

NEW RADIATION CURABLE PREPOLYMERS PREPARED FROM PALM OIL

The present invention relates to a process for the production of prepolymers, a polyester acrylates (hereinafter referred to as PEPP), and in particular, to a process for the production of palm based prepolymers suitable in the production of radiation curable coatings such as inks, varnishes, release coatings, wood coatings and paints which contain PEPP and of good surface characteristics. These coatings are curable by ultraviolet radiation as well as by electron beam radiation and plasma radiation, which for the present purposes shall be deemed to be a form of radiation curing. In particular, this invention relates to palm based polyester acrylates prepolymers modified for radiation curable by introduction of suitable modifiers.

Radiation curable or hardenable compositions, particularly for coating applications are known in the art. Examples of reactive monomers and oligomers also referred to as radiation-curable diluents, are multi-functional acrylates and methacrylates of alkoxyated and non-alkoxyated polyols. These compounds are characterized by their low viscosity and good solvating power and are thus utilized as viscosity enhancers in UV-curing formulations. However, majority of these acrylates are derived from petrochemical refining of crude oil and coal of which are rapidly diminishing natural resources. Due to shortage of petroleum oil and the growing use of vegetable oil, it is the object this invention to synthesize the polyesteracrylates prepolymers from palm oil/or its products such as palm kernel oil, palm stearin and palm olein of both refined and crude form. The invention also included fatty acids and their esters. The invention also relates to a method for preparing such oligomeric polyester acrylates. The polyester acrylates, can be formulated into coating polymers with appropriate cross-linking agents. More particularly, the invention is directed to such polyesters having large hydrocarbon side chains which act to reduce viscosity of coating composition and provide coatings with enhanced flexibility.

It is an object of this invention to provide radiation curable coatings applied in the form of prepolymers-monomers mixture that will give abrasion resistance and solvent resistance after curing and especially to provide radiation curable film forming prepolymers.

It is further object of the invention to provide hard, abrasion and solvent resistant polymerized film without the use of solvents.

BACKGROUND OF INVENTION

The main raw materials used in the production of radiation curable coatings, particularly UV-curable coatings are oligomers, monomers, photoinitiator and additives.

The common oligomers are polyesters acrylates. Currently, majority of these polyesters acrylates prepolymers are derived from petrochemical refining of crude oil and coal both of which are rapidly diminishing natural resources. Due to shortage of petroleum oil and the growing use of vegetable oil, it is the object this invention to provide a process for preparing PEPP from palm oil products and the like. The invention also include fatty acids and their esters.

Polyesters acrylates are prepared from polyols. Polyols are generally synthesized by one or two possible chemical routes, namely alkoxylation and esterification. Alkoxylation, by far the most common way, involves the reaction between a hydroxyl functional initiator (e.g. glycerol, pentaerythritol, trimethylol propane etc) and either propylene or ethyl oxide (epoxy functionalities). This reaction is carried out at elevated temperatures.

In the preparation of polyol, CPO and RBD palm oil (PO) is used. Firstly, epoxidised palm oil is derived from CPO and RBDPO by epoxidation process, and is then converted to polyol by reaction with a hydroxyl containing initiator, such as glycerol and a catalyst.

Polyol and Polyesters polyols are a most common reactant for the syntheses of polyesters or polyesters acrylated prepolymers. The production of polyester acrylates involves the reaction between an acrylic acid or acylated monomer and polyols.

The process as herein before described involves initially the synthesis of epoxidised palm oil products via epoxidation process. For this purpose, in particular, peroxyacetic acid (PAA) and performic acid (PFA) generated in situ is found to be suitable. However, in this invention, the use of PAA is preferred because PAA gives a better yield and better controlled epoxidation process.

The product formed during this process is known as epoxidised palm oil and palm oil products (EPOP). The resulting EPOP is then reacted with pure glycerol (99%), preferably derived from palm oil and palm oil products, in the presence of boron tri-fluoride in ether (as catalyst) to yield polyols. The polyols obtained from EPOP are then allowed to react with acrylic acid or methaacrylic acid to yield the acrylated polyester prepolymers.

The acrylated polyesters prepolymers are then formulated with other monomers, oligomers and photoinitiator to be used as UV-radiation curable coatings.

The invention encompasses novel acrylated polyesters prepolymers PEPP-1 and PEPP-2 useful as prepolymers for radiation curable compositions. PEPP-1 was synthesized from RBD (refined, bleached and deodorised) palm oil or its products and product PEPP-2 was from crude palm oil (CPO) or its products. Basically, both are physically and/or structurally the same but for formation of thin polymeric film, PEPP-1 showed better performance than PEPP-2. These polyol derivatives have been found to exhibit distinct process advantages over the corresponding previously described acrylated polyesters. The prepolymers is compatible with other ingredients and improve the uniformity of films prepared from such coating formulations. The compounds of the present invention cure at a faster rate when they are

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subjected to ultraviolet (UV) radiation. Overall, the claimed prepolymers display uniquely fast curing and formulation properties, features highly desirable in the UV-curing practice.

The coating composition of this invention is prepared by mixing the polyester of this invention, alone or in admixture with other polyesters and other additives. Coating employing the polyesters of the present invention are useful for a wide variety of applications. They can be used for inks, varnishes, release coatings. Also, they can be used for other coating applications such as paints. The coating compositions made possible by the polyester of this invention are particularly useful for coating wood. It may be achieved in 2-4 passes (when conveyor speed 4m/min. and delivery current 8A).

The polyester composition of the present invention may be used as the sole polyester components of a coating composition, and coatings formed from such a composition exhibit surprisingly good flexibility.

EXAMPLES

(1) Preparation of palm-based polyols:

The palm oil product, GA-1 (1 mole equivalent, gm) and Phenothiazine (1 ppm) were placed in a 1 liter multineck reactor with an attached mechanical stirrer. The reactor was heated in an oil bath. Added 1% (mole equivalent weight) of catalyst BF_3 dropwise to reaction mixture and at the same time, the reaction temperature was increased. Once the temperature reached 80°C , palm oil product EPOP (RBDEPOP) (equivalent weight, gm) was slowly added in reaction mixture into the reactor. Completion reaction time was 4 hours. Then reaction mixture was allowed to cool, thin and then purified. For purification, reaction mixture was washed with hot water to remove unreacted GA-1, phenothiazine and the catalyst. The obtained polyol was highly viscous and white creamy color. The product was labeled as Pol-1. Pol-2 was similarly prepared as in the above procedure by using CPOEPOP.

(2) Polyester acrylates resins preparation:

Pol-1 or Pol-2 (1 mol equivalent weight, gm), acrylic acid (2 mole equivalent weight, gm), catalyst (0.05%) and inhibitor (1 ppm) and 40 ml of dichloroethane were charged in a five necked reactor flask. Reactor was equipped with a thermometer, a vacuum inlet tube, a mechanical stirrer and a water collector containing condenser. While stirring, the mixture was heated using an oil bath heating system. The reaction temperature was maintained at $< 90^{\circ}\text{C}$, under vacuum condition.

The reaction was monitored by measuring acidity number and hydroxyl values (OH) and FT-IR spectra analysis of the reaction mixture. When acidity and OH values are almost constant and the OH functionality in the reactants Pol-1 and Pol-2 were almost disappear and as well as vinyl functionality ($\text{C}=\text{C}$, IR spectra 1629 cm^{-1} and 810 cm^{-1}) of polyester acrylates, PEPP-1 and PEPP-2 appeared by the observation of FT-IR spectra, then the reaction was stopped. Reaction completion time was observed 14-16 hours.

AOCS official method Cd 1d 13-60 was used to measure the acidity values while pyridine-acetic anhydride titration technique was used to determine the hydroxyl (OH) values. FT-IR spectra was carried out by coating the samples on potassium bromide (KBr) pellets. The solvent and acrylic acids or acrylic monomers were evaporated by rotary vacuum pump and the residue of excess acrylic acid monomer was removed through water and base solution and also ion-exchange column.

After purified the products PEPP-1 and PEPP-2, their iodine value and viscosity were determined by AOCS official method Cd 1d-92. A typical results of the iodine value, hydroxyl values, viscosity of PEPP-1 and PEPP-2 are shown in Table 1.

Table 1: Iodine value, hydroxyl value, viscosity and acidity of the polyester acrylates (PEPP-1 and PEPP-2)

Properties	PEPP-1	PEPP-2
Iodine value (average)	6.71	7.26
Acidity value (average)	28.67	31.34
Hydroxyl value (average)	81.67	73.0
Viscosity (average in CPs at 25°C)	650	1000

(3) Preparation of clear coatings:

The polyester acrylates PEPP-1 or PEPP-2 from example (2) were converted into clear coatings by combining the prepolymers (PEPP-1 & PEPP-2) with synthetic oligomers, synthetic monomers, photoinitiator and curing agent according to the following formulations:

PEPP-1 or PEPP-2	(10% - 90%)
Synthetic acrylates resins	(90% - 10%)
or synthetic monomer	(90% - 10%)
photoinitiator	(1% - 6 %)
curing agent	(0.5% - 2.5%)

The ingredients were blended until uniform and then the formulated solution was coated on a clean glass plate (5 cm x 3 cm x 3 cm) and cured under UV lamp (2 kW, Type of lamp: MC200; UV range: 180-450nm) using IST-UV-Minicure (U-200-M-1-Tr, Germany). The coated plate was irradiated up to 12 passes under UV lamp at a conveyor speed of 4m/ min. in order to achieve maximum cross-linking and gel formation. The supply current was 8A of which the giving energy per pass was approximately 0.18J/cm². The

relative degrees of cure was measured by qualitative simple tests, e.g. odor, tackiness and finger marking.

The physical and mechanical properties of some UV curable palm oil based polymeric films are shown in Table 2.

Table 2: Physico-mechanical properties of UV curable palm oil based polymeric films

F	Curing Speed (UV)	Viscosity (cPs)	Pendulum hardness (%)	contact angle (0°)	TS (Mpa)	Young Modulus (Mpa)	Eb (%)	Gel (%)
RP-11	4	115.4	25	69.0	18.35	120.78	23	90.40
RP-12	4	120.5	22	68.5	10.44	108.50	28	89.84
RP-13	4	135.8	20	68.0	9.84	43.63	28	87.27
RP-14	4	146.1	20	67.83	9.62	45.78	29	85.75
RP-15	4	151.2	18	67.67	6.94	45.78	38	84.65

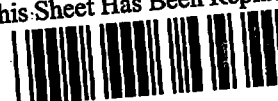
F = formulation; cps = centipoise; TS = tensile strength; Eb = elongation at break; Mpa = mega pascal (1 Mpa = N/mm²)

Table 2 shows the polymeric film properties which was prepared from both the newly synthesized palm oil prepolymers. The curing speed of 4 means that the film prepared from the prepolymer cured at 4 passes at a conveyor speed of 4m/min. Pendulum hardness properties of the UV cured polymeric films ranges from 18% to 25% depending on their formulated compositions. Contact angle is a property which shows their wettability performance. Higher contact angle means less wettability and results in better film properties. Higher tensile strength was achieved in the films that have higher hardness properties. Higher hardness or tensile films showed less elongation properties. The higher the gel content means that the films has higher cross-linked under UV radiation curing.

**CLAIMS**

1. A process for preparing polyester acrylates, a prepolymer from palm oil or a product thereof, the process comprising:
 - (i) preparing epoxidised palm oil by epoxidation of palm oil;
 - (ii) reacting the epoxidised palm oil with a monohydric or polyhydric alcohol in the presence of a catalyst to form a polyol;
 - (iii) reacting the polyol from 1(ii) with acrylic acid (AA), methacrylic acid (MA), methamethacrylic acid (MMA) in the presence of a catalyst and inhibitor to form polyester acrylates.
2. A process according to claim 1, wherein it includes palm oil, palm stearin, palm olein, palm kernel oil, palm kernel olein, palm kernel stearin, all of which could be refined or crude.
3. A process according to claim 1, wherein the alcohol used in step 1(ii) is glycerol.
4. A process according to claim 1, wherein the glycerol is derived from palm oil, or a product thereof.
5. A process according to claim 1, wherein acrylic acid is used in step 1 (iii).
6. A process according to claim 1, which is carried out at atmospheric pressure.
7. A process according to claim 1, where methacrylic acid is used in step 1(iii).
8. A process according to claim 1, wherein the acid is peroxyacetic acid.

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9. A process according to claim 1, wherein the catalyst is used in step 1(iii).
10. A process according to claim 1, wherein the inhibitor used in step 1(iii) is from hydroquinone or p-phenylthiazine or nitrobenzene.
11. The process of claim 1(iii) wherein the reaction is conducted at a room temperature from about 80°C to 90°C.
12. The polyols of claim 1(iii) wherein said polyols has a hydroxyl number of 38-53, viscosity of 113000 - 115000 cps at 25°C.
13. The EPO of claim 1, wherein said EPO has an oxirane number of 2.32% - 3.12%.
14. A clear coating prepared by blending a mixture comprising
 - (a) PEPP-1 or PEPP-2 (10% - 90%)
 - (b) Synthetic oligomers-Polyester, urethane, epoxy-triacrylate, tetraacrylates or hexaacrylates (90% - 10%)
 - (c) Synthetic monomers - monoacrylates, diacrylates, triacrylates (10% - 90%)
 - (d) Photoinitiator (1% - 6%)
 - (e) curing agent (0.5% - 2.5%)
15. A composition according to claim 14, further include 1-2% by wt. of a photosensitizer for promoting rapid cure under exposure of ultraviolet light.
16. A composition according to claim 14, wherein said higher viscosity monomer having three or more acrylate group is trimethylolpropane triacrylates.

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17. A composition according to claim 14 wherein said monomer is present in a ratio to said prepolymer within the range of about 1:1 & 4:1.
18. A radiation curable prepolymer material as defined in claim 2, containing 1-6% by wt. of a photoinitiator selected from the group consisting of acyloins and acyloin derivatives.
19. A radiation curable prepolymer material as defined in claim 14, containing 1-6% by wt. of a photoinitiator selected from the group consisting of benzoin lower alkyl ether, acetophenone, benzophenone, benzil & ketail mixtures of two or more of them.
20. The method of claim 14, wherein from 10% to 90% of the polyester acrylate is PEPP-1 or PEPP-2.
21. A prepolymer according to claim 14, in which the prepolymer is palm oil based.
22. The oligomer of claim 14, is polyester, urethane epoxy - triacrylate, tetraacrylates and hexaacrylates.
23. The monomer of claim 14, is monoacrylate, diacrylates and triacrylates.
24. The photoinitiator of claim 14, is benzophenone, benzil & ketails.
25. A radiation curable coating composition as recited in claim 14, in which said composition includes a photosensitiser rendering the composition curable with ultraviolet light.
26. A film forming coating incorporating a composition according to claim 14.

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27. Composition according to claim 15, containing in addition a curing agent.
28. Composition according to claim 15, wherein the photoinitiator is chosen from at least one of the groups consisting of acetophenone, benzophenone, & benzoin and derivatives thereof.