Scientific Research Publishing

Open Journal of Polymer Chemistry, 2022, 12, 80-92
https://www.scirp.org/journal/ojpchem
ISSN Online: 2165-6711
ISSN Print: 2165-6681

Application of Thermally Expandable Microspheres in Adhesives: Review

Ravindra Vilas Indubai Gadhave[1*], Chaitali Ravindra Gadhave[2]

[1]Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, India
[2]Department of Microbiology, Savitribai Phule Pune University, Pune, India
Email: *ravi.gadhave3@gmail.com

How to cite this paper: Gadhave, R.V.I. and Gadhave, C.R. (2022) Application of Thermally Expandable Microspheres in Adhesives: Review. *Open Journal of Polymer Chemistry*, **12**, 80-92.
https://doi.org/10.4236/ojpchem.2022.122005

Received: March 24, 2022
Accepted: May 15, 2022
Published: May 18, 2022

Abstract

Adhesives are used to bond various substrates such as metals, polymers, ceramics, rubber, wood and wood-based products. The use of adhesive as bonding agent rather than mechanical fasteners like nails results in the potential for reduced cost and weight of assemblies. However, adhesives are unprotected to a wide range of conditions, such as thermo-mechanical cycling in the environment, creep and fatigue imposed by structural joint configurations, and residual stress due to mismatch of thermal expansion between adhesives and objects. Thus, there will be a need for development of new chemistries and processes for easy repair and reprocessing of bonded structures are becoming of current great interest for the industries. In some cases, to improve the protection of various items/objects during handling and transportation, currently used protective products such as padded wraps, envelopes, packages and containers need to be modified. One technology which can solve the problem is the adhesives modified with thermally expandable particles (TEPs) which can be dismounted by heating the joint in a few seconds. The expandable composition is providing the necessary protective insulation and cushioning required in packages and containers. This paper reviews the application of unexpanded microspheres in the adhesive segment.

Keywords

Microspheres, Expandable, Adhesive, Heat, Packaging

1. Introduction

Recently, novel products consist more and more of a combination of special new raw materials, which need to be contributed according to their specific properties. Adhesives can be used to adhere polymers, metals, ceramics, rubber, wood, wood composite and combinations of any of these materials. Adhesive has found applications in various areas from high end industries such as aerospace, aeronautics, electronics, and automotive to conventical industries such as construction and packaging [1]-[6].

Adhesives are classified into water-based adhesive, solvent-based adhesives, hot melt adhesives, and pressure sensitive adhesives depending upon chemistries. The adhesives used in the various industries are made from renewable, compostable, or biodegradable materials to further decrease the carbon footprint and dependency on petroleum resources of the final product. However, bio-polymers are moisture unstable and mechanical properties of natural polymers are poorer than those of synthetic polymers, which restricts widespread use of these materials in adhesive industries. Preferred adhesives suitable for end use in the described products include, for example, adhesives comprising ethylene-vinyl acetate (EVA), polyvinyl acetate (PVA), polyvinyl alcohol (PVOH), ethylene vinyl alcohol copolymer (EVOH), acrylic, acrylate, polyurethane, epoxies, polyolefins, and combinations thereof [7].

However, adhesives are unprotected to a wide range of service loading conditions, such as thermal and mechanical cycling in space environments which resulted in mismatch of objects. Thus, the development of new chemistries and processes for easy repair and recycling of bonded structures are becoming of great interest for the industries. If bonds can be broken without damage to the components, recycling is easier. Also, for an environmentally friendly disassembly of bonded structures, it is necessary to separate the joint between the bonded components so that the different materials can be reused on a qualitatively high level. One example is the adhesives modified with thermally expandable particles (TEPs) which can be dismounted by heating the joint in a few seconds [8] [9] [10]. In some cases, to protect various items during handling, shipping or transportation, protective products such as padded wraps, envelopes, packages and containers are currently used. Such protective products may be placed in surrounding engagement with the product to protect the product from potentially damaging contact. To help insulate the hand of the consumer from the heat of a hot beverage, or keep the desirable temperature of the contents of a food or beverage container longer, heat-expandable adhesives and coatings have been developed by the inventors for use with packaging substrates, for example, with multilayer corrugated board, paper or paperboard [11]. This paper provides an overview of the recent developments in the use of unexpanded microspheres in adhesives and their application in adhesives.

2. Microspheres

Thermally expandable microspheres were developed by Dow Chemical Co. in the early 1970’ [12] and are microspheres made up of a thermoplastic shell filled with liquid hydrocarbon. They are commercialized worldwide by the companies Expancel Nobel Industries, under the trademark of Expancel [13], and Matsumoto Yushi Seiyaku, under the trademark of Micropearl [12]. Owing to this unique performance, thermally expandable microspheres are used by the industry in a wide variety of applications [11] [14] [15] [16] [17]. However, the use of this technique applied to adhesives started in Japan by Nishiyama *et al.* [18] to bond plywood boards. Technique for bonding wallpaper on plywood or plasterboards in construction fieldshas been extended to structural adhesives for recycling purposes by Nishiyama *et al.* [18].

The microspheres are the thermoplastic resin whose high polymer forms the shell material. The shell contains a low boiling point liquid hydrocarbon which is encapsulated inside it. On heating such a microsphere, rising temperature will induce two transformations. One is the softening of shell material while the other is the gasification of the hydrocarbon liquid inside it. With both changes happening almost simultaneously, as a result the shell will expand as the increased inner pressure pushes the softened shell wall from inside out producing a remarkable growth in size as shown in **Figure 1**. Microspheres are thermo-expandable have an average particle size of 5 to 50 μm.

The hydrocarbon gas works as a blowing agent. The microspheres can stand up to 300 kg/cm^2 of mechanical pressure and has solvent resistant. Microspheres must be stored indoors where temperature does not exceed 40˚C so that the product maintains its stability [19].

The heat-expandable microspheres have an initial expansion temperature range of from about 35˚C to about 110˚C and a maximum expandable temperature range of about 50˚C to about 150˚C. These microspheres may be made from a variety of materials, but generally have a polymeric shell and a hydrocarbon core. A blowing agent generally comprises the core and it is designed to activate upon reaching a specified temperature. One particularly useful heat-expandable micro sphere comprises a polyacrylonitrile shell and a hydrocarbon core, such as those sold under the trade names Dualite and Expancel®. The expandable microspheres may have any expanded size, including from about 5 microns to about 30 microns in diameter. Microspheres are not bio-degradable but adhesives in which microspheres added are biodegradable. In the presence of heat, the microspheres may increase from about 3 to about 10 times their diameter. The expandable microspheres have a particular temperature at which they begin to expand and a second temperature at which they have reached maximum expansion. Microsphere grades are typically sold with specific expansion (T_{exp}) temperatures and maximum expansion temperatures (T_{max}). The initial expansion

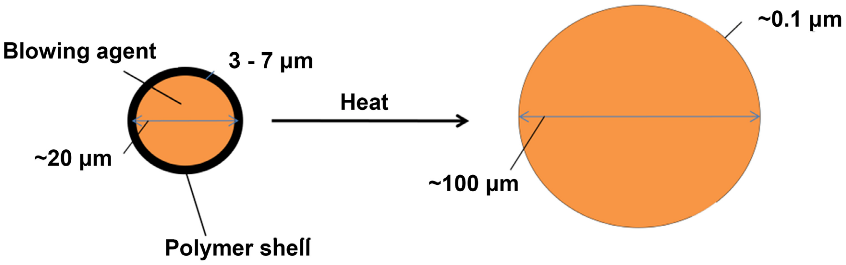

Figure 1. Expansion of unexpanded microspheres under application of heat.

temperature (T_{exp}) is the typical temperature at which the microspheres start to expand (T_{exp}), and the maximum expansion temperature (T_{max}) is the temperature at which about 80% of the microspheres have expanded. If the microspheres are exposed to temperatures far greater than T_{max}, the micro spheres start to explode and deflate. Depending on the fully expanded size of the micro spheres, the amount of the expandable microspheres in the composition can be adjusted [20] [21].

The Dielectric heating, electronic heating, radio frequency (RF) heating, high frequency heating microwave heater may heat the material at any of various points of the manufacturing process after the application of the heat-expandable adhesive. A multi-layered sheet material may be laminated with any combination of suitable materials aforementioned, and conveyed to final processing, such as to be printed, die cut, formed, and/or otherwise assembled into product containers. The heat-expandable adhesive or coating may contain expandable microencapsulated microparticles, like microspheres or microtubes from multiple different sources [22] [23].

3. Application of Microspheres

The heat expansion system of heat-expandable microspheres was used in inks for three-dimensional prints, ultra-lightweight paper, undercoating materials for automobiles, lightweight shoes, coating materials for non-polyvinyl chloride (PVC) wallpaper, delustering agents for PVC wallpaper, and heat-separable adhesives, and for preparation of lightweight polyethylene and polypropylene [24]. In the expanded form they are used as very low-density lightweight fillers in paints, sealants, adhesives, putties, etc. They also improve application properties and help reduce the costs of final products in expanded form [25]. The expandable composition is providing the necessary protective insulation and cushioning required in packages and containers. The packages and containers may be formed as envelopes, pouches, bags, boxes, cartons, cases, lids, wraps, clamshells, cups, food containers, and the like [26] [27].

4. Microspheres Application in Adhesive

4.1. Dis-Bondable Adhesive

The cost of repair is huge and, in many cases, impossible due to limited access or risk of further degradation of the structure. If bonds can be broken without damage to the components, recycling is easier. Thus, an adhesive with a built-in mechanism to repair cracks by restoring broken bonds is of great interest for numerous applications to extend the service life and improve the safety of bonded structures. All these aspects are the motivations behind the increasing development of novel adhesive technology. Novel adhesive joints can be thought of as joints capable to bond, re-bond and de-bond in response to a stimulus like mechanical, thermal, electrical, magnetic, etc. [28].

End-of-life vehicle legislations and recycling issues for future multi-material vehicles necessitate the development of new joining solutions that enable rapid disassembly for automotive vehicle maintenance or recycling scenarios [29]. In the search for a dis-bondable adhesive system suitable for automotive applications, an adhesive system containing TEMs has been identified as one of the most promising approaches with satisfactory dis-bonding performance observed in previous research conducted within the Joining Technology Research Centre (JTRC) at Oxford Brookes University [30]. TEMs are micron scaled spherical particles composed of a thermoplastic shell material and an encapsulated hydrocarbon core which has a low boiling temperature. At elevated temperature, shell softening and hydrocarbon gasification allows TEMs to expand 30 - 80 times in volume, which can lead to fracture of the adhesive bond line [29] [30] [31] [32] [33]. Although adhesion was a very convenient method of joining materials, it is difficult to dismantle joints bonded adhesively. This aspect has become a problem in terms of recyclability. A conventional way to solve the problem is use of thermoplastic adhesives. Recently, another way to use a new kind of adhesive which includes thermally expansive particles has been proposed. The particles were originally used as fillers of core form placed in sandwich panels of composite materials [34]. Another special application of the particles was fillers of removable coating used in car painting lines [35]. Ishikawa modified and improved the method in order to apply it for use in bonding thin metal sheets as wallpaper on wood or plasterboards in construction fields [36] [37]. In this case, soft adhesives such as vinyl copolymers were used because high strength was not required for the applications. The layer of the adhesive also fractured cohesively and the metal sheets could be peeled off easily by hand [38]. Recently, a new kind of adhesive including TEMs has been proposed as an alternative method [39]. Originally, the microspheres were used as an expanding and pressurizing agent for the molding of composite materials in sandwich panels [40]. This research successfully improved the compatibility between TEMs and an adhesive system for enhanced performance. TEMs were grafted with poly (glycidyl methacrylate) chains via atom transfer radical polymerization (ATRP) with activators regenerated by electron transfer (ARGET) or ARGET and ATRP technique. The temperature effect on the surface modification of TEMs was investigated for an optimum modification condition. Compared to adhesive incorporating unmodified TEMs, up to 15.8% increase in tensile lap shear strength and 24.0% increase in ultimate tensile strength were achieved. Surface modification of the TEMs substantially improved the compatibility with the adhesive via the formation of strong covalent bonds. It was also shown that the modified TEMs system obtained better moisture resistance. Most notably, the ultimate tensile strength of the adhesive system containing modified TEMs after environmental conditioning was higher than the strength of the adhesive system containing unmodified TEMs before environmental conditioning [41]. In pressure sensitive adhesives, the thermal expansion of adhesives and microspheres was measured by a pressure volume temperature apparatus under any pressure [42]. Even when epoxy resin was used, the joints bonded with the dismantlable adhesive including 30 wt% of the TEMs could be totally dismantled. In these cases, interfacial fracture in the joint occurred [43] [44] [45] [46].

4.2. Microspheres in Water-Based Adhesive

Paper converting and packaging operations require bonding cellulosic sheets like paperboard or cardboard, together with adhesives. Typically, waterborne or hot melt adhesives are applied onto one or both Substrates and the Substrates are compressed together to adhere to one another to form cases, cartons, bag handles, agricultural boxes, bulk box laminations, glued laps, and the like. Hot melt adhesives are favoured over waterborne adhesives in certain areas of the paper converting and packaging operations, where high compression cannot be achieved. Extruded hot melt adhesive lines have high amplitude with a bead-like profile that allows the substrates of the paper products to bond together even with the presence of small gaps. The rapid setting nature of the hot melt adhesives also allows for fast and efficient through-put packaging or converting operations. However, drawbacks to hot melt adhesives include low heat resistance, high energy usage, and non-repulpability [47]. Waterborne adhesives are typically utilized in paper converting and packaging operations where thin adhesive films rather than thick beads are applied, and where solid and lengthy compression can be achieved; however, the water borne adhesives do not readily gap-fill between two uneven Substrates such as those from the undulation of corrugated papers. Although increasing the viscosity, in particular the low shear viscosity, of the waterborne adhesives will help to overcome bead sagging problem and thus achieve gap-fill. The viscous adhesives are difficult to extrude due to their high viscosity. Furthermore, water evaporates from the viscous waterborne adhesive layers or beads ever so slowly that the through-put of such adhesive was much lower than that of hot melt adhesives.

In some of the research work, there were provided a hot melt assist waterborne adhesive composition comprising an emulsion polymer, a preservative, water and TEMs. The volume fraction of the micro spheres in the hot melt assists waterborne adhesive ranges from about 10 to about 40 Volume/Volume%. The hot melt assist water borne adhesive replaced some or all portions of hot melt adhesives for paper converting and packaging operations.

The method of joining two substrates together with a hot melt to assist waterborne adhesive composition consists of the following steps:

1) Preparing the hot melt assist waterborne adhesive composition comprising an emulsion polymer, a preservative, water and a plurality of pre-expanded hollow microspheres;

2) Extruding the hot melt assist waterborne adhesive composition onto the first Substrate;

3) Joining the second Substrate onto the adhesive;

4) Evaporating the water from the hot melt assists waterborne adhesive com-

position, whereby the two Substrates are joined.

The application or the extrusion pressure of the hot melt assist waterborne adhesive comprising the expanded hollow micro spheres is less than the application pressure of a conventional waterborne adhesive without the expanded hollow microspheres [48]. Normally, 0.1 to 30, preferably 0.5 to 20 and most preferably 1 to 15, parts by weight of the blowing agent were added to 100 parts by weight of acrylic emulsion, namely the "heat-expandable pressure-sensitive adhesive". However, it is also feasible to add more than 50 parts by weight of the blowing agent as needed [49] [50] [51]. TEMs reduces the environmental problem caused by traditional chemical foaming agents, and it can further realize weight reduction of forming material, lifts buffering and thermal insulating properties of lightweight paper material [52] [53]. The sheets comprise pressure-sensitive adhesive layers containing TEMs on at least one side of substrates, wherein the center average roughness of the substrate surface on the adhesive layer side is 0.10 - 5.00 μm, thus, an adhesive comprising acrylic acid-Butyl acrylate copolymer, an isocyanate crosslinker, and blowing agent microspheres [54] [55]. A flexible, insulating laminate comprising a first ply formed of paper, a second ply formed of paper, and an expandable insulating material comprising thermally activated expandable microspheres between the first ply and the second ply. An adhesive may be applied to provide a barrier between the insulating material and an outer edge of the laminate. The flexible laminate may be formed into a variety of end products such as bags, sheets, pillows, pads, and the like [56] [57]. In some case, TEMs based adhesives comprises a thermoplastic polymer shell and a propellant entrapped therein, a partially water-soluble polymer selected from starch [58] [59], gums, celluloses, chitins, chitosan, glycans, galectins, pectin's, mannans, dextrin, polyacrylic acid, esters, and amides and copolymers thereof [50] [60] [61] [62] [63].

This type of inventive products can be applied in papermaking, automobile chassis, coating, etc. The coating composition may be applied onto the surface of the substrate in any configuration desired, including in a series of dots, stripes, waves, checkerboard patterns, any general polyhedron shapes, and combinations thereof. In addition, if desired, the coating composition may be applied to the entire surface of the substrate of the package. In certain embodiments, the outer edges of the substrates are not coated with the coating composition and are reserved for an adhesive. The substrates are then adhered together at the edges to form the multi-substrate layers, which can form the protective package, e.g., envelope, pillow, Gusseted bags, and the like [64] [65] [66].

Test methods for TEMs based adhesive

1) *Solid* %:

Percent solids were measured by weighing about 1.0 ml of sample in a pre-weighed pan on an analytical balance and then placing it in a 120˚C oven for 90 minutes.

2) *Foam height*:

The foam height is the height of the sample after it has been expanded. A known mass of expandable sample, normally 20 to 100 milligrams, was placed on thin glass coverslip as a semi-spherical dot/drop and placed in a 1 kW household microwave oven directly on the turntable near the edge above the ring track. This was then heated for 10 seconds at full power. The semi spherical dot expands to a symmetric "mushroom cap" or very close to it. The freshly expanded foam will still contain moisture upon expansion, so it is left to dry or set. The side view of the dry foam was then photographed with a reference of known width and the profile was digitized with Image Analysis software to enable the determination of the height and volume of the foam.

3) *Expansion ratio*

The Expansion Ratio is the volume of expanded dry foam divided by the volume of liquid sample. A sample size of 20 to 100 milligrams was used to form the expanded foam dot height to about 4 and 8 mm with the microwave oven, as described above. Since the wet density of the sample is known, the wet volume was calculated, and therefore, the expansion ratio was obtained. Alternatively, the side profile of the wet drop was photographed and digitized to work out the wet volume.

4) *Biodegradability and compostability*

Products produced according to the disclosure can be biodegradable. Standards for biodegradability include OECD 301, 304A, and 306. Products produced according to the disclosure can be compostable. Standards for compostability include ISO 17088, ISO 18606, ASTM D6400 and ASTM D6868. Products produced according to the methods of the disclosure may also conform to ASTM D5929-18 [67] [68].

5) *Application technique*

Flexographic coating allows for the coating composition to be applied in a precise manner, focussing on placement of the coating composition in an ideal patterning, and location, to maximise the protective properties of the protective packaging whilst avoiding the need to apply the coating composition throughout the layer. In an embodiment, the flexographic coating technique may further comprise a pan roller, a transfer cylinder and a plate cylinder. This arrangement allows a pan roller to collect the liquid coating composition in a controlled manner before this is transferred to a layer of the substrate using a transfer cylinder to collect the coating composition from the pan roller and to apply the composition to a backing sheet arranged on the plate cylinder. The plate cylinder can then be used to transfer the composition from the backing sheet onto a layer of the substrate [69] [70].

5. Conclusion

There is an increasing interest in the use of novel adhesive technologies in various applications in industry due to their advantages over old technologies. In bonded assemblies, the damage or cracking in the adhesive line initiates at the interfaces between the adhesive and the objects, due to the presence of high stresses. Easily removable adhesive joints would allow for simplified dismantlement and recycling. To avoid mechanical destruction, dis-bondable adhesive is a novel system suitable for various applications and an adhesive system containing TEMs has been identified as one of the most promising approaches with satisfactory dis-bonding performance observed. In packaging industries, in order to protect various items during handling, shipping or transportation, protective products such as padded wraps, envelopes, packages and containers are currently used. Such protective products traditionally used polystyrene foam to form a cushion material which relies on an air gap or bubble between the plastic layers, to form the protective cushion. Recently developed water-based heat-expandable adhesives include heat-expandable microspheres. This review discussed newly developed smart adhesive technologies and these adhesives open up new exciting opportunities for development in automotive and packaging fields and offer promising potential in the future.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Abbreviations

TEPs: Thermally expandable particles
PVA: Polyvinyl acetate
PVOH: Polyvinyl alcohol
EVOH: Ethylene vinyl alcohol copolymer
EVA: Ethylene-vinyl acetate
T_{exp}: Specific expansion temperatures
T_{max}: Maximum expansion temperatures
RF: Radio frequency
PVC: Polyvinyl chloride
ATRP: Atom transfer radical polymerization
ARGET: Activators regenerated by electron transfer