Hot-Melt Adhesives: Fundamentals, Formulations, and Applications: A Critical Review

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Abstract: Hot-Melt Adhesives (HMAs) are typically used in applications where instant sealing is critically required. HMAs are generally preferred for those applications where processing speed is critical. These materials are widely used in various engineering applications, mainly as sealants in leakages and crack filling of walls and roofs. The industrial use of HMAs is most common in glassware and automobiles for gluing glasses in buildings and bonding heavy motor parts. The formulation of HMAs contains a polymer of suitable nature that makes the base for a strong adhesive, and waxes are added to increase the settling time of adhesive. The tackifiers are used to dilute the polymer to adjust the Glass Transition Temperature (T_g) and to reduce the viscosity for proper flow of hot-melt. This review intends to comprehensively discuss the preparation and formulations of HMAs using various polymer matrices, along with their applications and mechanics. The designing of green HMAs has been discussed in the literature and have been promoted over conventional solvent-based HMAs due to their functionality without Volatile Organic Compounds (VOCs). Various measures, challenges, and resolutions for making hazard-free HMAs have been discussed in the present review.

Keywords: Hot-melt adhesives, formulations, applications, challenges, engineering and industrial sectors

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1. Introduction to Hot-Melt Adhesives (HMAs)

HMAs are solvent-free thermoplastic materials that are applied in molten state, which upon cooling become solid. An HMA is generally composed of a high molecular weight polymer which is a synthetic elastomer with enhanced viscoelasticity, and a resin for enhancing the properties like gluiness and wetting [1–3]. Here, the polymer provides an appropriate melt viscosity and cohesiveness upon cooling. The precise HMA formulation is dictated by its bonding properties, and application conditions such as time, pressure and temperature. The most common additives for HMAs are rosins, alkyds, and phenol-formaldehyde (PF) resins. Various ranges of suitable polymers are used to make HMAs such as PVAc [poly(vinyl-acetate)], PBA [poly (butyl acrylate)], polystyrenes, polyesters, EVA (ethylene-vinyl acetate), polyethylene (PE), polyamides, amorphous polypropylene and others. A classic HMA is composed of four core constituents: polymer (~33%), resin (~33%), wax (~32%), and antioxidant (~1%). Here, the resin defines the tackiness of the HMA and also maintains the wetting of an HMA (i.e., for how long the HMA remains in liquid state after its application on the substrate). Relatively, resins have low molecular weights than the polymers but it can be said that a resin is an uncured polymer as most of the available HMAs in the market usually come in two components: resins and hardener. When these parts are mixed, the polymerization starts and the resultant product is a cured polymer. The choice of resin is always determined by its affinity with the main polymer. The resin is insoluble in water, but soluble in alcohol. Resin can also be added directly to the polymer to enhance the mechanical and chemical properties of the particular polymer. Due to the fact that the resins are usually tri- or tetra-functional molecules, and when mixed with difunctional polymers give weak mechanical properties. But, when these materials are allowed to mix with a compatible polymer, they form a cross-linked structure which is mechanically stronger than the polymer itself [4]. With higher quantity of resin, tough and strong hot-melts can be produced, while with less resin, soft and fast settling HMAs can be produced. The variety of primary constituents for a typical HMA are shown in Table 1 [3, 5]. HMAs generally exist in granules, powders, films, and blocks forms, where these can be applied to a surface as a solution or emulsion to be heat activated later after evaporation of solvent [6].

For the liquification of Hot-Melt Films (HMFs), thermal activation and solvents are used, and their solidification depends on their open time and set time, where open time is the time interval where the applicable surface remains tacky for pressure-sensitive adhesives (pressure-sensitive adhesives are a type of non-reactive adhesives which make a bond when pressure is exerted to affix the adhesive with the adherend). On the other hand, the set time is defined as the time interval required to obtain bond strength between the surface and adhesive in a temperature range of 20°C to 30°C [1, 5] (Figure 1).
HMAs have outstanding mechanical and physical properties in comparison to conventional solvent-based adhesives. Generally, HMAs are insensitive to aqueous media which means their bond strengths can rarely be influenced by water or moisture. If HMAs are used on a moist or wet surface then their bonding with the adherend may grow weak with time. Additionally, the technology of HMAs
exhibits various unique advantages in comparison to other types of adhesives. The prime benefits of HMAs are their low-cost, elimination of VOCs (Volatile Organic Compounds) discharge in manufacturing, no risk of heat burst (mainly occurs due to the chemical reaction processes in mixing two or more solvents in solvent-based adhesives), no need for adhesive dryers which are conventionally needed to dry the applied adhesive for good settling and maintaining it for long time, and modest application cost, i.e., mainly using a hot glue gun [7].

HMAs are widely used in consumer goods, and engineering sectors for manufacturing pressure-sensitive adhesive tapes, grooved boards, laminated panels of wood, etc. For instance, HMAs with trademarks KR-16-20, Krol, Krok, Krus-2, Stek, and Teplager provided by Jowat Adhesives are being widely used in metal-nonmetal bonding along with sealing of polymer composites. For a number of bonding applications, a variety of HMAs perform their function adequately. HMAs are generally preferred for applications requiring critical speeds (critical speed is the theoretical angular velocity of a rotating object such as shaft, lead-screw, gear, etc.). Hot-melts are carrier-free and solidify swiftly upon cooling, and for this reason, they have limited capability to: (i) penetrate the substrates of low-porosity, (ii) dissolve or absorb contaminants on the surface, and (iii) wet-out metals. HMAs are good choices in automated production due to their fast speed of setting. A large variety of HMAs are chemically inert and remain thermoplastic during their use. In this review, we discuss the formulations, design principles, mechanical behavior, HMA tests, and applications, along with the current challenges of HMAs and how to meet them.

2. Formulation of Hot-Melt Adhesives

2.1 Theories or Mechanisms of Adhesion

Adhesion usually is classified by physical, chemical, and/or mechanical bonding processes, which give the interfacial strength to the joint. The adhesion bonding occurs between the adherend and the adhesive. Over the years, various theories have been established to describe the phenomenon of adhesion. Mechanical bonding is a highly efficient technique for creating joints, but it fails to join smooth surfaces. Chemical bonding is strong but it is difficult to produce in an efficient manner [8–12]. Each theory of adhesion for bonding of materials is discussed in more detail below.

2.1.1 Mechanical Interlocking Theory

Mechanical theory is the common and the oldest theory of adhesion. It involves penetration of adhesive in pores, cavities, and irregularities on the surface of adherend and was proposed by McBain and Hopkins in 1925 [13]. It displaces the trapped air at the interface, which determines the adhesive penetration into both
adherends. It was also found that adhesives form good bonds with porous and irregular surfaces as compared to smooth surfaces [8–11].

2.1.2 Electrostatic Theory
According to this theory, adhesion takes place at the adhesive-adherend interface due to exchange or transfer of electrons across the interface. Such transfer forms an electrical double layer at the adhesive-adherend boundary and results in Coulomb attraction forces between the mating partners [8–11].

2.1.3 Diffusion Theory
According to this theory, diffusion is only valid when both the adhesive and the adherend are polymers with relatively long chain-like structures, which deliver mobility, and permit the possibility of the chains to have molecular movements in the sub-molecular range. The diffused interfacial layer has a thickness in the range of 1–100 nm, and it is dependent on various parameters such as pressure, time, temperature, molecular size, and mutual solubility [8–11].

2.1.4 Physical Adsorption or Wetting Theory
According to adsorption theory, the forces responsible for adhesion between two materials are secondary valence or van der Waals forces. The process of forming contact between the adhesive and the adherend is known as “wetting”. For an adhesive to wet a solid surface, the adhesive should have a surface tension lower than the critical surface tension of the solid. This is the reason for surface treatment of plastics, which increases their surface free energy and polarity [8–11].

2.1.5 Chemical Bonding
This mechanism is quite similar to the physical adsorption but it involves the formation of hydrogen, covalent, and ionic bonds between the adhesive and the adherends. In general, there are four types of interactions during bonding such as covalent, hydrogen, Lifshitz-van der Waals forces, and acid-base interactions, but the exact nature of bond depends on the chemical structure of the adherend (substrate). The fabrication of adhesives based on chemical bonding theory has been adopted for decades by various industries, but the results have been disappointing due to their contamination with external environmental factors like air, moisture, temperature, etc. which made the adhesion unstable and weak [8–11].

2.2 Intermolecular Forces between Adhesives and Adherend
The numerous adhesion theories imply the existence of physico-chemical interactions across the interface of adherend and adhesive. The development of an adhesion bond relies on increasing the intermolecular attraction between the two
surfaces, both in the polymer bulk and between the adhesive and adherend. Among the different forces accountable for intermolecular attraction, primary forces are dispersion forces acting in all atoms and are responsible for all of the molecular attraction or cohesion in all molecules, excluding the polar molecules. Dispersion forces are short-range interaction forces that are effective at a distance of 4 Å, and rapidly decrease with the inverse 6th power of the intermolecular distance. Hence, the molecules of adhesive polymer must be sufficiently flexible to come within this interaction range with a rigid adherend surface under bond formation conditions. Additional interaction arises between dipoles in molecules, where dipoles arise when the chemically bonded electrons among atoms are shared unequally, thus creating positive and negative charge centres in the molecule. The force of interaction due to permanent dipoles of polar molecules depends on strength of the two dipoles, and is reduced with the inverse 6th power of the distance. Evidently, the dipolar interaction of adhesives will be strong when they possess polar chemical groups [14]. A strong dipolar attraction occurs when the positive centre is connected with the H-atom attached to an electronegative atom, generally N or O, as shown in the following examples

\[ \delta^+ \delta^- \quad \delta^+ \delta^- \quad \delta^- \delta^+ \quad \delta^- \delta^+ \]

\[ -\text{C=O} \ldots \quad \text{H-N} \ldots \quad -\text{O-H} \ldots \quad \text{O-H} \]

This sharing of proton between electronegative atoms is called the hydrogen bond. It arises in polymers carrying amide (-CONH-), carboxyl (-COOH), or hydroxyl (-OH) groups, and is responsible for adhesion of materials such as proteins, starch, poly(vinyl alcohol), epoxy resins, phenolics to polar substrates, especially to wood which has an abundance of hydroxyl groups [15, 16].

2.3 Thermodynamic Model of Adhesion

The thermodynamic work of adhesion, wetting surface tension, solubility parameter or interfacial free energy are responsible parameters for the strength of adhesive bonds. Adhesive bonding is controlled by intermolecular forces, where the attraction forces between adhesive and adherend are defined by an energy interaction that can be characterized by the Lennard-Jones potential [17].

\[
F = \frac{d}{dr} \left[ \frac{A}{r^6} + \frac{C}{r^8} \right]
\]

where, F denotes the force of attraction, r denotes the separation distance between an adhesive and adherend with the variables A and C as adhesion constants. The Force of Attraction vs Distance of Separation graph is illustrated in Figure 2.

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The basic equations provided by Dupre and Young-Dupre for the thermodynamics of adhesion are as follows:

(I) Dupre Equation: 
\[ W_A = \gamma_S + \gamma_L - \gamma_{SL} \]  

(II) Young-Dupre Equation: 
\[ W_A = \gamma_L (1 + \cos \theta_{LS}) \]  

where, \( \theta_{LS} \) is the equilibrium contact angle made by L (liquid) phase in contact with S (solid) phase.

The maximum strength and flexibility of an HMA bond are obtained when the interfacial free energy is minimum [18]. The interfacial free energy of the system is obtained by reorganization of Equations (2) and (3) as:

\[ \gamma_{SL} = \gamma_S - \gamma_L \cos \theta_{LS} \]  

### 2.4 Bonded Joints

The lap-shear tests determine the various HMA designs based on the strength of joints and Length of Overlapping (LO). There is an approach known as IAI (Incorrect Assumption Inherent) which defines that the stress in hot-melt joints is uniform; therefore, doubling the LO can bear double the loads in an HMA. The fundamental principle for designing an HMA bond is to formulate the bond in such a way that the adhesive strength is always higher than the strength of the adherends. This approach facilitates the formation of stronger HMA joints in comparison to the parent material from which the HMA is formulated. The facility to design bonded HMA joints occurs in such a way that the adhesive part can never be the weakest portion of the joint. If the HMA will not fail due to the applied...
load, then there is no requirement to make comprehensive design of the HMA joint because the load will never cross its limit for parent material used for fabricating HMA. It has been shown that if the load capacity is greater than the strength of the parent material, the adhesive will not fail and will provide an adequate joint (eq 5) [19]. This work was proposed by Hart-Smith at the Douglas Aircraft Company and was mentioned in a technical report NASA CR 112236 [20].

\[ P = \sqrt{2\eta \tau_p \left( \frac{1}{2} \gamma_e + \gamma_p \right) E_0 \eta t_0 \left( 1 + \frac{E_0 t_0}{E_i t_i} \right)} \]  

(5)

where, \( E_i \) denotes the elastic modulus, \( \tau \) denotes the adhesive shear stress, \( \gamma_e \) denotes the elastic adhesive shear strain, \( \gamma_p \) denotes plastic adhesive shear strain, \( P \) denotes the applied load on the joint, \( \eta \) denotes the thickness of the adhesive layer, \( t_i \) is the thickness of the adherend, \( t_o \) is thickness of substrate, \( \tau_p \) is the plastic adhesive shear stress, and \( E_0 \) represents the adhesive peel modulus. It is a well-known fact that a higher adherend bending stiffness imposes a greater strain concentration on the adhesive than a low bending stiffness. Most of the structural engineering studies show the resilience of an HMA joint to be related to fatigue. This assumption is not completely true because most of the issues are provoked by ambient factors rather than fatigue loads. Various experimental models explain that accurately formulated HMAs do not exhibit fatigue failures. Adhesive fatigue test is to confirm that the LO is adequate to qualify shear stress of an HMA to make a creep-resistant joint [21].

2.5 Surface Preparation for HMA Application

The misunderstanding in the preparation of a surface is that the only condition for a good HMA bond is a requirement of clean surface. It is an essential condition for adhesion but is not enough for the durability of bond. Most of the structural HMAs work by chemical bond formation, mainly covalent, among the surface atoms of adherends and the components (polymers) forming the adhesive. In general, an adhesive can be defined as a material used to transfer loads between adherends in service environments that are typically load bearing, i.e., an adhesive is a substance that is capable of holding materials together by surface attachment. Bond strength on a short-term basis can be easily obtained by less surface preparation like normal cleaning, air pressure cleaning, and is independent of other factors, but long-term strength relies on the chemical bond resistance and degradation time of HMAs [22]. It is crucial to prepare metallic surfaces before bonding because poor metallic surfaces form oxides due to hydration, which leads to a displacement reaction on the surface and eliminates the chemical bonding of adhesives and adherends, leading to
adhesion failure. The fundamental requirement for surface preparation is that the surface must be (i) contamination-free, (ii) active for chemicals to facilitate chemical bonding between adhesives and adherends, (iii) environmentally corrosion resistant [23].

2.5.1 Solvent Degreasing

Solvent degreasing is an imperative step to eradicate contaminants from an adherend surface which otherwise prevent the development of chemical bonds. Solvent degreasing provides a perfect surface condition but does not result in surface free energies required for bond stability over a long time as some adhesives need a minute etching on the surface for their better adhesion, and this molecular requirement cannot be fulfilled by solvent degreasing completely. Solvent degreasing must be done in meticulously clean conditions to avert re-contamination of adherend surface. Removal of contamination from the adherend surface is the main step in the preparation of surface as degreasing treatment with chemicals leaves a thin contaminant layer of solvent that can later affect adhesion. Maintenance of adherend surface is necessary such that the solvent should not degrade the surface structure. For instance, acidic chemical greases like HCl and other chlorinated hydrocarbon compounds can lead to surface corrosion. Solvents with fast evaporation rate are the best for use in hand degreasing because of their rapid evaporation. The faster the evaporation, the lesser the contamination of surface occurs. The degreasing of the surface should always be completed using evaporable solvents, not by any soap or detergents [19, 24, 25].

2.5.2 Chemically-Active Surface

A fresh chemically active surface is required for an HMA bonding process, where abrasion and etching can be useful in producing such surfaces. Industrial applications use etching methods for surfaces of metals and laboratory applications use the process of abrasion. The real purpose of abrasion is to make a fresh and chemically active surface for HMAs. Abrasion can be done using pads, papers, hands or by grit blasting. The method of grit blasting is much more effective than the hand abrasion but facilitates the formation of folded (cavity-based) surfaces that can trap moisture and contaminants. The HMA bonding relies only on the chemical reactivity and cleanliness of the surface. Sometimes, it is challenging to eradicate sand particles from the surface; therefore, it becomes necessary to use a suitable solvent after abrasion that can completely wash-off the particles from the surface. These particles can be removed by incorporating a dry wipe-out process until completely clean. The process of grit blasting is a much more effective technique in making an active surface as it is contactless process. One of the primary requirements of grit blasting is that the abrasive material should just scratch the active surface, not punch it [26]. For this reason, beads of glass, husks, metal shots, and sand powders are not well-suited and are not used. Aluminium oxides and
zirconia powders are also very effective as abrasive materials [27]. Along with all the properties and functionalities, the abrasive material or powder should not be re-used to prevent re-contamination of active exposed surfaces [28, 29].

3. Fundamental Aspects of Adhesive Behavior of HMAs

There are a variety of methods available to test the adhesive property and bonding quality of HMAs. The methods are also known as tensile creep tests as these tests involve the application of an opening stress on the bond at a temperature at which it starts to resist adhesion after a particular period of time [30]. The key role of an HMA is to bond two materials; so, it is vital to predict the adhesion behavior and factors affecting it. The behavior of an HMA also depends on the two adherends in the adhering system as well as on the active working medium and environment. Here are some HMAs performances in different conditions.

3.1 Mechanical and Physical Behaviors

To recognize the adhesion behavior between two substrates, it is essential to examine several properties and functionalities of HMA films responsible for adherence [31], mainly, mechanical behavior. A study by Park et al. [32] examined the miscibility, thermal, and viscoelastic properties. They also demonstrated the lap shear strengths of Poly (EVA) (poly (ethylene-vinyl acetate)) HMAs combined with EVA copolymers with Aromatic Hydrocarbon Resin (AHR) using the calorimetric techniques of Differential Scanning Calorimetry (DSC) & Dynamic Mechanical Thermal Analysis (DMTA) at 1 Hz frequency at 3°C under the effect of liquified nitrogen. The blending of polymers was done using EVA-20, EVA-150 and EVA-400 and mixing them with tackifier P-120 in an internal mixer of 300 g at 30 RPM at a temperature of 170°C. Firstly, the EVA copolymers and antioxidant Irganox 1010 were used to prepare a blend ratio of 5:5 to make EVA-HMA films using compression molding. This research group verified the relationship between thermal-viscoelastic behavior and adhesion (lap shear strength). The adhesive joint was obtained by applying pressure to the HMA film in between two plates of stainless steel at 180°C for a time interval of 5 minutes. The thickness of bond-line was 0.1 mm. Single lap shear strengths were measured using a Z101 Testing Machine at speeds of 10, 50, 100, 300, 500, and 1000 mm/min and temperatures of 25, 40, 55, and 70°C (Figure 3).

The thermal properties of EVA-CoP and AHR copolymers were determined using DSC. Figure 3(A) shows Tg and melting temperature (Tm) of copolymers. The EVA copolymers exhibited Tg approximately at 30°C and a strong endothermic peak, whereas AHR, P120 exhibited Tg approximately at 70°C. Generally, the Tm of EVA copolymers was influenced by VA (vinyl acetate) constituent of EVA copolymers but less influenced by the melting index of EVA copolymers. The Tm values of EVA copolymers are comparable, in that their heat of fusion reduced
with growing melting index of EVA copolymers. $T_g$ and $T_m$ of EVA copolymers are alike whereas their heat of fusion and melt viscosity diminished with cumulative melting index because there is a requirement for less energy for mobility and flow. Figure 3(B) demonstrates the EVA copolymer blends’ thermograms with 50 wt% of AHR, P120.

### 3.2 Blending Behavior and the Effects of Other Ingredients

The blending behavior of HMAs is very vital, as an HMA is a complex blended system. Noteworthy experiments and studies have been reported in the literatures [33]. Saiz-Arroyo et al. [34] examined the blends of poly(ε-caprolactone-lactic acid) and poly(lactic acid) (PLA) for application in HMAs. The outcome of this study identified partial miscibility in the amorphous phase of the blend, but no random miscibility could be spotted in the block copolymers. The stereochemistry of PLA could be accountable for morphology and the adhesive property of holt-melts. Duffy et al. [35] examined the structural effect of polyester on morphological developments and structural interactions in ternary blends. This group also examined the adhesion performance of HMAs and poly-PO (propylene oxide) and poly MMA-co-nBMA (methyl methacrylate-co-$n$-butyl methacrylate) blended with poly (HMA). The study found that changing the structure of polyester firmly changed the miscibility behavior and BIP (Binary Interaction Parameter) that can be used to analyse spinodal and binodal structures. The above examinations can be used for an overall understanding of blending behavior of a simple HMA using investigational techniques like DSC. A range of physicochemical and mechanical behaviors may occur due to the interchanges between ingredients and additives for complex HMA systems. Therefore, it is problematic to fully recognize contributions of respective ingredients in defining the overall performance of an HMA. To improve the action of an HMA, it is also essential to balance tacky resins, waxes,
plasticizers, etc. For this reason, it is also essential to understand every ingredient, mainly its configuration and structure in shaping the bulk properties of HMAs. Fernandes et al. [36] used thermogravimetry, DSC, and a universal tensile machine to examine the adhesive strength of a 3-component HMA. The study found that all HMA preparations displayed a direct connection between the Glass Transition Temperature and the adhesive shear strength.

3.3 Polymeric Behavior

The polymers used in HMAs play a decisive part in their mechanical behavior such as strength and toughness. Therefore, it is tremendously vital to determine the role of HMA polymer. In a general system of HMA, polymers mostly affect the following properties: (i) Viscosity and Rheology, (ii) Cohesive strength, (iii) Flexibility, and (iv) Adhesive strength [5, 37]. EVA is the most commonly used copolymer in the current engineering applications. A range of EVA grades engineered with variable VA fillings coupled with variable melt indices (viscosities) are used due to their substantial importance. It has been documented that larger contents of VA produce greater adhesion with enhanced flexibility. The higher content of VA requires higher cost. For instance, EVA based hot-melts utilize an average of 28% VA and usually 40% binder in the formulations [30]. The adhesion property of HMAs was dominated by the use of polymers which affected HMA performance. Various polymers with their functional characteristics are shown in Table 2.

4. Preparation of HMAs Using Various Polymers

In general, hot-melts are the thermoplastic materials that are used for adhesive purposes by melting them. The preparation of HMAs involves a series of experiments followed by some initial processes like the selection of appropriate polymers, additives, resins/wax and other components that can be helpful in enhancing the HMA performance. The three latest significant researches in the preparation of HMAs are as follows.

4.1 HMAs by Grafting Acrylic and Crotonic Acids on Metallocene Ethylene-Octene Polymers

A recent study by Pavlinec et al. [38] discussed the preparation of an HMA by grafting of acrylic and crotonic acids onto metallocene ethylene-octene copolymers. In preparation of the sample, an atmospheric plasma generator was used to treat Resinex RXP (commercial polymer) powder under a flow of O$_2$ + O$_3$ (Oxygen and Ozone) at a temperature of 25°C where the generator was operated at a power of 300 W, 5 l/min of O$_2$ input, and 5 l/min flow of gas (O$_2$ + O$_3$). After polymer activation for 3 hours, the concentration of H$_2$O$_2$ on RXP was determined by analytical
4.1.1 Solution Grafting

Grafting in solution was done by dissolving activated 7.5 g of Resinex PE RXP 1502 (RXP), a commercial metallocene ethylene–octene polymer in 150 ml of toluene at a temperature of 70°C. The system was purged with N₂ to produce an oxygen-free condition, about half an hour before the reaction. After adding NaLS (sodium lauryl sulphate) and AA (acrylic acid), the process was initiated at a temperature of 110°C. The reaction temperature was maintained for about 120 minutes. Then, by adding methanol to the reaction mixture, the grafted RXP-g-AA was precipitated. During the reaction process, the unreacted AA and the PAA (poly (acrylic acid)) appeared in the mixture as sediments that were dissolved in methanol to remove them out of the precipitated RXP-g-AA by repeated extraction using methanol.

Table 2 Some most common polymers used in hot-melts with their characteristics.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Vinyl Acetate (EVA)</td>
<td>Most common polymer for HMAs, versatile adhesive, good compatibility with various tackifiers, and wax/resin can control the set time</td>
</tr>
<tr>
<td>Polyolefin (PO)</td>
<td>General-purpose adhesive, good thermal stability, high resistance to acids, and can blend with other polymers</td>
</tr>
<tr>
<td>Amorphous Polyolefin (APO)</td>
<td>Soft and flexible, high open time, low surface free energy, compatible with wet surfaces, high fuel and heat resistance</td>
</tr>
<tr>
<td>Polyamides (PAs)</td>
<td>High-performance HMA, low melting points than amides, need fewer additives, high temp. resistance, slightly more expensive than others</td>
</tr>
<tr>
<td>Polyurethane (PUR)</td>
<td>Cross-links in humid conditions, has terminal isocyanate groups, reacts with ambient moisture and changes to thermoset instead of thermoplastic</td>
</tr>
<tr>
<td>Styrene Block Copolymer (SBC)</td>
<td>High resistance to heat, fast setting of HMA, can blend with other polymers like SBS (Styrene-Butadiene-Styrene) and SEBS (Styrene-Ethylene-Butadiene-Styrene)</td>
</tr>
</tbody>
</table>
4.1.2 Melt Grafting
Brabender Plasticorder with a chamber of 30 ml at a temperature of 110°C for about 30 minutes was used to adjust the activated RXP powder. The filling of the system chamber with a polymer solution and polymer melt with the wetting agent such as NaLS was done at 80°C for 5 minutes. The temperature was kept marginally higher than the RXP melting temperature. The initial blade speed was 15 RPM and was increased to 30 RPM after 5 minutes. Then, the monomer was added in steps for the next 5 minutes. At the same time, the reaction mixture was heated at 110°C to initiate the grafting procedure, and the speed of mixing was maintained at 50 rpm for 30 min during the reaction.

4.1.3 Preparation of HMAs
HMAs were formulated by mixing of RXP polymer with 10% GTL Sarawax SX105 (a synthetic hard paraffin wax) in a Brabender Plasticorder mixer of 30 ml chamber at a temperature of 110°C for 30 minutes.

4.2 Cross-Linked Polyurethane Hot-Melt Adhesives (PUR-HMAs)
A PUR-HMA generally means a low molecular weight, cross-linked, permanent structure arising from the reaction of polyurethane with the ambient moisture [40]. In comparison to thermoplastic Polyurethane-HMA (PUR-HMA), a cross-linked PUR-HMA has higher adhesion strength, and improved heat, acid, and chemical resistance [41]. Chemical structural design of a dynamic PUR-HMA is shown in Figure 4 (DBTDL denotes Dibutyltin Dilaurate).

The polycondensation of DMG (Dimethylglyoxime), poly-THF (tetrahydrofuran), glycerol, and 4,4′-methylenebis (phenyl isocyanate) was used to synthesize the dynamic PUR-HMA. The monitoring of this reaction was done by ATR-FTIR (Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy). The formation of a urethane component was indicated by the disappearance of isocyanate signal at 2275 cm$^{-1}$ and introduction of a new signal at 1733 cm$^{-1}$. For evaluation studies, 1,4-butanediol-CPU (Cross-linked Polyurethane) was produced to replace dimethylglyoxime as a regulator of the chemical process. The formation of a carbonyl peak was observed around 1720 cm$^{-1}$ and disappearance of NCO (isocyanate) peak at 2275 cm$^{-1}$ confirmed the completion of reaction. The TGA (Thermogravimetric Analysis) studies showed that the PUR-HMA displayed thermal stability with a weight loss of only 5% up to a temperature of 214°C. The dissociation of oxime-carbamate bonds was indicated by a consistent weight loss of PUR-HMAs about 13% from a temperature of 186°C to 240°C. The PUR-HMA was found to be a stiff elastomer with tensile strength of 7.64 MPa with an error margin of 1.06 MPa and elongation of about 56%. A high elastic modulus of 77.60 with a margin of 14 MPa was found for PUR-HMA, which was found to be valuable for durable adhesion. The dynamic PUR-HMA was produced with favorable mechanics for numerous potential adhesive applications.
4.3 Soybean Protein Isolate and Polycaprolactone Based HMAs (SPIP-HMAs)

The combination of synthetic biodegradable thermoplastics with natural polymers can have practical advantages in minimizing the environmental impact, low toxicity, inherent biodegradability, and overall low-cost of the adhesives [42]. Soybean proteins can be incorporated in HMAs due to their good adhesive compatibility and other properties [43, 44]. Soybean proteins are also available commercially in various forms in different concentrations of proteins like Isolated (SPI, >90% protein), Concentrated (SPC, 50–70%) and Flour (SF, <50%). Tous et al. [45] demonstrated the preparation of HMAs using Soybean Protein Isolates and Polycaprolactone. The materials used in the preparation of SPIP-HMAs were SPI (87% w/w), and Polycaprolactone. In the preparation technique, the adhesives were produced by combining SPI (Soy Protein Isolate) (25% w/w) and PCL (polycaprolactone) (50% w/w) in a two-step process initiated at a temperature of 80°C for 5 minutes and later at 140°C for 15 minutes. Once the PCL was melted, the castor oil was added to the mixture at 25% and 50% w/w PCL. As a tackifier, the pine rosin was used to enhance the adhesive strength. Different tackifier concentrations were used to formulate various SPIP-HMAs for testing purposes. The rheological study on produced HMAs was carried out by applying them in molten form and allowing to flow with the purpose to wet the surface of the substrate and for assurance of adhesion. Figure 5 shows a representative rheological curve for PCL blended with 25% SPI and 25% of CO (Castor Oil). In this curve, three stages can be recognized:

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Firstly, a viscous behavior is seen at a temperature of 120°C ($G'' > G'$), secondly, point of gelation ($G' = G''$) and lastly, the solid behavior ($G' > G''$), where $G'$ is the storage and $G''$ is the loss modulus.

5. Mechanical Analysis of Hot-Melt Adhesives

Mechanical analysis of HMAs is used to characterize materials and to analyse their mechanical properties. Both the temperature and time contribute to the variation of mechanical properties of a polymeric HMA in a deformed (distorted) state. The polymeric components in a material exhibit properties of viscous liquids and elastic solids as they both are viscoelastic materials [46].

5.1 Fracture Mechanics of HMAs

Fracture mechanics is an important approach for understanding and avoiding failures of HMAs for different engineering applications. Debonding propagation can occur swiftly for quick growth of crack during critical fracture of an HMA [47]. An HMA for specimen in the fracture test can be designed for test purposes where some steps are taken during manufacturing to prevent the formation of defects. A fracture in an HMA can arise in a pure manner or combination of the three modes (i) Opening-Mode I (ii) Forward Shear-Mode II, and (iii) Tearing-Mode III is shown in Figure 6. By using the SERR (Strain Energy Release Rate) approach, a critical fracture is presumed to occur when the driving force or SERR ($G$) reaches critical SERR ($G_c$) for a bonded system. For a subcritical fracture, the crack propagation rate depends on various factors such as the available energy release rate, viscoelastic property of materials, ambient conditions, and the mode.

Figure 5 Rheological Curve for PCL blended with 25% SPI as well as 25% CO (Reprinted with Permission from Elsevier, Copyright © 2019 Elsevier).
of fracture. In accordance with this theory, the strain energy release rate is the quantity of energy per unit crack area imposed by conditions of loading given by the relationship [48]:

$$G = \frac{\partial (W - U)}{\partial A} \quad (6)$$

In this expression, $W$ is the work done externally, $U$ is the energy stored elastically and $A$ is the crack area. The failure criterion states that the crack shows applied energy rates which extend to a certain critical level. This critical level is also termed as fracture energy, $G_c$.

The SERR method is broadly used in various bonded systems. For homogeneous materials, SIF (Stress Intensity Factor) approach (used for predicting the stress state near the crack tip) and strain energy release rate can be equivalent [49]. For analysing cracked systems, a fracture can be used very efficiently for the system subjected to linear loads and deflections [50]. In this case, the rate of energy dissipation can be defined as [49]:

$$G = \frac{1}{2} p^2 \frac{dC}{dA} \quad (7)$$

where, $C$ denotes the compliance of the system, which is related to the generalized displacement like rotation, volume, etc. and $P$ denotes pressure, momentum, etc. The various other mechanical tests like peel test and stretching of membranes can also be explained by this equation [51]. The most common difficulties and arguments against the fracture mechanics approach is the need to examine and study an actual crack. The early errors can be minimized by maintaining good quality of the preparation of surface and bonding. The classical fracture mechanics cannot be conducted without incorporating a crack. This challenge was overcome by the advancement of the Cohesive Zone Method (CZM) that can facilitate damage progression from the starting point through crack propagation [52, 53].
5.1.1 Fracture Energy Measurement

The critical strain energy release rate \( G_c \) for a perfectly brittle material should be the energy required to generate new surfaces. For satisfying this ideal thermo-dynamic condition, the \( G_c \) for crack propagation would be doubled because of the two faces of crack. The work of adhesion (thermodynamic) at the interface of two materials in debonding can be given by \( W_{adh} = \gamma_1 + \gamma_2 - \gamma_{12} \), where, \( \gamma_1, \gamma_2, \) and \( \gamma_{12} \) are the surface free energies of materials 1, 2 and the interface, respectively. \( W_{adh} \) is usually calculated using the measurement of energy released in the process of wetting and is expressed as mJ m\(^{-2}\). These parameters are enormously valuable in formulating the thermodynamics of an adhesive on an adherend \([54, 55]\). Fracture energies are correlated with the ratios of viscoelastic loss and storage modulus in polymers and adhesive joints \([56, 57]\). If a fracture test needs to be performed at an infinitely slow rate at elevated temperatures, \( W_{adh} \) should be definitely minimized. The \( W_{adh} \) calculated at critical test speeds is sometimes of larger magnitude than intrinsic adhesion. Although the intrinsic and practical \( W_{adh} \) are significantly higher than the thermodynamic \( W_{adh} \) \([58]\). In general terms, practical \( W_{adh} \) is the result of several adhesion tests like shear, peel, tensile, etc. and intrinsic \( W_{adh} \) is the limiting fracture energy when a fracture test is performed at an infinitesimally slow rate at an elevated temperature or under Time-Temperature Superposition Principle given by Ferry. This practical relationship can be stated in various forms where one of them is: \( G_c = W_{adh} \{1+\varphi(a,T,\ldots)\} \) and \( G_c = G_0 \{1+\psi(a,T,\ldots)\} \), where, \( G_c \) depends on either \( \varphi \) or \( \psi \) which are dissipation functions and depend on temperature, debonding and other aspects. Figure 7 illustrates that the magnitudes of adhesion (thermodynamic, intrinsic and practical) which shows that \( G_c \) depends on temperature and debonding rate \([59]\).

5.2 Stress-Strain, and Frequency-Temperature Sweep Tests for Viscoelasticity

In a DMA, the HMA sample of a particular polymer is distorted at regular intervals, generally under forced vibrational setting. The strain in such materials is measured to govern the complex modulus for monitoring the relationship between stress and strain with altering temperatures. Park and co-workers \([60, 61]\) carried out mechanical analysis on an EVA-based HMA-hydrocarbon resin at temperature from 100°C to 75°C, as higher temperatures can also lead to melting of polymers. In the study, the Storage Modulus (\( E' \)) of the blend material was observed in the range of 0°C and 25°C (Figure 8), and the Loss Modulus (\( E'' \)) of the blend material was found to increase at 30°C, 27°C, and 17°C, for P-90, P-120 and P-140, respectively.

Apart from this study, some other test techniques used to measure the viscoelastic properties of polymers constituting an HMA are Sweep Methods (frequency and temperature). Frequency sweep is usually used for representing the
time-dependent behaviour of an HMA material in non-destructive deformation region. Fast motions are accelerated by using high frequencies on shorter time scales, and slow motions are accelerated at low frequencies on longer time scales. The inner structures and behaviors of an HMA polymer can be seen by using these proven FS (Frequency-Sweep) methods. In the FS procedure, the HMA

Figure 7 Relationship between Thermodynamic, Intrinsic and Practical Adhesion. (Reprinted with Permission from Elsevier, Copyright © 2010 Elsevier).

Figure 8 $E'$ and $E''$ versus Temperature for EVA-20 HMA Blends with 50 wt% of P-90, P-120, and P-140. (Reprinted with Permission from Elsevier, Copyright © 2006 Elsevier).
sample is held at a static temperature and subjected to testing at varying frequency ranges. This method is intended to study the mechanical behavior of HMAs from higher to lower frequencies as this process reduces the test procedure time. The viscoelasticity can also be given by Maxwell’s equation which states:

\[ E'' = \frac{E\tau_0\omega}{\tau_0\omega^2 + 1} \]

where \( E \) is the elastic modulus, \( \omega \) is a function of frequency, and \( \tau_0 \) is the Maxwell relaxation time. The two modes for presenting the deflection are (A) Controlled Strain (B) Controlled Shear Stress. In the temperature sweep method, the frequency at which the sample is to be tested is kept constant, and the range of temperature is varied to determine the complex modulus [62]. A prominent peak can be observed at the \( T_g \) of the polymer constituent of the HMA sample. This test can be advantageous for new resins and raw materials and to control the viscosity of HMAs as a function of temperature. To positively predict the processability of HMAs, it is vital to describe properties like viscoelasticity and its dependence on temperature [63].

6. Industrial Applications of Hot-Melt Adhesives

HMAs offer numerous advantages and benefits over other materials, and thus find innumerable applications in different fields. There is a variety of HMAs with distinct melt index values along with outstanding adhesive property. The properties and features of HMAs can also be modified depending on the desired application as they offer the advantage of being compatible with additives (plasticizers, tackifiers, etc.) incorporation. For instance, EVA-based HMAs can be used for the prevention of corrosion, but often face failure on industrial level applications due to poor adhesion and processing difficulty. This problem was solved by incorporation of magnetite (Fe\(_3\)O\(_4\)) nanoparticles into EVA-based hot-melt adhesives. The incorporation of magnetite nanoparticles improved the interfacial adhesion property of EVA-HMAs and made their industrial application possible. The typical applications of hot-melt adhesives (HMAs) are drug delivery, medical aids, bone repair, food packaging, heat sealing, electronic assembly, textiles, and anticorrosion applications. Some of these applications are described in this section.

6.1 Medical Applications

HMAs have a large number of fascinating applications in the medical field. The Hot-Melt Pressure-Sensitive Adhesives (HMPSAs) are used to fabricate medical adhesive bandages or tapes with high moisture removal rate, which are beneficial in reducing skin problems caused by the accumulation of moisture. Another important application of HMPSAs is the transdermal drug delivery. The most common pressure-sensitive adhesives used for drug delivery are acrylics with excellent adhesion property. The transdermal drug delivery using PSAs (Pressure-Sensitive Adhesives) is possible via two ways, either by holding the drug in the patch reservoir attached
to the skin or by adhesives (commonly silicone-based PSAs) acting as drug carrier. The transdermal drug delivery can be accomplished via both routes along with the advantage of minimum toxicity. PSAs are also used as a connector between skin and gel contacting metal electrodes in electromedical devices (electrically connecting skin and apparatus). Peel models for cell adhesion are also available using HMA polymeric substrates [64]. The most common polymers for this connector application include water-swollen hydrophilic crosslinked polymers, for instance, acrylic acid-based UV curable PSA crosslinked by a multifunctional acrylate [65]. The hot-melt adhesives also act as bone glue (for instance, 2-component dextran and chitosan) for fast bone repairment [66, 67].

6.2 Electronic Applications

Hot-melt adhesives are commonly used in the electronics field to assemble distinct parts of electronic devices. Thermally Conducting Adhesives (TCAs) with electrical resistivity and thermal conductivity are the popular adhesives for this purpose. HMAs are also widely used in EMI (Electro-Magnetic Interference) shielding to prevent interference from mobile electronic devices [68]. These thermally conducting adhesives containing aluminium nitride, beryllia, alumina, boron nitride, etc. have applications in power devices, capacitors, heat sinks, edge connectors, transformers, thermal coatings [69–71], heat shields in thermal protection systems, etc. thus, providing an ideal packaging system [72, 73].

6.3 Anticorrosion Applications

The industrial level gas and oil pipelines may suffer from corrosion on their external surfaces. The hot-melt adhesives provide a solution to this problem by allowing fabrication of three-layer anticorrosive coatings on external pipeline surfaces. These three layers consist of innermost epoxy layer, a middle thermoplastic adhesive layer, and outermost polypropylene (PP) layer. These three-layer coating systems are used for systems having high-temperature internal fluid. This three-layer system provides auxiliary protection against corrosion and is widely adopted on industrial level. Critical engineering applications for anti-corrosion surfaces can also be accomplished by HMA polymer coatings [74, 75].

6.4 Food Packaging Applications

HMAs have been widely used in the food industry as packaging materials, sealants, laminates, etc., to provide additional protection against unfavorable environmental conditions (pH, temperature, microbial attack) to maintain the freshness and nutrient content of food. In addition to these basic food packaging applications, HMAs also offer smart applications to examine food quality over time. One such application is the CO$_2$-sensitive smart adhesive to check the freshness of food. This adhesive contains CO$_2$-responsive pigment (pH-sensitive phenol red
dye coated nano-dimensional silica particles dispersed in hot melt). This smart adhesive is then coated onto polymeric substrate to produce the CO₂-stimulating adhesive tape. This tape is then placed inside the food package to detect the presence of CO₂. The adhesive tape changes from deep purple to yellow/orange color in the presence of CO₂ and then turns back to its original color (deep purple) when exposed to air outside the food package, thus, determining the freshness of the food [76].

6.5 Textile Applications

Hot-melt adhesives have been extensively used in textile industries for several distinct applications. The various hot-melt textile adhesives include Low-Density Polyethylene (LDPE) for automotive carpets, EVA (in footwear and bonding of leather and paper), polyamide and its copolymers (in garments), etc. Hot-melt adhesives have been used for the fabrication of various designs and attachment of distinct decoration substances on garments, carpets, and other accessories [77].

7. Current Challenges and Future Scope of HMAs

HMAs have been used in various engineering and industrial applications for a long time [6]. Many of the foremost applications of HMAs are in non-woven materials (diapers and sanitary napkins), packaging materials (case and carton sealing), labelling of bottles, book binding, and pressure-sensitive tapes and films. HMAs cover almost all the industrial sectors based on consumer goods and services. In terms of electronics, the swelling problem in electronic circuits and telecommunication has aggravated the problem of EMI (Electromagnetic Interference). EMI becomes a concern in the performance of electronics which can lead to an inappropriate function or failure of the total system. This problem can be rectified by using HMAs of a suitable polymer component. Intrinsic HMAs of particular conductance (IC-HMAs) based on polypyrrole were developed by Pomposo et al. [78] for electrical and telecommunication applications for EMI shielding. These advanced IC-HMAs are designed to display remarkable shielding effects of EMI, without losing the properties of primary conventional HMAs. HMAs also have some environmental issues which should be kept in mind while preparing them. For instance, solvents like TCE (Trichloroethylene) and Toluene are basically VOCs, but are used in various HMAs as a carrier fluid which is challenging the environment. There is a need to produce eco-friendly HMAs by using recyclable components like PUR-HMAs which can be easily separated and detached from the fibres of papers in the process of recycling.

The working strategies need to aim in the direction of use of raw materials for the development of new risk-free HMAs. The particular constituents should be proposed after an appropriate evaluation for diverse engineering and industrial
applications. For instance, Viljanmaa et al. [79] developed a PLLA-PCL copolymer of high thermal stability which proved to be a suitable HMA for many lamination applications and industrial polylactide films. Extraordinary efforts have been dedicated to developing green raw materials that can be capable substitutes for HMA constituents, but over the past 20 years, green HMAs have not been announced in the marketplace. An example of green HMA ingredients are the terpenes-based tackifiers derived from the trees for use as a substitute for petroleum-based HMAs [7]. Apart from this, various biochemically-derived polymers have been produced using plant extracts and modified into HMAs. But still there is a need to move these researches from laboratories to industries. There have been various remarkable researches in the field of HMAs that need to be carried forward for wider industrial implementation. Broos et al. [80] developed a novel HMA for the woven and non-woven bonding of papers, cartons, films, and glasses using polyesters and polyamides with the functionality of dicarboxylic acid. One more instance of this category is the manufacturing of a lactic acid-based polymer that has been claimed to be an excellent potential component for HMA preparations for hot-melt coatings, fibres, films, and non-woven blown melts developed by Lewis and team [81]. Such HMAs have not been introduced to the market due to high material cost, poor thermal stability, and foul odour. More work should be emphasized on the cost-cutting factors and compatibility with environment for newly emerging HMAs. The environmental threats of using HMAs, along with cost, are due to their ingredients and additives because most of them are produced from chemical components of petroleum, mostly non-biodegradable. Therefore, the necessity for a healthy environment is biodegradability of raw materials, and it is indispensable to eliminate these petroleum-based HMAs.

7. Summary

An HMA should be designed in such a way that the bonding property is not negatively impacted. For this, there is a need to balance all the involved factors like environmental conditions, surface properties, polymeric matrices of HMA, fracture mechanics, etc. An ideal HMA should be VOC-free and based entirely on eco-friendly ingredients. However, solvent-based HMAs are more important adhesives than polymer-based HMAs, but polymer-based HMAs can be prepared using green methods, whereas the solvent-based cannot. New polymeric HMAs can replace these solvent-based HMAs by eliminating the risk of VOCs. This review was intended to discuss the fundamentals, formulations, principles, mechanical tests and applications of HMAs. The fracture mechanics has been discussed as it is a very important tool for determining the durability and bonding of an adhesive to an adherend. Many of the novel and newest HMA preparations are discussed in this review with their formulation procedures. Latest challenges have been introduced along with their solutions and future scope that can widely extend HMAs on industrial scale by making eco-friendly HMAs.
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