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Current Research in Biopolymers

Mitchell GR, et al. Curr Res Biopolymers: CRBP-102.

DOI: 10.29011/CRBP-102.000002

Review Article

Biopolymers Based on Rosin

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Citation: Mitchell GR, Mahendra V, Sousa D (2018) Biopolymers based on Rosin. Curr Res Biopolymers: CRBP-102. DOI: 10.29011/CRBP-102.000002

Received date: 8 February, 2018 ; **Accepted date:** 23 February, 2018; **Published date:** 2 February, 2018

Abstract

Rosin is a material, which can be obtained from pine resin using a green technology with no waste output. It is a mixture of terpenes with a functionality that make them a rich chemical resource. Rosin is a material which has been available for hundreds of years and has developed many niche applications some old, some new. The authors review the potential of this material for preparing sustainable biopolymers and composites by identifying the reaction paths. The authors conclude that foams and composites may be the most effective route to high volume applications based on rosin.

Introduction

In 2018 there is strong renewed interest in sustainable materials; in particular for biodegradable plastics to circumvent the problems arising from plastic waste in the oceans [1]. Polymer Science is a rich area for materials, for example, as well as naturally occurring polymers such as cellulose and polysaccharides [2] there are synthetic polymers such as polylactides [3] and polyethylene [4] coming available, which are produced from natural raw materials. It is known that the polyolefin-based polymers developed over the last 60 years have been hugely successful in terms of providing excellent insulation for electrical cables and high-quality water piping for water distribution. The success of such polymers in these applications, rests on the ability not to degrade, so as a consequence any plastics which enter the environment will retain their form for many years. This paper considers an alternative raw material, which is obtained in a sustainable manner and is rich in potential chemistry for preparing high performance materials. The focus is on rosin, which is extracted from the resin tapped from pine trees. The complete process from tree to rosin is very environmentally friendly, producing distilled water and distilled turpentine as by products [5]. Rosin itself at room temperature is a brittle glassy material and but has found application in a wide variety of fields [5,6]. Here the authors look for the potential beyond established applications.

Rosin, Applications and Limitations

Rosin, sometimes referred to as colophony, is produced at the end of the extraction system from pine-resin. Rosin glass is a brittle glassy material consisting of small molecules, basically terpenes with a molecular formula of $C_{20}H_{30}O_2$ and the weight 302g/mol. It is an approved food additive in the EU with the E number of E915. It is a mixture of different isomers [5]. Over a long period, it has attracted a variety of applications ranging from treating a violin bow through to flux for soldering and a viscosity modifier for printer inks and a glaze for paper [5,6]. These are very much niche applications. To date there has been no large volume application in for example engineering or building materials, although various approaches have been explored for example [7]. The basic problem is that rosin is a particularly brittle material. Sousa et al [8] have attempted to improve the mechanical properties by mixing with nanoclay and polymers.

Polymers Based on Rosin

Intrinsic Structural Characteristics

Rosin is a mixture of small molecules consisting of different isomers. These isomers are commonly known as resin acids. The chemical structure of a resin acid typically consists of cyclic rings, conjugated double bonds and a carboxylic group. These features provide rosin with many potential routes to structural alterations. Although they consist of cyclic ring structures, they remain anti-aromatic, which is conducive to chemical reactions, hence the ease of modifications. These modifications are useful in various applications (Table 1).

Product name/ scheme	PRODUCT	ACID VALUE (mg KOH/g)	SOFTENING POINT (^{O}C)	COLOUR (50% toluene)	Properties and application recommendations
POLIMELT Tall oil rosin ester/i	P 88	≤10	80-90	≤4	Light and stable glycerol rosin ester recommended for hot melt adhesives.
	P 90	≤6	85-92	≤4	Highly stable glycerol rosin ester with medium softening point, ideal for pressure sensitive adhesives.
	P 98	≤10	95-100	≤4	Light and stable pentaerythritol rosin esters with low odour. Recommended for hot melt adhesives for packaging, bookbinding and pressure sensitive.
	P 101	≤10	97-102	≤4	
	P 105	≤10	102-108	≤3	High softening point pentaerythritol rosin ester with improved heat stability.
	P 115	≤10	112-117	≤6	Very high softening point pentaerythritol rosin ester with very low odour and volatility.
	P 120	≤20	114-120	≤6	Pentaerythritol rosin ester with high softening point and high heat resistance.
	P 6302	80-90	80-90	≤4	High acid value and medium softening point glycerol rosin ester designed for specialty packaging hot melt adhesives.
TERGUM Gum rosin ester/ii	T 100	≤20	92-98	≤5	Pentaerythritol rosin esters with excellent stability. Recommended for hot melt adhesives for packaging, bookbinding and pressure sensitive.
	T 103	≤20	98-105	≤5	
	T 120	≤15	114-120	≤6	Pentaerythritol rosin ester with high softening point and high heat resistance. Recommended for hot melt adhesives.
	T 385	≤12	80-86	≤5	Glycerol rosin ester for hot melt adhesives with increased tack requirements. Recommended for packaging and flooring adhesives and depilatory waxes.
	T 390	≤10	85-91	≤5	
Tergum Non-crystallising gum rosin/iii	T 19	135-155	85-95	≤8	Non-crystallising gum rosin with low volatile content. Ideal for flooring adhesives and pressure sensitive adhesives.
Gum rosin	Gum rosin	162-182	72-87	≤8	Recommended as tackifier for use in adhesive, varnishes, inks and raw material for modified resins.

Table 1: Physical properties of rosin and rosin derived esters for recommended application. The contents of the Table are reproduced from Respol Resinas, S.A. with permission

There are commonly known resin acid isomers such as abietic acid, levopimaric acid, pimaric acid and isopimaric acid (Figure 1). Clearly these are not polymers. These isomers tend to undergo isomerisation at higher temperatures and interchange their structural arrangements, for an example abietic acid rearranges as levopimaric acid at higher temperature.

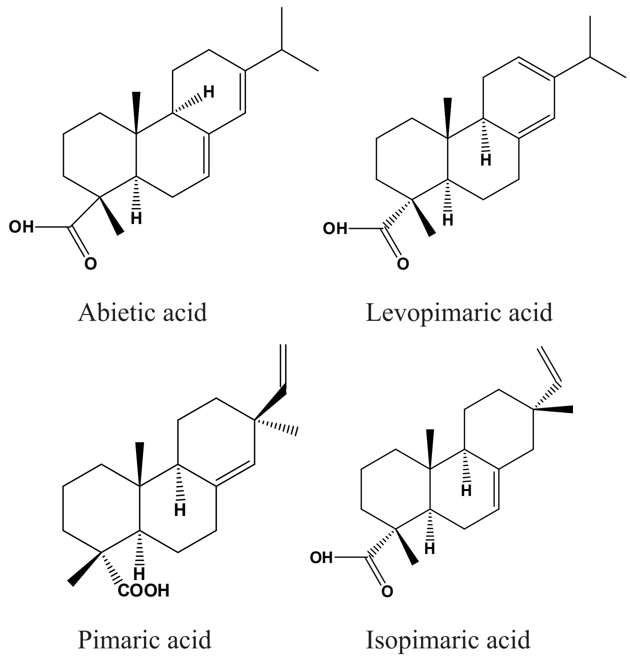

Figure 1: Structures of resin acids

The modified rosins exhibit different softening points and acid values that provide advantage for various applications (Table 1).

- Tall oil rosin is a synonym for pine oil rosin. [9] scheme 1
- Gum Rosin esters are obtained by the esterification reaction of the resin acids of the pitch or resin acids of the pitch modified with polyols [10].
- Non-crystalline gum rosin is obtained by the addition of a hard rosin ester [11].

The ester form of rosin is obtained in the laboratory using the following reaction scheme. The resin acid is treated with a desired alcohol (glycerol, pentaerythritol etc.) at an elevated temperature and the resulting water is removed to isolate the rosin ester as the principal product (Figure 1). Similarly, in the presence of an appropriate base, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), the resulting water is removed to obtain rosin soap as the principal product as a viscous liquid. In such reactions, the presence of a metal atom attached to the end of the carboxylate group makes it ionic (Figure 2). Unlike rosin, the soap enables interaction with hydrophilic chemical reactions.

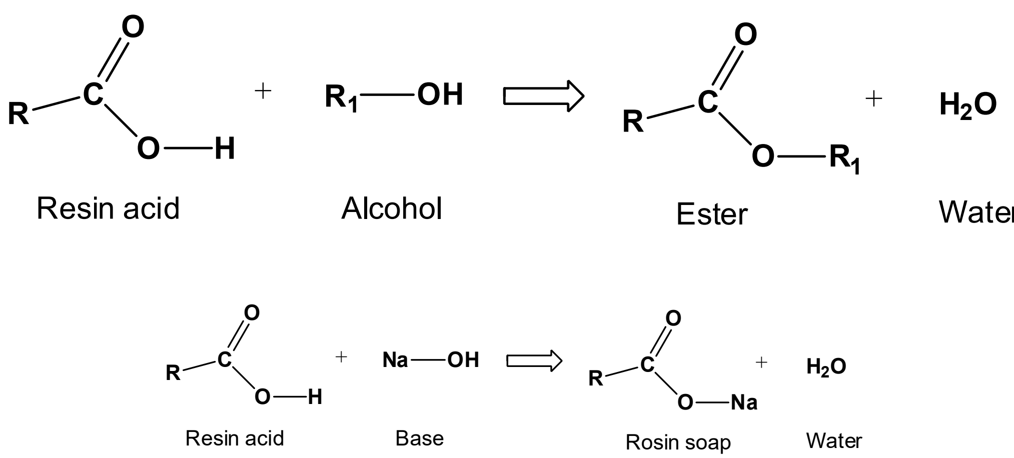

Figure 2: Saponification reaction of resin acid in the presence of a base.

Possible polymerisation route: Rosin is primarily used as an adhesive material and some of the applications along with its properties are listed in the Table 1. However, the applications of rosin which would require good mechanical properties have been limited due to the brittle nature of the rosin glass. Chemical reactions such as cross-linking, grafting and polymerisation of resin acids may be potential pathways to overcome this brittleness. The conjugated double bonds in the resin acid ring system makes it favourable for polymerisation. Polymerisation of rosin has been reported for a long time for making industrially useful products. The most commonly known reaction scheme of polymerisation of rosin is the dimerisation of resin acid [12] that is achieved via acid catalysis (Figure 3).

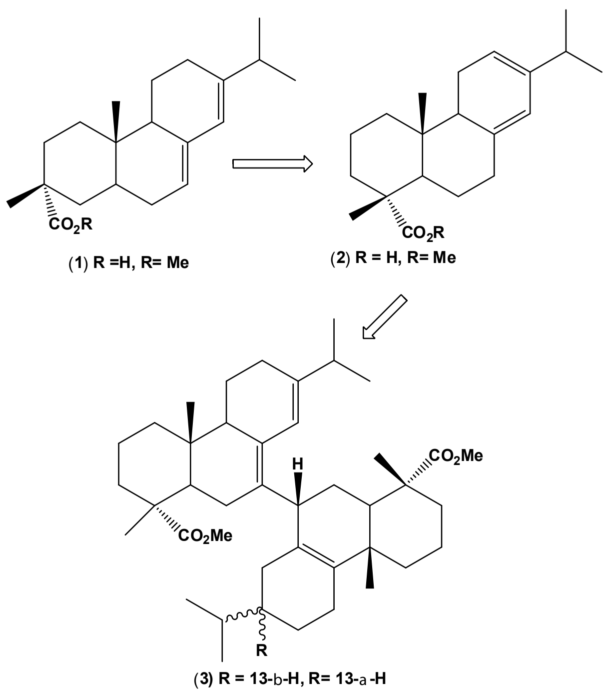

Figure 3: The dimerisation pathway of abietic acid via acid catalysis

According to Gigente et al. [13], the dimerisation takes place in a two-step mechanism; a fast-initial isomerisation followed by slow dimerisation reaction. Sinclair et al. [12] have reported some improvements on rosin by producing its dimer with a softening point of 162°C as compared with 60°C of the monomer, and the mass spectrometric confirmation of its value at m/e = 632. However, the polymerisation of the dimerised rosin has not been reported.

Mahendra et al. [14] have previously reported the formation of rosin foam, a bio-foam in a single-pot scheme via using a foaming agent for potential thermal insulation (Figure 4). The resulting bio-foams have been compared with the industrially established Urea Formaldehyde Foam Insulation (UFFI), proved to be a better alternative with no harmful gas emission subsequently foam making. Carbon dioxide is formed during the reaction process and liberated as a by-product.

$$\text{R-COOH} + \text{R}_1\text{N=C=O} \rightarrow \text{R-CONHR}_1 + \text{CO}_2$$

(resin acid) (an isocyanate) (an amide) (liberation of carbon dioxide)

Scheme 4: Schematic route to foam developing.

Composites of Mixtures Based on Rosin

Rosin Biocomposites: Lately there has been more awareness about the environment, climate change, the fact that fossil resources may be limited combined with the need for a green way for discarding materials when they reach their end-of-life that is not burning or burying, synthetic biopolymers have been developed which led to an intensive research of alternatives to fossil-based polymers [15]. Therefore, the polymer industry began looking for alternative sources and biological materials were studied for the production of polymers.

Biopolymers may be naturally occurring like those formed in nature during the life cycles of plants, animals, bacteria and fungi. These include the polysaccharides such as cellulose, starch and animal protein-based polymers such as wool, silk, gelatin and collagen [16]. The word biopolymers seem to imply that these are sustainable, but it depends on the source material, the production process and how it is handled at the end of its life cycle [17]. According to Riggle [18] for materials to claim to be biodegradable and compostable they should satisfy ASTM tests showing “conversion to carbon dioxide at 60% for a single polymer and 90% for other materials in 180 days or less and leave no more than 10% of the original weight on a 3/8-inch screen after 12 weeks (84 days).”

Since the mechanical properties of rosin are very poor as it is extremely brittle at room temperature and there is a need for improvement in such properties to make it a useful natural material. The term brittleness is used but there is no commonly accepted quantitative definition [19]. Physical properties of polymers, particularly mechanical properties are related with molecular architectures [20]. The incorporation (mixture) of rosin and biopolymers could possibly increase the physical properties of the rosin composite. Gennusa et al [7] analyzed the structural behaviour of a biocomposite material that consisted of a natural resin (rosin) and vegetal fibres (hay). Compressive tests and three-point flexural tests were performed. Samples with a smaller amount of fibres revealed to be more resistant, however, the brittle behaviour also increases, shown by the absence of a plastic behaviour in the stress-strain curve. When these mechanical tests were compared with a mixture of lime and hay, they show that the mechanical properties strongly increase by substituting the lime with rosin as a binder.

Pharmaceutical Properties and Biocompatibility: Plastics can be divided in to two types, common plastics and bioplastics. Common plastics also called petrochemical-based polymers are derived from petroleum or natural gas and bioplastics derived from renewable biomass sources such as vegetable fats and oils, corn starch or microbiota [21]. Bioplastics degrade rapidly as compared with the fossil-fuel plastics due to their consumption by microorganisms such as bacteria [22]. However, these bioplastics are extensively investigated prior to applications in human biology, such as cytotoxicity, cell adhesion, cell propagation and lifecycle assessments. There are number of recent developments reflected to rosin as a material for bio applications. Rosin and its derivatives are expected to be biodegradable and biocompatible [23] as they are of natural origin. Satturwar et al. [24] studied the degradation of rosin biocomposites *in vitro* and *in vivo* and revealed rosin has shown faster degradation *in vivo* as compared with *in vitro* studies, in the *in vivo* studies films were subcutaneously implanted on the backs of male wistar rats and showed mass weight loss of 100% after 90 days. The biodegradation and biocompatibility characteristics of rosin were investigated *in vivo* and confirmed by the absence of necrosis or abscess formation in the surrounding tissues.

Rosin and its derivatives have been extensively studied in pharmacy as film-coating and microencapsulating materials for a sustained and controlled drug release [25]. Nande et al. prepared derivatives of rosin reacting polyethylene glycol 200 and maleic anhydride, these proved suitable for sustaining drug release from matrix tablets and pellets [26]. PEGylated materials were prepared by Morkhade et al. [27] by reacting ester derivatives of rosin with PEG 400 & maleic anhydride at high temperatures. These were tested for sustained drug delivery. Microcapsules of diltiazem hydrochloride with rosin were synthesized by Reddy et al. [28] through an emulsion solvent-evaporation technique. The authors added different amounts of drugs to get different drug to polymer ratios. The physical properties, loading efficiency and release rate depended on the drug to polymer ratio.

Rosin-PEG 1500 derivatives were successfully synthesised by Kanlaya et al. [29] from natural rosin and PEG using ZnO 2% as a catalyst. These derivatives were completely soluble in water.

Different studies on the film forming and coating properties of rosin and the glycerol ester of maleic rosin demonstrated their potential to be used as coating materials for pharmaceutical products as well as in sustained-release drug delivery systems. *In vitro* studies demonstrated the potential of rosin to produce effective nanoparticulate drug delivery systems [30]. Fulzele et al. [31] investigated the application of polymerised rosin films. Films were produced by casting/solvent evaporation from plasticizer free and plasticizer containing solutions. Plasticizer containing films showed excellent potential as coating materials for the preparation of sustained release dosage forms. Mandaogade et al. [32] studied rosin derivatives as novel film forming materials for controlled drug delivery. Two new rosin derivatives free of plasticizer were produced by a casting/solvent evaporation method and evaluated for their physicochemical properties.

Rosin and rosin derivatives have many advantages for pharmaceutical applications; they have excellent film forming properties for granules, tablets and pellets, the ability to form moisture protective films for hygroscopic drugs, impermeability to air and oxygen for protecting drugs from oxidation damage, resistance to acids for enteric coating and for delayed or slow release and excellent binding ability in wet granulation [33].

Summary

It is clear that rosin is a versatile chemical resource and it has found many niche applications either as rosin or a near derivative. The richness of chemical reactivity provides opportunities for exploiting rosin as a feedstock for polymer-based materials. The authors are optimistic that large scale applications are possible either an insulation foam or a structural plastic for use in composites. It is believed that any such approaches must maintain the green credentials of the rosin by using simple reactions which do not need subsequent purification.

Acknowledgements

This work form part of the Green Thermosets project PT-DZ/0001/2015 funded by the Foundation of Science and Technology (FCT) in Portugal. We acknowledge most helpful discussions with our Algerian partners, Dr Amine Harrane of the university of Oran and his research group in this project. The authors thank Respol for permission to reproduce Table 1 in this paper.

References

1. Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, etal. (2015) Plastic waste inputs from land into the ocean. Science.347: 768-771.
2. Plackett D. (2011) “Biopolymers: New Materials for Sustainable Films and Coatings” Wiley 354 pages.
3. Aguirre EC, Franco FI, Samsudin H, Fang X, Aurasa R (2016) Advanced Drug Delivery Reviews 107: 333-366.
4. Hustad PD (2009) Science. 325: 704-707.
5. Zhang J (editor) (2012) Rosin-based Chemicals and Polymers Smithers Shawbury UK.
6. Silvestre AJD and Gandini A in Monomers, Polymers and Composites from Renewable Resources 2008 Chapter 4 Edited by Belgacem M and Gandini A, Elsevier: Oxford
7. La Gennusa M, Llorach-Massana P, Montero JI, Peña FJ, Rieradevall J, et al. (2017) Sustainability 9: 373.
8. Sousa D, Biscaia S, Viana T, Gaspar M, Mahendra V, et al. (2018) Advanced Materials in press 2018.
9. Biermann CJ (1993). Essentials of Pulping and Papermaking. San Diego: Academic Press, Inc. p. 107.

10. Sourced from GUM ROSIN ESTERS

11. NON-CRYSTALLIZING ROSIN, U.S. PATENT DOCUMENTS (1978) 4,105,462, Aug. 8,

12. Sinclair RG, Berry DA, Schuler WH and Lawrence RV (1970) 'Influence of reaction conditions on the dimerisation of abietic acid and rosin'. Industrial & Engineering Chemistry Product Research and Development 9: 60-65.

13. Gigente B, Jones R, Lobo A, Marcelo-Curto MJ, Prabhakar S, et al (1986). 'The structure of an Abietic Acid Dimer'. Journal of the Chemical Society, Chemical Communications. 1038-1039.

14. Mahendra V, Mitchell GR. and Mateus A.J.S. (2015) The Development of Rosins as Potential Eco-Foams from Pine Derived Resins, 5th International Conference on Biofoams. Sorrento 13-16,

15. Dodiuk H. and Goodman S. (2013) Handbook of Thermoset Plastics, Chapter 15, 3rd edition, PDL Handbook Series, 577-621.

16. Yadav P, Yadav H, Shah VG, Shah G, Dhaka G (2015) Biomedical Biopolymers, their Origin and Evolution in Biomedical Sciences: A Systematic Review, Journal of Clinical and Diagnostic Research, Vol-9(9): ZE21-ZE25.

17. Álvarez-Chávez CR, Edwards S, Moure-Eraso R, Geiser K (2012) Sustainability of bio-based plastics: general comparative analysis and recommendations for improvement. Journal of Cleaner Production, 23 (1): 47-56.

18. Riggle D (1998) Moving Towards Consensus on Degradable Plastics, BioCycle Journal of Composting & Recycling, 39, No.3, 64-70.

19. Brostow W, Lobland HEH, Narkis M (2001) Polymer Bulletin, 67: 1697–1707.

20. Wool PR (2005) Fundamentals of Fraction in Bio-based Polymers, Chapter 6, 3rd edition, 149-201.

21. Chua H, Peter HF, Chee KM (1999) Applied Biochemistry and Biotechnology, 289-399.

22. Chen CG (2010) Plastics from Bacteria, Natural functions and applications, Springer Heidelberg, 1-6.

23. Satturwar PM, Fulzele SV, Panyam J, Mandaogade PM, Mundhada DR, Gogte BB, Labhasetwar V, Dorle AK (2004) Evaluation of new rosin derivatives for pharmaceutical coating, International Journal of Pharmaceutics, Volume 270, Issues 1–2, 11, 27-36.

24. Satturwar PM, Fulzele SV, Dorle AK, Biodegradation and in vivo Biocompatibility of Rosin: a Natural Film-Forming Polymer, AAPS PharmSciTech 2003; 4 (4) Article 55, 1-6.

25. Kumar S, Gupta SK (2013) Rosin: a naturally derived excipient in drug delivery systems, Polim Med. 2, 43(1): 45-8.

26. Nande VS, Barabde UV, Morkhade DM, Patil AT, Joshi SB (2006) Synthesis and characterization of PEGylated derivatives of rosin for sustained drug delivery. Reactive Funct. Polym, 66, 1373-1383.

27. Morkhade DM, Nande VS, Barabde UV, Patil AT, Joshi SB (2007) PEGylated Rosin Derivatives: Novel Microencapsulating Materials for Sustained Drug Delivery, AAPS PharmSciTech, 8 (2) Article 47, E1-E9.

28. Reddy MN, Shirwaikar AA (2000) Rosin, a polymer for microencapsulation of diltiazem hydrochloride for sustained release by emulsion-solvent evaporation technique, Indian Journal of Pharmaceutical Sciences, 7, 308–310.

29. Kanlaya P, Sumrit W, Amorn P (2016) Synthesis and Characterization of Water Soluble Rosin-Polyethylene Glycol 1500 Derivative, International Journal of Chemical Engineering and Applications, Vol. 7, No. 4, 277-281.

30. Lee C-M., Lim S., Kim G-Y., Kim D-W., Joon HR, Lee, K-Y (2005) Rosin nanoparticles as a drug delivery carrier for the controlled release of hydrocortisone, Biotechnology Letters, 27, 1487-1490.

31. Fulzele SV, Satturwar PM, Dorle AK (2002) Polymerized rosin: novel film forming polymer for drug delivery, International Journal of Pharmaceutics, 249, 175-184.

32. Mandaogade PM, Satturwar PM, Fulzele SV, Gogte BB, Dorle AK (2002) Rosin derivatives: Novel film forming materials for controlled drug delivery, Reactive & Functional Polymers 50, 233–242.

33. 33. Pratapwar AS, Sakarkar DM (2015) Applications of rosin derivatives in the development of novel drug delivery system (NDDS): a contemporary view, Journal of Quality Assurance and Pharma Analysis, Vol 1 (1), 100-109.