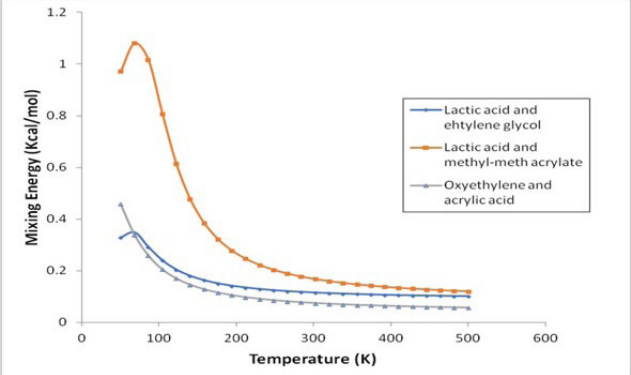

Figure 4: Mixing energy and temperature plot.

readily miscible and have an inverse relationship with temperature. With the results from blend analysis showing the miscibility of combinations at 298 K, we further estimated mechanical and thermo-physical properties by using SYNTHIA analysis. The module gives the results based on the predictive model. The random copolymerization of monomers at different composition ratios shows the physical and thermal properties. The copolymerization process obtained at 298 K temperatures for a mixture of unit molar composition.

Table 1 specifies the mechanical properties for lactic acid and methyl meth-acrylate random copolymers. The analysis shows an increase in the molar composition of lactic acid increases density and decreases in the elastic constants. Table 2 represents thermophysical properties for all molar compositions of lactic acid. The increase in lactic acid increases the cohesive energy and solubility parameter; there is a decrease in glass transition temperature with a minimum of 285.13 K for 90% molar composition of lactic acid. Tables 3 represents mechanical properties of acrylic acid and oxy-ethylene mixture.

The random copolymer of lactic acid and ethylene-glycol was analyzed to increase the molar composition of lactic acid at the set temperature of 298 K. The properties for the increasing molar composition of lactic acid illustrated in table 4.

Table 5 gives the mechanical properties of lactic acid and ethylene-glycol composition at a temperature of 298 K. The analysis shows that an increase in molar concentration of lactic acid decreases the density, Young's modulus, and bulk modulus. Table 6 presents the thermophysical properties of the mixture. The analysis shows the decrease in glass transition temperature and an increase in permeability of oxygen and carbon dioxide.

Glass transition temperature

The glass transition is the gradual and reversible transition in amorphous materials from a hard and relatively brittle state into a viscous or rubbery state as the temperature increased. The glass transition temperature is always lower than the melting temperature. The glass transition temperature for the mixtures shown in fig as a function of mole fraction of compound forms a total of 1 mole. From figure 5, the glass transition temperature for lactic acid and ethylene glycol is increasing for the increase in the mole fractions of lactic acid. The glass transition temperature values are decreasing with an increase in mole fraction for lactic acid and methyl meth-acrylate mixture and acrylic acid and oxy-ethylene.

Comparison with poly(propylene)

The properties of random copolymers of the different molar composition of lactic acid, methyl methacrylate, acrylic acid, oxy-ethylene, and ethylene glycol are compared with

Table 1: Mechanical properties of lactic acid and methyl meth-acrylate mixture.

Composition of lactic acid and methyl methacrylate	Density (g/cc)	Poisson's ratio	Young's modulus (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)
0/100	1.159	0.371	2.65	0.967	3.43
10/90	1.16	0.378	2.54	0.923	3.47
20/80	1.162	0.384	2.45	0.883	3.5
30/70	1.163	0.389	2.35	0.846	3.53
40/60	1.165	0.394	2.27	0.812	3.56
50/50	1.167	0.399	2.18	0.78	3.58
60/40	1.169	0.403	1.96	0.7	3.36
70/30	1.171	0.407	1.74	0.617	3.1
80/20	1.173	0.41	1.51	0.534	2.8
90/10	1.175	0.414	1.28	0.454	2.48
100/0	1.177	0.417	1.06	0.374	2.13

Table 2: Thermo-physical properties of lactic acid and methyl meth-acrylate mixture.

Composition of lactic acid and methyl methacrylate	Glass transition temperature (K)	Temperature of half decomposition (K)	Cohesive energy (Fedors) at 298 K (Kcal/mol)	Solubility parameter (Fedors) at 298 K ($cal^{1/2}.cm^{-3/2}$)	Permeability of O_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)	Permeability of CO_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)
0/100	353.6807	600.1797	35.09723	20.1531	180.68	836.494
10/90	347.0428	600.8646	35.43518	20.407	152.466	695.255
20/80	340.1855	601.5691	35.77313	20.6656	127.97	574.502
30/70	333.0987	602.2943	36.11109	20.9291	106.809	471.827
40/60	325.7722	603.0411	36.44904	21.1978	88.6234	385.024
50/50	318.1949	603.8103	36.787	21.4719	73.0811	312.082
60/40	310.355	604.603	37.12495	21.7516	59.8745	251.176
70/30	302.24	605.4204	37.46291	22.0373	48.7207	200.659
80/20	293.8365	606.2636	37.80086	22.329	39.361	159.053
90/10	285.1303	607.1338	38.13882	22.6271	31.5597	125.039
100/0	276.1063	608.0324	38.47677	22.932	25.1036	97.4486

Table 3: Mechanical properties of acrylic acid and oxy-ethylene mixture.

Composition of acrylic acid and oxyethylene	Density (g/cc)	Poisson's ratio	Young's modulus (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)
0/100	1.127	0.43	2.88	0.961689	1.26
10/90	1.156	0.426	2.9	0.968789	1.54
20/80	1.183	0.423	2.88	0.962724	1.86
30/70	1.209	0.42	2.83	0.946664	2.23
40/60	1.232	0.417	1.36	0.478905	2.72
50/50	1.254	0.414	1.71	0.603501	3.29
60/40	1.275	0.41	2.09	0.74034	3.88
70/30	1.295	0.407	2.47	0.87836	4.43
80/20	1.313	0.404	2.79	0.992584	4.82
90/10	1.33	0.4	3.08	1.10E+03	5.14
100/0	1.347	0.397	3.37	1.21E+03	5.44

Table 4: Thermo-physical properties of lactic acrylic acid and oxy-ethylene mixture.

Composition of acrylic acid and oxyethylene	Glass transition temperature (K)	Temperature of half decomposition (K)	Cohesive energy (Fedors) at 298 K (Kcal/mol)	Solubility parameter (Fedors) at 298 K ($cal^{1/2}.cm^{-3/2}$)	Permeability of O_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)	Permeability of CO_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)
0/100	204.933	594.863	13.03	18.26	658.412	3.42E+03
10/90	226.29	596.672	15.26	19.406	293.792	1.42E+03
20/80	245.155	598.277	17.49	20.415	138.645	626.895
30/70	261.951	599.711	19.719	21.314	68.8123	292.278
40/60	277.007	600.999	21.949	22.122	35.7435	143.197
50/50	290.583	602.163	24.179	22.854	19.3481	73.381
60/40	302.891	603.219	26.409	23.521	10.8732	39.17
70/30	314.102	604.183	28.639	24.132	6.32286	21.702
80/20	324.358	605.066	30.869	24.695	3.79333	12.439
90/10	333.776	605.877	33.099	25.214	2.34178	7.355
100/0	342.455	606.626	35.329	25.696	1.48415	4.475

Table 5: Mechanical properties of lactic acid and ethylene-glycol mixture.

Composition of lactic acid and ethylene-glycol	Density (g/cc)	Poisson's ratio	Young's modulus (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)
0/100	1.351	0.422	2.97E+03	1.05E+03	6.35E+03
10/90	1.324	0.421	2.65E+03	9.32E+02	5.61E+03
20/80	1.3	0.421	2.37E+03	8.33E+02	4.97E+03
30/70	1.279	0.42	2.12E+03	7.46E+02	4.42E+03
40/60	1.26	0.419	1.90E+03	6.70E+02	3.93E+03
50/50	1.242	0.419	1.71E+03	6.04E+02	3.52E+03
60/40	1.227	0.418	1.55E+03	5.46E+02	3.16E+03
70/30	1.213	0.418	1.40E+03	4.94E+02	2.85E+03
80/20	1.2	0.418	1.27E+03	4.49E+02	2.58E+03
90/10	1.188	0.417	1.16E+03	4.10E+02	2.34E+03
100/0	1.177	0.417	1.06E+03	3.75E+02	2.13E+03

Table 6: Thermo-physical properties of lactic acid and ethylene-glycol mixture.

Composition of lactic acid & ethylene-glycol	Glass transition temperature (K)	Temperature of half decomposition (K)	Cohesive energy (Fedors) at 298 K (Kcal/mol)	Solubility parameter (Fedors) at 298 K ($cal^{1/2}.cm^{-3/2}$)	Permeability of O_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)	Permeability of CO_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)
0/100	313.6934	563.3237	38.4444	29.4068	0.037	0.08025
10/90	309.2947	569.4667	38.4477	28.5021	0.10086	0.23927
20/80	305.1105	575.1195	38.4509	27.6762	0.24554	0.63063
30/70	301.1048	580.3386	38.4541	26.9183	0.54351	1.49854
40/60	297.2485	585.1719	38.4574	26.2195	1.10995	3.26168
50/50	293.5174	589.6608	38.4606	25.5726	2.11578	6.58595
60/40	289.891	593.8408	38.4638	24.9715	3.80063	12.4655
70/30	286.3515	597.7428	38.4671	24.4109	6.48428	22.3062
80/20	282.8835	601.3935	38.4703	23.8865	10.5761	38.0061
90/10	279.4727	604.8165	38.4735	23.3946	16.5811	62.0262
100/0	276.1063	608.0324	38.4768	22.932	25.1036	97.4486

Table 7: Properties comparison with poly(propylene).

Random copolymer	Density (g/cc)	Young's modulus (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)	Permeability of O_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)	Permeability of CO_2 ($.10^{-14}$ $cm^3.cm/cm^2.s.Pa$)
Lactic acid and methyl methacrylate	1.16	2.54	0.923	3.47	152.465	695.254
Acrylic acid and oxyethylene	1.15	2.9	0.968	1.54	293.792	1420.5
Lactic acid and ethylene-glycol	1.32	2.65	0.932	0.561	0.10086	0.23927
Poly(propylene)	0.885	1.8	0.4	0.182	6635.4	42375.4

polypropylene in table 7. The permeability values of mixture materials are much less than polypropylene. And the table shows that the elastic modulus of these materials is comparatively the same as polypropylene. The simulation results conclude that these materials can be further used for the testing process to determine the best material satisfying the objectives of PPE kits.

Conclusion

This study's outcomes have shown that the copolymerization of various potential alternate materials portrays higher strength and resilience than the standard materials presently employed for manufacturing PPE gowns. The study also proves that the resultant copolymer materials have higher molecular density due to the presence of heavier

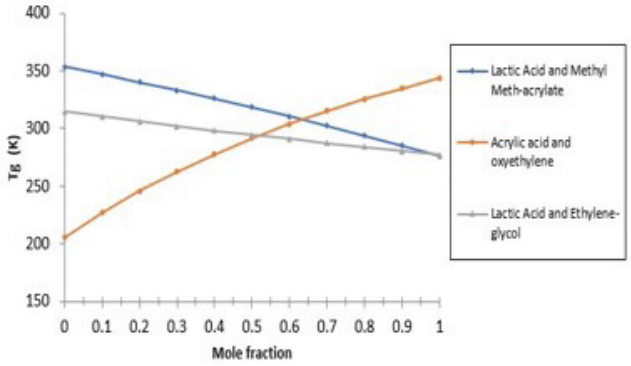

Figure 5: The glass transition temperature of all compositions.

oxygen atoms compared to propylene's carbon atoms. This outcome substantiates a significant reduction in air and water permeability. It has also observed that although the study so performed does not display the efficacy of the materials suggested, the required details and facts supplemented with experimental results.

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Conflict of Interest

None.

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