Development of a Transparent and Highly Heat-Resistant Polymer Film Derived from Biomass

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Abstract

We have prepared high-purity methyl dehydroabietate (DHA-Me) from disproportionated rosin consisting of many compounds via methylation and subsequent reaction or recrystallization. DHA-Me was converted into various bifunctional compounds useful as monomers. Among these, 12-carboxy dehydroabietic acid (CDHA) and dimethyl methylenebis-dehydroabietate (MDA-Me) were particularly applicable and both were transformed into corresponding bio-based polyesters or polyamides. The synthesized polymers were cast as thin films, and the resulting films were characterized. In comparison with commercially available super-engineering plastic films, the aforementioned films are more flexible, are more heat resistant, and exhibit high transparency and low density. The porous film formed via the film-making process has characteristics similar to those of an ordinary film.

1. Introduction

As growing demands for low carbon society and resource recycling society, materials using biomass has been developed. For example, plastics such as polylactic acid (PLA), polybutylene succinate (Bio-PBS) and polycarbonate (Bio-PC) are already put into practical use. General purpose plastics, such as polyethylene, polypropylene and polyethylene terephthalate are increasingly produced from biomass instead of fossil resources [1].

Biomass materials currently being used include fermented glucose produced from starch which is made from grains such as sugar cane and corn , oil and fat derived from oil plants (fatty acid glycerin ester) and wood-based chemicals such as cellulose, natural rubber and rosin. In addition to having little influence on the environment, biomass materials to be used in the future should be preferably inexpensive and also inedible considering the potential food shortage in the future.

Rosin is an inedible biomass produced from pine-family plants. It has been used for a wide variety of purposes since the days before Christ [2].

Rosin can be divided into three types according to the manufacturing method. (1) Gum rosin is made by distilling raw pine resin extracted from a cut in the pine tree's bark. (2) Tall rosin is made by distilling crude tall oil, a by-product of pulp production from pine. (3) Wood rosin is made by solvent extracts of chips of pine tree stumps. To produce gum rosin, pine trees are not logged. To produce tall rosin, although pine trees are logged, pine trees grow fast and the forests are renewed in 20 years after planting. Therefore gum rosin and tall rosin are considered renewable chemicals. Rosin has characteristic structures and physical properties (Fig. 1). It is a complex mixture consisting of ten or more types of six-membered-ring tricyclic terpene compounds. Rosin has rigid and bulky structures and is highly hydrophobic. In addition, it has a carboxyl group as a functional group. We have explored methods of derivating a single-compound from rosin. In other words, we considered producing various functional materials from rosin by fine chemical transformation (Fig. 2). This report describes transformation of rosin to single-compounds and characteristics of highly functional polymers made from those substances.

Rosin (Complex Mixture)

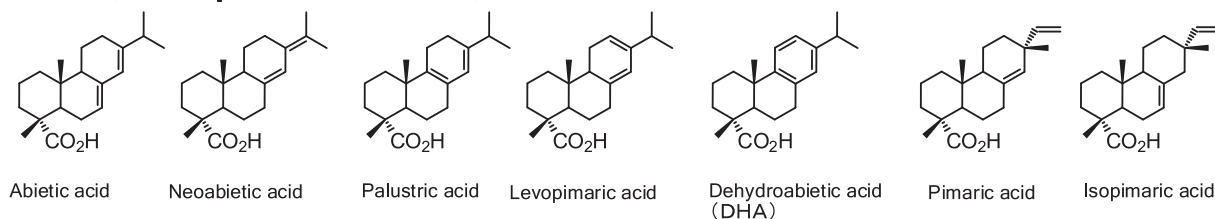Abietic acid　Neoabietic acid　Palustric acid　Levopimaric acid　Dehydroabietic acid (DHA)　Pimaric acid　Isopimaric acid
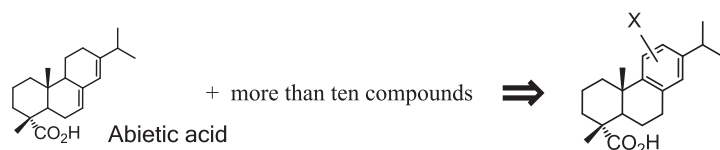
Applications taking advantage of the Complex Mixture.
ex. Sizing agents for paper, Emulsifying agents, Dispersing agents, Toners, Soldering flux, etc.

Fig. 1　Structures and properties of Rosin

Complex Mixture ⇒ Single Compound

Abietic acid　+ more than ten compounds ⇒

Approach to take advantage of the structural features to the fullest potential
(The features : rigid / bulky / hydrophobic / hydrophilic / Optical activity, etc.)

Fig. 2　Application strategy of Rosin

Disproportionated Rosin (DPR)

Rosin → catalyst / Heat

Dehydroabietic acid (DHA)　Dihydro or Tetrahydroabietic acid　Pimaric acid　Isopimaric acid
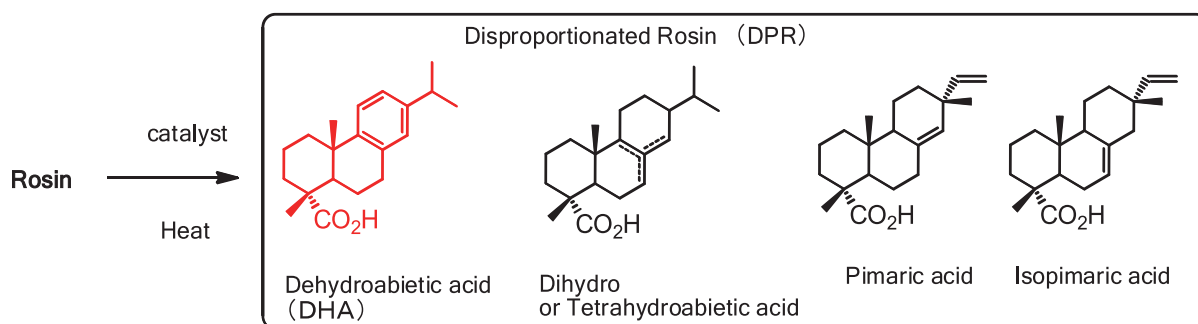
Fig. 3　Disproportionation products of Rosin

2. Preparation of high-purity methyl dehydroabietate (DHA-Me) from disproportionated rosin (DPR)

We sometimes use Rosin derivatives produced by Diels-Alder reaction using the conjugate double bond of conjugate resin acid, the main component of rosin. However, in many cases, the conjugate resin acid is easily oxidized and colored, so we use stable disproportionated rosin.

Disproportionation is usually carried out by heating rosin for several hours at 250 to 280℃ under the presence of a Pd catalyst (Fig. 3). During this reaction, dehydrogenation and hydrogenation occur concurrently and dehydroabietic acid (DHA) and dihydro or tetrahydroabietic acid are produced. Normally, disproportionated rosin contains 50 to 60% DHA as the main component (the rest are tetrahydroabietic acid, dihydroabietic acid, both less than 20%, and several types of pimaric acid). We think it is reasonable to extract DHA from disproportionated rosin (DPR) because DHA is the main component of DPR. In addition, it is preferred that DHA is considered easy to transform chemically because it contains a benzene ring.

Based on that, we examined methods of extracting DHA as a single compound (Fig. 4). Upon examination of distillation and recrystallization, it was difficult to purify DHA as it contains a free carboxylic acid. So we esterificated

DPR (DHA content ～ 70%) → DHA

Method	DHA content	Yield ratio
Distillation	72%	75%
Recrystallization		
(1st. crop)	73%	68%
(2nd. crop)	79%	29%

Esterification

Methyl-esterified DPR → Dehydroabietic acid methyl ester (DHA-Me)

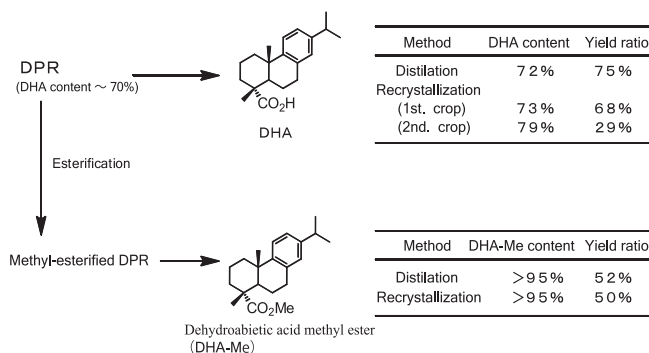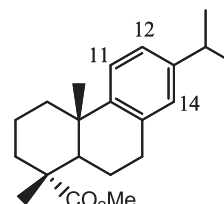| Method	DHA-Me content	Yield ratio
Distillation	＞95%	52%
Recrystallization	＞95%	50%

Fig. 4　Purification scheme of DPR

DHA to produce a DHA-Me, and we could obtain high-purity DHA-Me by distillation or recrystallization. Finding this purification method was a valuable breakthrough. It made it possible to mass-produce high-purity DHA-Me at low cost. After that, we conducted examinations using high-purity DHA-Me.

3. Preparation of monomer from DHA-Me

We have studied producing a derivative from DHA-Me, as it is necessary to introduce another functional group to utilize DHA-Me as a polymer material. The benzene ring in DHA-Me is considered to have relatively high electron density, indicating that various substituents can be introduced by aromatic electrophilic substitution reaction. At first, in order to clarify the reactivity of DHA-Me, we examined the typical electrophilic substitution reaction on benzene ring. Although DHA has been well known compound from a long time ago and many derivatives have been synthesized, few of them have been commercially available and used in the fine chemical use. The only example we have known is a derivative sulfonated at 12-position carbon which is used as a gastric mucosal protective agent [3] [※1]. Generally, aromatic electrophilic substitution reaction on DHA occurs at 11-, 12- and 14-positions. The regioselectivity depends on the type of electrophilic reagent and reaction conditions. Fig. 5 shows the outline of the regioselectivity of aromatic electrophilic substitution reaction on DHA-Me we have studied. Reactivity is the highest at 12-position, followed by 14-position. Reactivity is low at 11-position due to steric hindrance. We have found that the reactivity is almost similar to that of p-xylene or m-xylene and those reactions occur under relatively mild conditions.

Hydroxyl group, amino group and carboxyl group can be introduced into DHA-Me as the second functional group. To use DHA derivatives for monomers of polyesters or polyamides, we thought a carboxyl group is the most favorable. So we examined various methods for introducing carboxyl group into DHA-Me and synthesized several types of dehydroabietic acid derivatives containing two carboxyl groups (or esters) (Fig. 6). Among those derivatives, we examined the polymerization of 12-carboxy dehydroabietic acid (CDHA) that has carboxyl group directly bonded to 12-position and dimethyl methylenebis-dehydroabietate (MDA-Me) that is dimerized via methylene group at 12-position carbon. As CDHA and MDA-Me are thermally and chemically stable and carboxyl group is in a sterically hindered position, they are expected to have high hydrolysis resistance when they are transformed to esters or amides.

Reaction Type	Carbon Position		
	11	12	14
Halogenation	−	+	+-
Nitration	+-	+-	+
Acylation	−	+	+-
Sulphonation	−	++	−
Alkylation	−	+	+-

++ : Exclusively   + : Preferentially
+- : Secondarily   − : No Reaction

Fig. 5   Regioselectivity of aromatic electrophilic substitution of DHA-Me
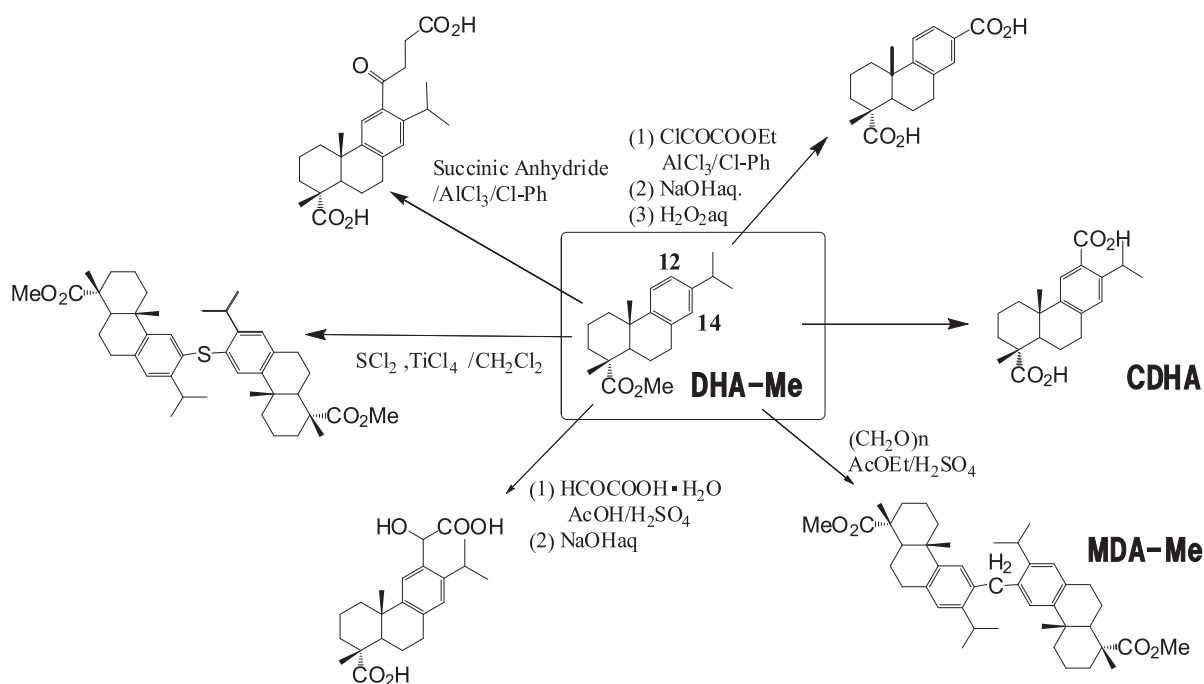

Fig. 6   Conversion of DHA-Me into dibasic acid derivatives

※1   Sulfodehydroabietic acid monosodium (Ecabet Sodium Hydrate) is sold as a gastric mucosal lesion improved pharmaceutical.

4. Polymerization from CDHA and MDA-Me

In the early development stage, we synthesized CDHA via haloform reaction with sodium hypochlorite after acetylation using acetyl chloride (Fig. 7). As environmentally hazardous methylene chloride was used as a solvent and toxic haloform was made as a byproduct, we studied other synthesis routes and finally established the synthesis route using ethyl oxalyl chloride. This route makes it possible to use chlorobenzene as a solvent and employ inexpensive hydrogen peroxide oxidation. Thereby we could prevent producing compound of haloform, and reduce steps in the manufacturing process [4].
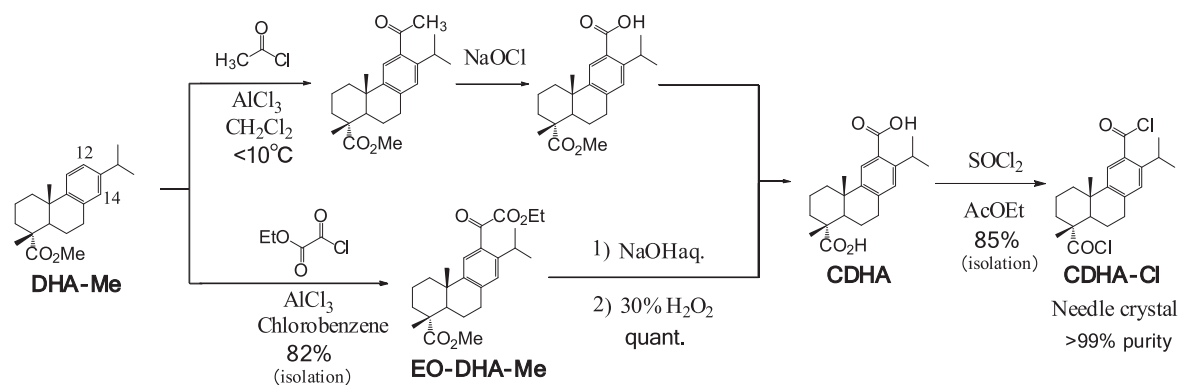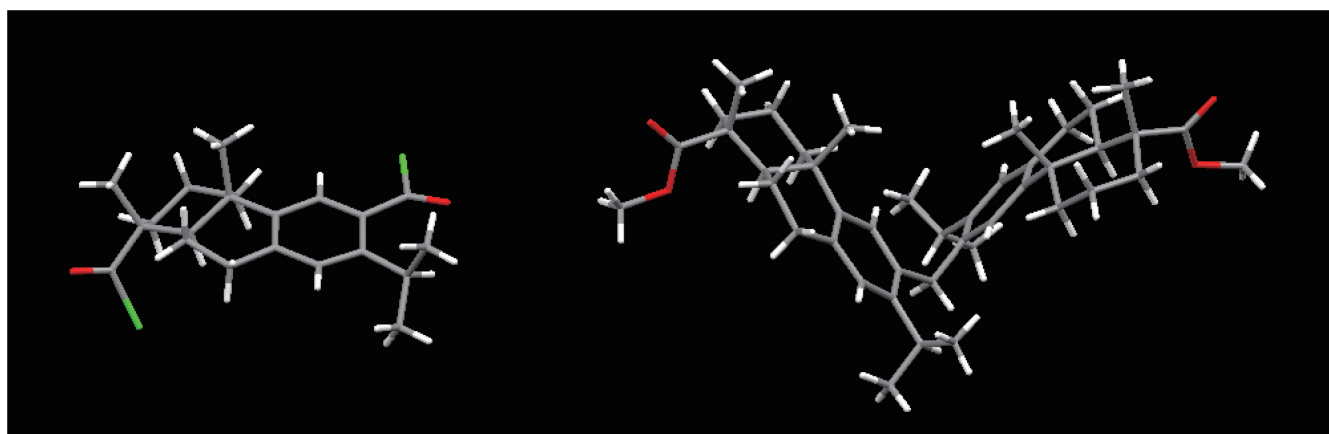

Fig. 7　Synthetic route of CDHA

Fig. 8　X-ray structural analysis　　Left：CDHA-Cl　Right：MDA-Me

Table 1　Synthesis of Polyesters

Sample No.	di-acid		di-ol		Mn (k) / Mw (k) [1]	Tg (℃) [2]	Biomass content (wt%) [3]	Thermal decomposition onset temperature (℃) [4]
PE- 1	CDHA	(50)	HO—〇—OH	(50)	46 / 100	278	67.5	420
PE- 2	CDHA	(50)	HO—〇—|—〇—OH	(50)	111 / 234	272	52.6	419
PE- 3	CDHA	(50)	HO〇—〇OH	(50)	54 / 150	283	49.0	432
PE- 4	CDHA	(50)	HO—〇—〇—OH	(50)	95 / 236	298	57.1	354
PE- 5	MDA	(50)	HO—〇—|—〇—OH	(50)	12 / 31	265	71.4	434
PE- 6	MDA	(50)	HO—〇—〇—OH	(50)	16 / 58	287	75.4	353

1) The molecular weight of the polymer was measured by GPC (solvent : NMP).
2) The temperature at which the film tangent loss (tan) exhibited the maximum value.
3) Mass originating from plants in the constituent components of the polymer/total mass of the constituent components of the polymer.
4) 2% weight loss temperature. Rate of temperature rise is 10 ℃/min under a nitrogen gas stream.

Next, CDHA was led to its acyl chloride derivative (CDHA-Cl), allowing for the isolation high-purity and stable needle crystals.
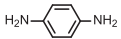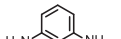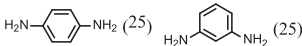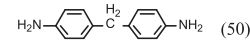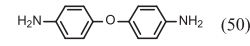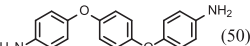
Fig. 8 shows the result of the single crystal X-ray structure analysis of CDHA-Cl and MDA-Me. It is evident that both compounds are sterically hindered around 12-position and that the molecules are bent. Next, we synthesized various polyesters and polyamides using CDHA-Cl and MDA-Me. Table 1 and 2 show those synthesized polymers and their properties.

5. Fabrication of films and evaluation

We prepared polymer solutions with concentrations of 10 to 15 wt% by dissolving synthesized polymers in a solvent. After removal of small dust and foreign substances by pressure filtration, the polymer solutions spread onto glass slides using an applicator and made into films by air blowing and vacuum drying.

We compared the physical properties of the PE-1 and PA-1 films with those of aromatic polyamide (Aramid), polyimide

Table 2   Synthesis of Polyamides

Sample No.	di-acid	di-amine	Mn (k) / Mw (k)[1]	Tg (℃)[2]	Biomass content (wt%)[3]	Thermal decomposition onset temperature (℃)[4]
PA- 1	CDHA (50)	H_2N—⟨⟩—NH_2 (50)	47 / 111	>350	67.8	407
PA- 2	CDHA (50)	H_2N—⟨⟩—NH_2 (50)	25 / 119	326	67.8	420
PA- 3	CDHA (50)	H_2N—⟨⟩—NH_2 (25) / H_2N—⟨⟩—NH_2 (25)	39 / 202	335	67.8	415
PA- 4	CDHA (50)	H_2N—⟨⟩—CH_2—⟨⟩—NH_2 (50)	33 / 85	323	55.7	427
PA- 5	CDHA (50)	H_2N—⟨⟩—O—⟨⟩—NH_2 (50)	28 / 78	316	55.5	433
PA- 6	CDHA (50)	H_2N—⟨⟩—O—⟨⟩—O—⟨⟩—NH_2 (50)	27 / 80	283	47.0	436

1) The molecular weight of the polymer was measured by GPC (solvent: NMP).
2) The temperature at which the film tangent loss (tan) exhibited the maximum value.
3) Mass originating from plants in the constituent components of the polymer/total mass of the constituent components of the polymer.
4) 2% weight loss temperature. Rate of temperature rise is 10 ℃/min under a nitrogen gas stream.

Table 3   Film properties of PE-1, PA-1, Aramid, PI and PEN

Polymer			PE−1	PA−1	Aramid	PI	PEN
Mechanical Properties (25℃ 60%RH)	Modulus	GPa	1.9	2.6	6.4	7.6	4.3
	Strength	MPa	100	130	238	332	158
	Elongation	%	64	60	18	20	95
Thermal Properties	10% TG N2 / Air	℃	454 / 419	452 / 347	448 / 445	>500 / >500	425 / 423
	Tg (tan δ)	℃	278	350	302	ND	166
	CTE (orientated)	ppm/℃	77 (26)	61 (ND)	31 (4)	13 (ND)	ND (16)
Optical Properties	Transmittance	%	90	89	67	26	87
	Haze	%	0.29	0.29	36	3.1	0.62
	Refractive index (n_d)		1.58	1.58	1.62	1.62	ND
	Abbe Constant		26	25	37	40	ND
Electrical Properties (10^6Hz)	Permittivity		3.20	4.53	4.10	3.55	3.26
	Dissipation factor		0.006	0.058	0.007	0.005	0.012
Water absorption(23℃ 24h)		%	0.44	6.4	2.7	1.5	0.62
Density		g/cm³	1.13	1.15	1.49	1.47	1.36
Film thickness		μm	50	50	50	50	100
Biomass content		wt%	67	67	0	0	0

Aramid
(Polyamide)
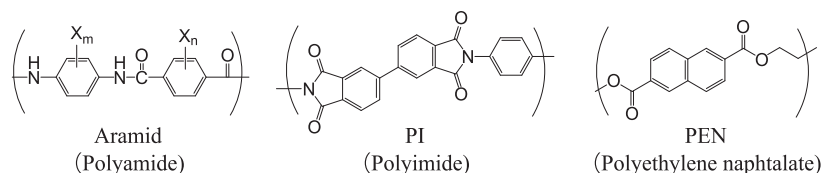
PI
(Polyimide)

PEN
(Polyethylene naphtalate)
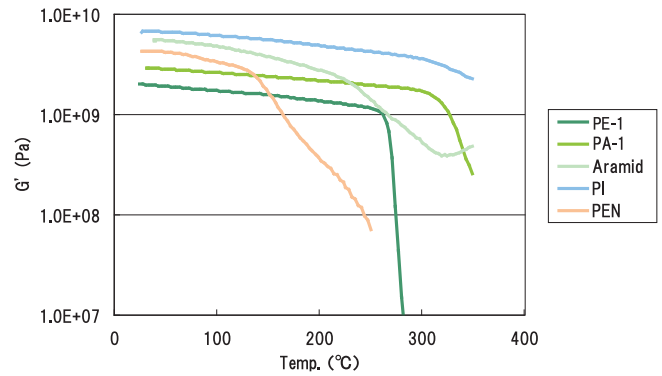
Fig. 9   Origami Crane used PE-1 film

Fig. 10   Temperature dependence of strage modulus of the films

(PI) and polyethylene naphthalate (PEN) well known as heat resistant plastics (Table 3). Distinct characteristics of DHA-based films include (1) high flexibility, (2) high heat resistance, (3) high light transmission and (4) low density. Those characteristics are explained in detail in the sections below.

5.1   Flexibility

As shown in Table 3, DHA-based films are lower in modulus and strength than other heat-resistant films, so it is suggested they are soft films. On the other hand, they have larger elongation. Those results show that DHA-based films are more flexible than general heat-resistant films. When PE-1 and PA-1 films are folded, white fold marks are not left and they are not easily cracked or torn. Surprisingly, these films can even be fold into paper crane (Fig. 9).

5.2   High heat resistance

As shown in Table 3, the glass-transition temperature (Tg) of PE-1 is 278℃ and that of PA-1 is 350℃ and these films are classified as a super-engineering plastic film just like as Aramid films. The temperature dependence of storage modulus (Fig. 10) shows that the modulus of PEN drops at around 130℃ and that of Aramid at around 200℃. On the other hand, PE-1 and PA-1 keep their modulus high till around Tg. That indicates DHA-based films contain similar self-supporting properties even at high temperature to those at room temperature.

5.3   High light transmission

As shown in Table 3 and Fig. 11, the total light transmittance of PE-1 is 90% and that of PA-1 is 89%. Showing higher transmittance than those of Aramid and PI or even that of PEN. As haze is small, those films are highly clear and transparent.
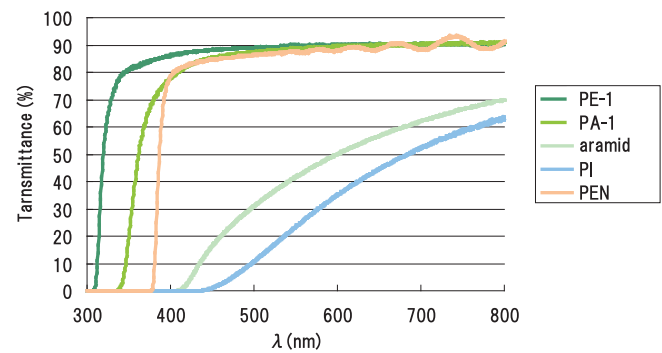

Fig. 11   UV-VIS spectra of the films

5.4   Low density

As shown in Table 3, the density of PE-1 is 1.13 g/cm^3 and that of PA-1 is 1.15 g/cm^3, much lower than those of Aramid (1.49), PI (1.47) and PEN (1.36). That reason, we suppose, is the polymer chains are bent and the free volume in the polymer film is large. It is supported a by the X-ray structure analysis of CDHA-Cl in Fig. 8.

6.   Application to finely structured films

As described above, we confirmed that DHA-based polymer films are flexible, high-heat-resistant, high-transparent and low-density. Next, we fabricated finely structured films, such a porous film and a honeycomb film, utilizing the self-assembly that occurs during drying process of films.

6.1 Porous film

In the process of examination of film making methods, we observed that the films clouded. Upon analysis of the phenomenon, we found that a porous was produced in the film. SEM observation of a cross section showed that a porous morphology was formed inside the film (Fig. 12). PE-1 film
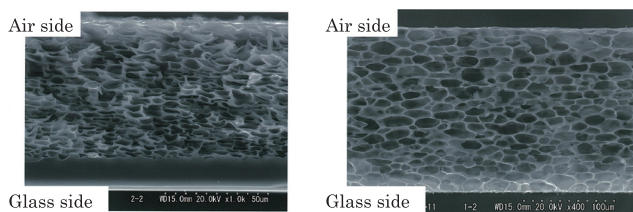
Fig. 12   Scanning electron microscopy Images of side view of films
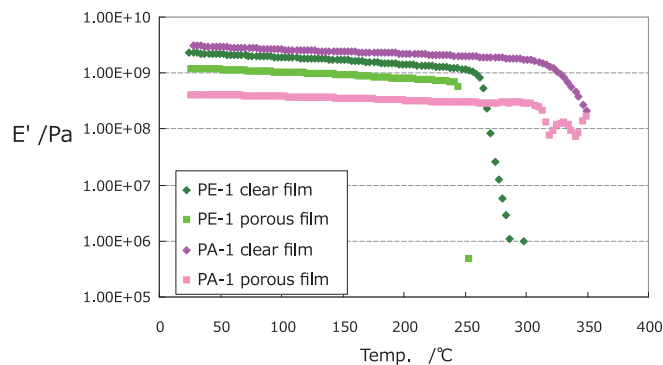Left: PE-1 film ,Right: PA-1 film

Fig. 13   Temperature dependence of strage modulus of the films
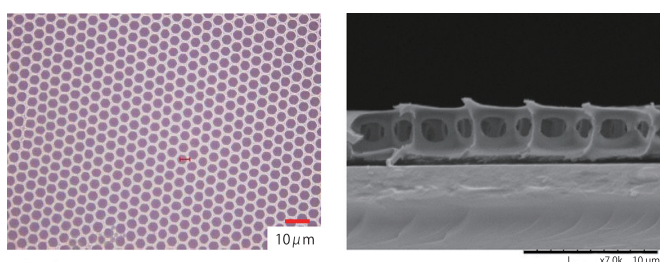

Fig. 14   Scanning electron microscopy Images of
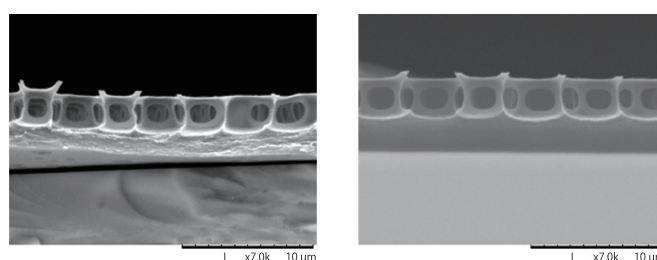PE-1 honeycomb film
Left: Top view ,Right: Side view

Fig. 15   Scanning electron microscopy Images of PE-1
honeycomb film after heat treatment for 30 minutes
at 250 ℃
Left: Before ,Right: After

Table 4   Film properties of the Porous films of PE-1, PA-1

Polymer			PE-1		PA-1	
			Clear Film	Porous Film	Clear Film	Porous Film
Mechanical	Modulus	GPa	1.9	0.90	2.6	0.35
Properties	Strength	MPa	100	40	130	14
(25℃ 60%RH)	Elongation	%	64	37	60	25
Thermal Properties	Tg (tanδ)	℃	278	247	350	325
Optical Properties	Transmittance	%	90	21	90	0.9
Density		g/cm³	1.13	～0.2	1.15	～0.2
Film Thickness		μm	50	80	50	100

had a two-layer structure with the porous layer on the air side and the uniform layer on the glass interface side (porous layer: about 65 μ m and uniform layer: about 15 μ m). Whereas, PA-1 film had only a porous layer.

As shown in Table 4, the density of porous films is about 0.2 g/cm³. This shows that the porosity is about 80%. On the mechanical properties, those films are low in strength. About the temperature dependence of storage modulus, they keep their modulus high till around Tg, just as the transparent films. It shows they maintain high self-supporting properties even at high temperatures (Fig. 13).

6.2   Honeycomb film

Honeycomb films are porous films with the pores arranged in the shape of honeycomb. Those pores are considered to form by the following mechanism. Water droplets are congealed during the film-making process and they are arranged regularly in the direction of film surface. They serve as a template and make the unique shape on the film surface [5]. Utilizing this process, we made a PE-1 honeycomb film (Fig. 14). This film consists of a two-layer structure with 5 μ m holes layer and a 10 μ m thick uniform layer. This film also has high heat resistance similar to its predecessors, for example, no deformation is observed after heat treatment at 250℃ for 30 minutes (Fig. 15).

7. Conclusion

Selecting inedible rosin as a biomass resource and using it as a starting material, we have produced various types of transparent heat-resistant films. Those films have high heat resistance, high transparency and low density that the conventional petroleum-based plastics don't have. Although at present these films are still lacking in some aspect, it is considered that there is a high possibility for better performance and more functions.

By extracting high-purity DHA-Me as fine chemicals from rosin, an inexpensive mixture, and producing dicarboxylic derivatives with a simple method; we have developed polyesters and polyamides that inherit the rosin's structural characteristics (e.g., rigidity, bulkiness and hydrophobicity a) of six-membered-ring tricyclic terpene compounds.

Utilizing these structural characteristics, we will further explore application of these films.

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