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Synthesis and characterization of polyesteramide based hot melt adhesive obtained with dimer acid, castor oil and ethylenediamine

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ABSTRACT

Polyesteramide based hot melt adhesives were synthesized from high purity dimer acid (composition: ~1% trimer acid, ~98% dimer acid and ~1% linoleic acid), ethylenediamine and castor oil. The effect of castor oil content on the properties of the hot melts, such as thermal properties: glass transition temperature (T_g), melting temperature (T_m), enthalpy of melting (H_m), crystallization temperature (T_c), enthalpy of crystallization (H_c) and softening point (T_s); mechanical properties: tensile strength, elongation at break and Shore D hardness; adhesion properties: lap shear strength (LSS) and T-Peel strength (TPS); and rheological properties were investigated. Ethylenediamine was replaced by 5%, 10% and 15% (molar basis) of castor oil. It was found that T_g, T_m, H_m, T_c, H_c, T_s, LSS, TPS, tensile strength, Shore D hardness and viscosity, all decreased with increased concentration of castor oil. This is due to the decrease in the crystallinity of the polyesteramide caused by conversion of amide linkages by ester linkages and increased distance between two ester linkages (due to the bulky nature of castor oil).

1. Introduction

Hot-melt adhesives (HMA) are solid adhesives which when heated are converted to a molten liquid state for application to substrates and on cooling quickly sets up the bond. [1] The substrates must be joined immediately on application of the HMA. [2] When hardened, HMA can have various degrees of tackiness depending on the formulation. Conventional HMAs cool to harden and do not chemically cross-link. HMAs have an open time from few seconds to few minutes [1].

Materials that are primarily used as HMAs include ethylene and vinyl acetate copolymers (EVA), polyethylene (PE), amorphous polypropylene (PP), block copolymers (styrene butadiene rubber, SBR), polyamides (PA) and polyester (PEster). HMAs are solid at temperatures below 80 °C. Typical application temperatures are 150–200 °C [2].

The most important advantage of HMA is the ability of being able to pre-apply e.g. as powder or adhesive spheres, in melt liquid form, as dispersion or as an adhesive foil. The joining procedure does not have to take place directly after applying the adhesive to the substrate; this can happen at any time later on [3]. The market for HMA is mainly in the manufacture of durable goods, such as shoe assembly, kitchen and bathroom cabinets, telecommunication cable repair sleeves, and window assembly [4].

First polyesteramide (PEA) based HMA was reported by Martins and Ashley in 1972. They prepared PEA HMA from dimer acid, sebacic acid, hexamethylenediamine and ethylene glycol, and had bond strength of about 13.8 MPa. PEA synthesized from dimer acid, diols and diamines have low crystallinity and wide range of melting temperatures, which make them particularly suitable to be used as HMA [5]. Krieger et al. synthesized hot melt pressure sensitive adhesive by reacting dimer acid with ethanolamine, and dimer acid with mix of ethylenediamine and dimethyl terephthalate. Prepared adhesives were found to have adhesion strength of 0.34 and 0.47 MPa respectively, and were used for sticking polystyrene labels to glass [6]. Martins and Donermeyer prepared spherical metal particles filled PEA HMAs for cavity filling applications. PEA consisted of 60% by weight of polyethylene terephthalate and 40% by weight of polyamide prepared from dimer acid and hexamethylenediamine with a minor amount of anti-oxidant. This PEA was filled with spherical alumina, iron, mild steel, stainless steel and zinc particles of varied particle size and concentration [7,8]. Veazey investigated the PEA HMA for joining vinyl based substrates. He synthesized PEA HMA by reacting 0.201 equivalents (eq.) of dimer acid with 1.82 eq. of sebacic acid, 1.95 eq. ethylenediamine, 0.21 eq. 1,4-cyclohexane dimethanol and 0.06 eq. stearic acid. Dimer acid used was of 95.6% purity. Viscosity of the polymer was determined to be 59 Pa s, softening point of 162 °C and had T-peel strength of 7.6 MPa [9]. Frihart and Veazey prepared PEA HMA by reacting 0.92 eq. dimer acid with 0.4 eq. sebacic acid, 0.41 eq. ethylenediamine, 0.97 eq. N-(2-hydroxyethyl)

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piperazine and 0.02 eq. stearic acid. Prepared HMA had viscosity of 15.5 Pa s at 195 °C and a softening point of 115 °C. It had improved adhesion strength to vinyl based substrates at low temperature (3.6 MPa at 0 °C) compared to ambient temperature (1.9 MPa at 22 °C) [10–12]. Hayes et al. synthesized PEA HMA from dimer acid (70%), sebacic acid (30%), ethylenediamine (45%) and 1,6-hexamethylenediamine (55%). Prepared HMA was found to have viscosity of 6 Pa s at 195 °C and lap shear strength of 5.7 MPa [13]. Swan and Hansen developed PEA based HMA suitable for bonding polyester and polycarbonate substrates by reacting dimer acid, adipic acid, hexamethylenediamine and ethylene glycol in varied proportion [14]. Chen et al. synthesized PEA of different viscosities using dimer acid, sebacic acid, ethylenediamine and diethylene glycolamine. They found an improvement in mechanical and adhesion with increase in inherent viscosity of the PEA [15]. They also investigated the effect of PEA addition on the properties of EVA based HMA, and found that PEA/EVA blend composition containing about 20% PEA showed highest miscibility and the best in adhesion [16].

Current study deals with PEAs synthesized from dimer acid (composition: ~1% trimer acid, ~98% dimer acid and ~1% linoleic acid), castor oil and ethylenediamine. The effect of the content of castor oil on the properties such as lap shear strength, T-peel strength, tensile strength, elongation at break, glass transition temperature, softening point, melting temperature, enthalpy of melting, crystallization temperature, enthalpy of crystallization and viscosity was investigated.

2. Experimental

2.1. Materials

Croda Chemicals, Mumbai, India, supplied dimer acid (Unidyme 18), with an acid value of 198 mg potassium hydroxide (KOH)/g sample. The contents were as follows: linoleic acid ~1%, dimer acid ~98%, trimer acid ~1%. Ethylenediamine was obtained from Ankita Chemicals, Mumbai, India. Castor oil, with hydroxyl value of 160 mg potassium hydroxide (KOH)/g sample, was procured from Adya Oils, Mumbai, India. Fatty acid composition of the castor oil was as follows: ~89.5% ricinoleic acid, ~4.2% linoleic acid, ~3.0% oleic acid, ~1.0% stearic acid, ~1.0% palmitic acid, ~0.7% dihydroxystearic acid, ~0.3% linolenic acid, ~0.3% eicosanic acid. P-toluene sulfonic acid was obtained from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. All chemicals were used as obtained without any purification or modification.

2.2. Preparation of polyesteramides

Fig. 1(a–e) shows the molecular structures of the reactants used in the study; while their molecular weights are listed in Table 1.

In order to obtain high molecular weight polymer with molecular uniformity, the ratio of total acid equivalent present in Unidyme 18 (consisting mainly dimer acid) to total amine equivalents present in ethylenediamine and hydroxyl equivalents present in castor oil was kept at, approximately, 1.

Unidyme 18 consists of ~1% trimer acid, ~98% dimer acid and ~1% linoleic acid. Basis of the reaction was 200 g Unidyme 18, which according to its composition had 2 g of trimer acid, 196 g of dimer acid and 2 g of linoleic acid. This means it had 0.002 mol of trimer acid, 0.35 mol of dimer acid and 0.007 mol of linoleic acid. Trimer acid and linoleic acid were present in a very negligible amount. So, their quantities were not considered in calculating the required quantities of ethylenediamine and castor oil. Accordingly, 200 g of Unidyme 18 was supposed to consist of 200 g dimer acid. Thus, Unidyme 18 provided about 0.36 mol of dimer acid. Number

Table 1
Molecular weight of the reactants used in preparing PEA HMA.

Sr. no.	Reactant	Molecular weight (g/mol)
1.	Trimer acid	840
2.	Dimer acid	560
3.	Linoleic acid	280
4.	Ethylenediamine	60
5.	Castor oil (major component)	934

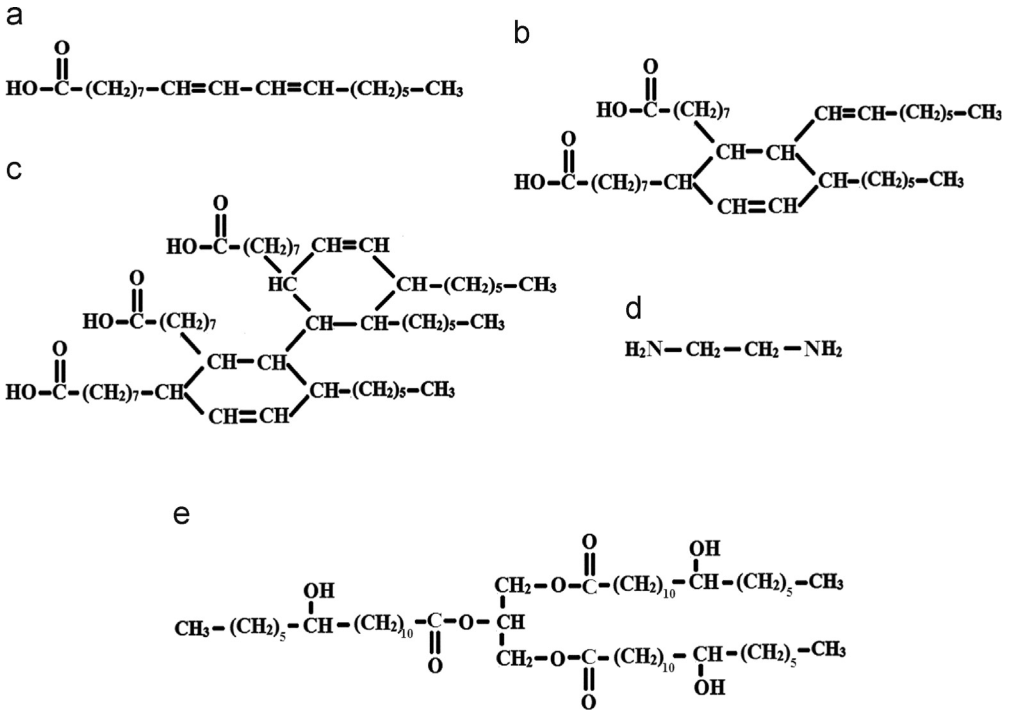

Fig. 1. Molecular structures of (a) linoleic acid, (b) dimer acid, (c) trimer acid, (d) ethylenediamine and (e) major component of castor oil.