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(71) Applicant: **VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.** [US/US]; 2200 Kraft Drive, Suite 1050, Blacksburg, Virginia 24060 (US).

(72) Inventors: **ZHANG, Keren**; Blacksburg, Virginia 24060 (US). **LONG, Timothy E.**; Blacksburg, Virginia 24060 (US). **PAUL, Charles**; Bridgewater, New Jersey 08807 (US). **DEJESUS, Maria Cristina Barbosa**; 43 Pheasant Run Drive, Basking Ridge, New Jersey 07920 (US).

(74) Agent: **GREENBAUM, Michael C.**; Blank Rome LLP, 600 New Hampshire Avenue NW, Washington, District of Columbia 20037 (US).

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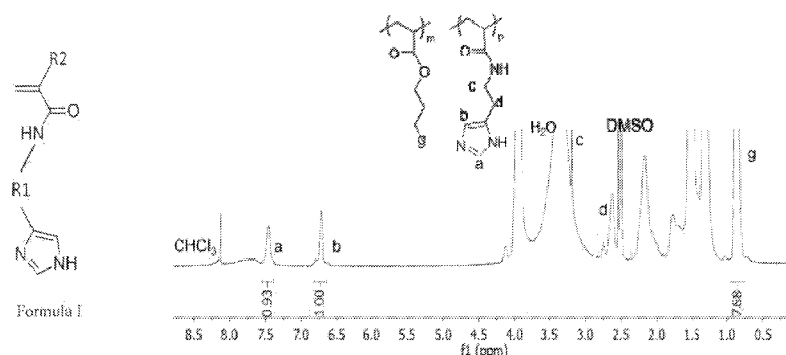


FIGURE 2

(57) Abstract: The present invention relates to copolymer compositions for making pressure sensitive adhesives. The copolymer contains a comonomer having the structure of Formula I, wherein R1 is an alkylene having 1 to 3 carbons; and R2 is hydrogen or an alkyl having 1 to 3 carbons.

ACRYLAMIDE COPOLYMERS FOR PRESSURE SENSITIVE ADHESIVES

[0001] This application claims the priority of U.S. Provisional Patent Application 61/892,509, filed October 18, 2013, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to copolymer compositions for making pressure sensitive adhesives.

BACKGROUND OF THE INVENTION

[0003] Acrylic polymers have advantages and superior qualities to other polymer based adhesives for use in pressure sensitive adhesives (PSA). Acrylics are transparent and chemically and oxidatively stable. They are less irritating to skin and often used for biomedical applications. Commercial PSAs commonly use permanent crosslinking to improve the cohesive strength and to obtain clean peeling. Noncovalent interactions can also provide a physically crosslinked polymer network while incorporating reversibility. Noncovalent interactions include van der Waals force, hydrogen bonding, pi stacking, and ionic interaction. Physically crosslinked polymers are responsive to heat, moisture, solvent, salt concentration, etc., depending on the specific noncovalent interaction.

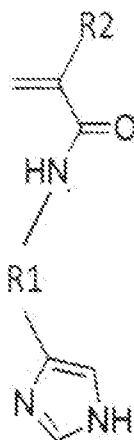
[0004] Histamine serves a wide range of biological functions, including allergic reactions to antigens and neuron regulation etc. The imidazole ring has both hydrogen bonding donor and acceptor to form noncovalent interactions. The aromaticity sustains the thermal and chemical stability of imidazole rings. Imidazole-containing polymers also exhibit anti-inflammatory

responses. The polarity of histamine also contributes to its potential in designing water-soluble adhesives and coatings.

[0005] However, there remains a need for PSAs based on hydrogen bonding. The reversible nature of noncovalent interaction in hydrogen bonding provides an opportunity to design thermal or solvent reversible adhesives and recyclable adhesives materials. Hydrogen bonding introduces physical crosslinks to enhance mechanical properties, especially cohesive strength of adhesive materials and maintains processability above the hydrogen bonding dissociation temperature.

SUMMARY OF THE INVENTION

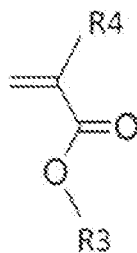
[0006] The present invention provides copolymers for making pressure sensitive adhesives (PSAs). The copolymer contains a first comonomer and a second comonomer. The first comonomer has the structure of Formula I



Formula I

wherein R1 is an alkylene having 1 to 3 carbons, preferably 1 to 2 carbons; and R2 is hydrogen or an alkyl having 1 to 3 carbons. Most preferably, R1 is an ethylene. Most preferably, R2 is hydrogen or a methyl.

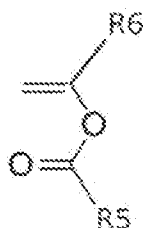
[0007] The second comonomer has the structure of Formula II, III, or IV, or combinations thereof. Formula II is given as follows:



Formula II

wherein R3 is an alkyl having 1 to 16 carbons or alcohol or acids thereof; and R4 is hydrogen or an alkyl having 1 to 3 carbons. Preferably, R3 is a butyl. Preferably, R4 is hydrogen or a methyl.

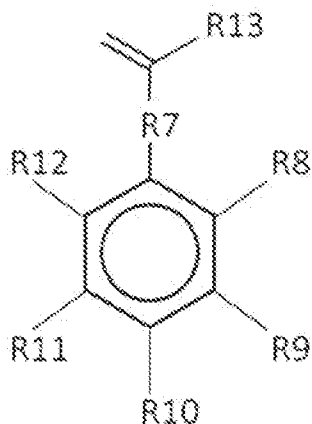
[0008] Formula III is given as follows:



Formula III

wherein R5 is an alkyl having 1 to 12 carbons, preferably 1 to 3 carbons; and R6 is hydrogen or an alkyl having 1 to 3 carbons. Preferably, R5 is a methyl. Preferably, R6 is hydrogen or a methyl.

[0009] Formula IV is given as follows:



Formula IV

wherein R7 is an alkylene having 0 to 2 carbons; each of R8 to R12 is independently hydrogen, a halogen, or an alkyl having 1 to 3 carbons; and R13 is hydrogen or an alkyl having 1 to 3

carbons. Preferably, R7 has 0 carbon atom. Preferably, R8 to R12 are all hydrogen. Preferably, R13 is hydrogen.

[0010] The copolymer may be a random copolymer or a block copolymer. A random copolymer is preferred. Additionally, the second monomer may contain any combinations of Formulas II to IV. For example, the copolymer may contain a monomer of formula I and a comonomer or several comonomers of Formulas II to IV.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is a drawing showing chemical structures of some preferred second comonomers.

[0012] Figure 2 is a graph showing an NMR analysis of Poly(HA-*co*-*n*BA) copolymers.

[0013] Figure 3 is a graph showing a TGA analysis of 11 mol% HA-containing polyacrylate which depicts a 5% weight loss at temperature of 272 °C.

[0014] Figure 4 is a graph showing a differential scanning calorimetry (DSC) of 11 mol% HA-containing polyacrylate which depicts a broad glass transition around temperature of -30 °C.

[0015] Figure 5 is a graph showing a size exclusion chromatography analysis of 11 mol% HA-containing polyacrylate which depicts a weight average molecular weight of 101 kDa.

[0016] Figure 6 is a graph showing the storage and loss modulus master curves of polyacrylates containing 11 mol% HA.

[0017] Figure 7 is a graph showing peel strength of 11 mol% HA-containing polyacrylate compared to polynBA and 3M Scotch® Magic™ tape.

[0018] Figure 8 is a picture showing that Mylar backing of scotch tape and HA-containing copolymer curls after peel and Mylar backing of polynBA remains flat.

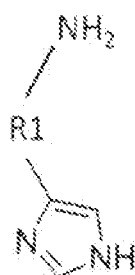
[0019] Figure 9 is a graph showing the thermodynamic mechanical properties of solvent casted polyacrylates films containing 13 mol% HA and 28 mol% HA.

[0020] Figure 10 are a series of picture showing the property changes of polyacrylates containing 0, 11, 28 mol% HA from left to right.

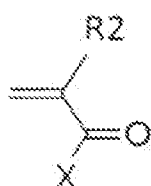
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] The present invention relates to compositions for pressure sensitive adhesive (PSA). The compositions provide physical crosslinking through hydrogen bonding. The compositions contain a copolymer having a first comonomer and a second comonomer. The first comonomer has the structure of Formula I; and the second comonomer has the structure of Formula II, III or IV. The copolymer may be a random or block copolymer. In the copolymer, the first comonomer serves to provide tackiness for the adhesive through hydrogen bonding between the imidazole rings; and the second copolymer is used to tune the desired properties of the PSA. Preferably, the copolymer contains about 3-28 mol %, more preferably 5-15%, of the first comonomer, and about 72-97 mol %, more preferably 85-95 mol %, of the second comonomer.

[0022] In an embodiment, the first comonomer may be made by reacting a suitable amino substituted imidazole (Formula V, where R1 is as described above) with an acryloyl halide (Formula VI, where R2 is as described above and X is a halide, such as fluoride, chloride, bromide, and iodide, preferably chloride and bromide)



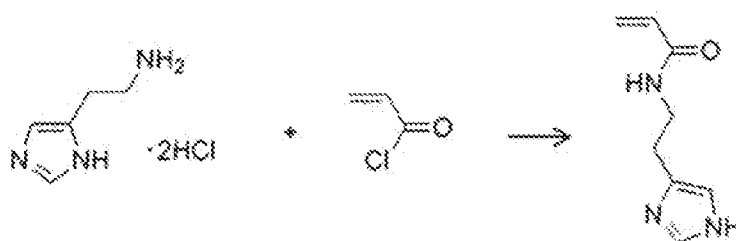
Formula V



Formula VI

Preferably, R2 is hydrogen or methyl, and X is chloride. The reaction between Formulas V and VI is preferably carried out in a solvent in the presence of a base. The base used can be inorganic, such as sodium hydroxide, potassium hydroxide, and sodium carbonate; and organic, such as triethylamine. The solvent can be, but is not limited to, water, dichloromethane (DCM),

chloroform, and ethyl acetate, with the preferred solvent being a mixture of water and DCM. An interfacial reaction was carried out at 0 °C. When R2 is methyl, crystallization occurs at the interface of DCM and water, allowing minimized purification process. In a preferred embodiment, histamine dihydrochloride is reacted with acryloyl chloride to form histamine acrylamide as shown in Scheme 1



Scheme 1

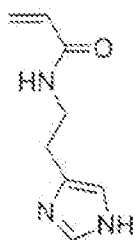
Alternatively, if histamine (meth)acrylamide is desired, the histamine dihydrochloride can be reacted with meth(acryloyl) chloride to form the histamine (meth)acrylamide.

[0023] The second comonomers are well-known in the art and may be obtained using previously described methods. Indeed, the second comonomers are available commercially from many sources. For example, butyl acrylate has CAS Number 141-32-2 and is available from Dow; butyl methacrylate has CAS Number 97-88-1 and is available from Dow; 2-ethylhexyl methacrylate has CAS Number 688-84-6 and is available from Sigma Aldrich; 2-ethylhexyl acrylate has CAS Number 103-11-7 and is available from Sigma Aldrich; methyl acrylate has CAS Number 96-33-3 and is available from Dow; and methyl methacrylate has CAS Number 80-62-6 and is available from Sigma Aldrich; styrene and its functionalized monomers are also available through Sigma Aldrich. Specific examples of the second monomer may be, but are not limited to, acrylates or methacrylates, such as methyl acrylate, methyl methacrylate, ethyl

acrylate, ethyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, i-butyl acrylate, i-butyl methacrylate, t-butyl acrylate, t-butyl methacrylate, hexyl acrylate, hexyl methacrylate ethylhexyl acrylate, ethylhexyl methacrylate, 3,3 dimethylbutyl methacrylate, lauryl acrylate; styrene and functionalized styrenes, such as bromostyrene, chlorostyrenes, butoxystyrenes, butylstyrenes, methylstyrenes, and propylstyrenes. The preferred second comonomers are n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof. The structures of some of those second comonomers are shown in Figure 1. The most preferred second comonomer is n-butyl acrylate, ethylhexyl acrylate, n-butyl methacrylate, lauryl acrylate, or combinations thereof.

[0024] The first and second monomers are reacted to form the copolymer of the present invention. Preferably, the reaction takes place in a solvent with the presence of an initiator. Preferably, the reaction is carried out at about 60-70°C for about 18-30 hours, more preferably 20-24 hours, under inert gas, such as argon or nitrogen. The solvent can be, but is not limited to, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and methanol, with DMSO being the preferred solvent. The initiator can be, but is not limited to, azobisisobutyronitrile (AIBN), 4,4'-Azobis(4-cyanovaleric acid), and organic peroxides, such as di-tert-butyl peroxide and benzoyl peroxide, with AIBN being the preferred initiator.

[0025] In a preferred embodiment, the adhesive composition contains a copolymer of histamine acrylamide (Formula IA) and n-butyl acrylate. In another preferred embodiment, the adhesive composition contains a copolymer of histamine acrylamide (Formula IA) and n-butyl methacrylate.



Formula IA

Formula IA is preferably obtained by reacting histamine with acryloyl chloride at conditions described above.

[0026] In a further preferred embodiment, the adhesive composition contains a copolymer of histamine methacrylamide (Formula IB) and n-butyl acrylate. In yet another preferred embodiment, the adhesive composition contains a copolymer of histamine methacrylamide (Formula IB) and n-butyl methacrylate.



Formula IB

Formula IB is preferably obtained by reacting histamine with (meth)acryloyl chloride at the conditions described above.

[0027] Without further description, it is believed that one of ordinary skill in the art can, using the preceding description and the following illustrative example, make and utilize the compounds of the present invention and practice the claimed methods. The following example is given to illustrate the present invention. It should be understood that the invention is not to be limited to the specific conditions or details described in the example.

Example**[0028]** Methods

[0029] *Synthesis of Histamine Acrylamide Monomer.* In a three-necked 250 mL flask equipped with a stirrer and two 200 mL dripping funnels, histamine dihydrochloride (8.00g, 43.6 mmol) was dissolved in 40 mL of distilled water. The solution was cooled to 0-5 °C in an ice bath. A solution of acryloyl chloride (3.932g, 43.6 mmol) in anhydrous dichloromethane (40 mL) and an aqueous NaOH solution (3.27M, 40 mL, 130.9 mmol) were simultaneously added dropwise while stirring vigorously for 1 h. The reaction was allowed to be warmed to room temperature and stirred for an additional 4 h. The aqueous layer was collected and freeze-dried. The residue was re-suspended in 200 mL of isopropanol and filtered. The filtrate was concentrated by rotary evaporation. The crude product was purified with column chromatography using 3:1 chloroform:ethanol as an eluent. The collected fractions were evaporated through rotary evaporation and dried in a vacuum oven at room temperature.

[0030] *Synthesis of Histamine Methacrylamide.* In a three-necked 100 mL flask including a stirrer and two 25 mL dripping funnels, histamine dihydrochloride (2.00g, 10.9 mmol) was dissolved in 10 mL of distilled water. The solution was cooled to 3°C in an ice bath. A solution of methacryloyl chloride (1.14g, 10.9 mmol) in anhydrous dichloromethane (10 mL) and an aqueous NaOH solution (3.27M, 10 mL, 32.7 mmol) were simultaneously added dropwise while stirring vigorously over 1 h. The reaction was allowed to be warmed to room temperature and stirred for an additional 4h. The flask was left in a 4°C refrigerator for 72 h to collect crystals.

[0031] *Synthesis of Histamine-Containing Copolymers.* Histamine-containing random copolymers were prepared using solution free radical copolymerization in DMSO or N,N-

dimethylformamide (DMF) with AIBN as initiator. Typical synthesis was conducted as follows. Poly(histamine acrylamide-co-*n*-butyl acrylate) poly(HA-co-nBA) polymers were prepared by radical polymerization of histamine acrylamide (HA) in the presence of 0.1 mol% AIBN (3mg) in DMSO at 65°C. Under an argon atmosphere, HA (0.5 g, 3.02 mmol), DMSO (2.83g, 17.1 mmol), and AIBN (3.3 mg, 20.2 μ mol) were added into a 10 mL Schlenk flask equipped with a magnetic stirrer. The flask was purged with argon for 20 min. The flask was then sealed and placed in an oil bath at 65°C. After stirring for 24 h, the polymer was precipitated using a 2:1 ratio of MeOH: distilled H₂O. After precipitation, the solid was collected and left in a vacuum oven at room temperature for 24h. The polymer was then dissolved in 10 wt% DMF. A film was then cast by evaporating the DMF at 50°C exposed to air for 72 h and then 40°C in a vacuum oven for 24h.

[0032] *Analytical Methods.* ¹H NMR and ¹³C NMR spectra spectroscopy was performed on a Varian Unity 400 at 400 MHz in deuterated chloroform or DMSO. Thermogravimetric analysis was completed using a TA Instruments TGA Q500 under N₂ at 10 °C min⁻¹. DSC was executed using a TA Instruments DSC Q2000 under N₂ using a heat/cool/heat cycle at 10 °C min⁻¹. All T_gs were obtained from the second heat. Size exclusion chromatography (SEC) was performed using a Waters size exclusion chromatograph. The instrument was equipped with an auto sampler, three 5 μ m PLgel Mixed-C columns, a Waters 2410 refractive index (RI) detector operating at 880 nm, a Wyatt Technologies miniDAWN multi-angle laser light scattering (MALLS) detector operating at 690 nm, and a Viscotek 270 viscosity detector with a flow rate of 1 mL/min at 50 °C in DMF with 0.05 M lithium bromide (LiBr). Reported molecular weights are relative to polystyrene. Prior to SEC analysis, all polymers were analyzed by DLS to confirm no aggregation in the utilized SEC solvent. DSC was performed under a nitrogen flush of 50

mL/min at a heating rate of 10 °C/min on a TA instruments Q1000 DSC, which was calibrated using indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards. Glass transition temperatures were measured as the midpoint of the transition in the second heating ramp. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Q800 Dynamic Mechanical Analyzer in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 15 µm, and a static force of 0.01 N. The temperature ramp was 3 °C/min. Polymers were dissolved in DMF and cast into a Teflon® Petri dish, followed by slow evaporation of the solvent and drying of the film in vacuo. Disposable 8 mm diameter aluminum parallel plates were used for rheometry. All measurements were strain-controlled at a constant nominal strain value within the linear viscoelastic range, determined with strain sweeps. Master curves were obtained from temperature/frequency sweep measurements using time-temperature superposition (TTS), which were described with the Williams-Landel-Ferry equation. G' curves were used as the reference curves for TTS. The peel force per unit width was measured in accordance with ASTM-D3300 standard. The polymer coated Mylar film was adhered to a ethyl acetate cleaned stainless steel substrate and rolled down once with a 1 kg roll. Adhesive strength was measured at 180 ° using a Cheminstruments AR-1000 Peel Tester. The cross-head speed was maintained at 12 in/min, and four measurements were performed on four different specimens to ensure reproducibility.

[0033] Results and Discussion

[0034] We prepared two histamine-containing monomers (Formulas IA and IB) and histamine-containing copolymers through free radical polymerizations (the histamine containing acrylamide is abbreviated herein as HA). The (meth)acrylamide monomers (FormulaIA and IB) provide facile synthesis to incorporate imidazole and histamine function groups in an adhesive formulation, offering reversible crosslinking sites to increase the apparent molecular weight and

to enhance mechanical strength. Acrylamide and methacrylamide monomers have different reactivity ratios; and corresponding homopolymers have different T_g due to the methyl group on the polymer backbone. For each histamine-containing monomer, a wide variety of commercial comonomers can be used in formulation to tune copolymer properties. In particular, soft acrylic monomers serve as the polymer matrix to maintain the tackiness and lower the cost for PSA applications. We can also utilize living radical polymerization to produce copolymers with well-defined architectures such as block or branched copolymers. Currently, we focus on the synthesis and characterization of random copolymers of histamine acrylate with *n*-butyl acrylate (*n*BA) for PSA fabrication to examine the structure-property relationships with histamine incorporation.

[0035] A DMF and MeOH mixture solvent with specific ratio or dimethyl sulfoxide (DMSO) was required to obtain a homogeneous polymerization solution with specific monomer feed ratio. Poly(HA-*co*-*n*BA) with 11 mol% HA is an example, which was polymerized in a DMF-MeOH 5:2 solvent mixture. ^1H NMR showed incorporated histamine composition in the copolymer in Figure 2. DMF SEC confirmed histamine-containing copolymers with high molecular weights were achieved in Figure 5. A poly(*n*-butyl acrylate) homopolymer with comparable molecular weight was synthesized as a control. Table 1 lists molecular weights of histamine-containing copolymers and poly*n*BA (relative to polystyrene standard). We can tune the histamine composition and molecular weight of copolymers through varying the monomer feed ratio, initiator concentration, and solution concentration.

Table 1			
Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
11 mol% HA	49k	101k	2.07
poly <i>n</i> BA	39k	102k	2.66

[0036] Polymer morphology and behavior change significantly with increasing HA content in a copolymer (Figure 10). The homopolymer of poly n BA with comparable molecular weight is a sticky liquid. Histamine-containing polyacrylates with 11 mol%, 13 mol%, and 28 mol% were tacky soft film, tacky free standing film, and free standing film, respectively. Thermogravimetric analysis demonstrated that the thermal stability of polyacrylates remained with histamine incorporation (Figure 3), which proved the potential of histamine containing polymers in hot melt PSA fabrication. The glass transition temperature increased with more histamine content, which was attributed to additional chain mobility restriction from intermolecular and intramolecular physical crosslinking. 11 mol% HA-containing copolymer has a glass transition temperature around -30 °C (Figure 4), which is in the range of -20---40 °C for typical PSA. Histamine-containing copolymers showed broad glass transitions in DSC and DMA (Figure 4 and 9).

[0037] In Figure 9, 13 mol% and 28 mol% HA-containing copolymers are free standing films to enable dynamic mechanical analysis. Lower tan delta peak of 28 mol% HA shows that higher density of histamine leads to less chain mobility. However, flow temperatures of 13 mol% and 28 mol% HA copolymers are the same due to similar hydrogen bonding dissociation temperature. Thermo-reversibility of hydrogen bonding of the imidazole groups can also maintain processability of adhesive materials as well as enhance mechanical strength.

[0038] Figure 6 shows the rheological characterization of Poly(HA-*co*- n BA) using time-temperature superposition. The master curves of storage and loss modulus versus frequency for 11 mol% HA polyacrylate were referenced to 25 °C and overlaid. One step decrease of modulus elicited the absence of phase separation morphology. Histamine-containing polyacrylates

exhibited slower molecular dynamics compared to polynBA. Histamine incorporation also contributed to higher shear modulus over the entire frequency range tested. The master curves demonstrate a marked improvement of cohesive strength upon introduction of histamine into polyacrylates.

[0039] Figure 7 shows the peel strength of 11 mol% HA-containing copolymer, polynBA, and 3M Scotch® Magic™ tape. Adhesive layer thickness of 11 mol% HA containing copolymer and polynBA was 0.103 ± 0.006 mm and 0.125 ± 0.030 mm. With comparable adhesive thickness, poly(HA-co-nBA) has over 100 times higher peel strength than polynBA. Histamine incorporation introduces hydrogen bonding to physically crosslink soft acrylic polymer, which significantly enhanced peel strength. The peel strength of 11 mol% HA-containing copolymer is about 6 times as high as peel strength of a 3M Scotch® tape. Figure 8 shows the Mylar backing after the peel test. Strong peel force leads to plastic deformation of the Mylar backing during the peeling process. Peel force of polynBA was too weak to deform the backing. (Adhesive backings are the curled portions in scotch tape and poly(HA-co-nBA) samples. Doubled back tapes on the left side were used to connect adhesive backings with peel tester clamp).

[0040] In conclusion, hydrogen bonding of the imidazole groups in histamine-containing copolymer provides physical crosslinks and reversibility of adhesive material.

Thermomechanical analysis, thermal analysis, peel test, and rheological analysis proved histamine incorporation enhanced cohesive strength and mechanical property of polymers. The reversibility of hydrogen bonding also maintained processibility of adhesive materials.

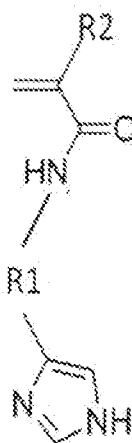
[0041] Although certain presently preferred embodiments of the invention have been specifically described herein, it will be apparent to those skilled in the art to which the invention pertains that variations and modifications of the various embodiments shown and described

herein may be made without departing from the spirit and scope of the invention. Accordingly, it is intended that the invention be limited only to the extent required by the appended claims and the applicable rules of law.

What is claimed is:

1. A copolymer comprising

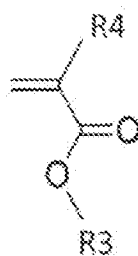
- a. a first comonomer having a structure of Formula I



Formula I

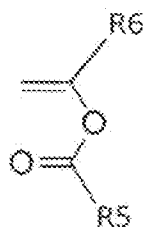
wherein R1 is alkylene having 1 to 3 carbons; and R2 is hydrogen or an alkyl having 1 to 3 carbons; and

- b. a second comonomer having a structure of Formula II, III or IV, or combinations thereof



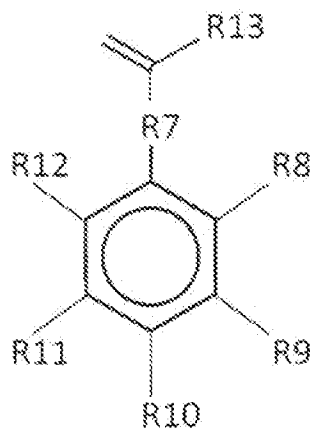
Formula II

wherein R3 is an alkyl having 1 to 16 carbons or alcohol or acids thereof; and R4 is hydrogen or an alkyl having 1 to 3 carbons;



Formula III

wherein R5 is an alkyl having 1 to 12 carbons or alcohols or acids thereof; and R6 is hydrogen or an alkyl having 1 to 3 carbons;



Formula IV

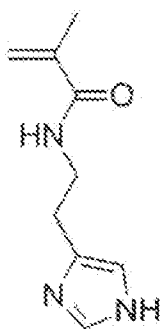
wherein R7 is an alkylene having 0 to 2 carbons; each of R8 to R12 is independently hydrogen, a halogen, or an alkyl having 1 to 3 carbons; and R13 is hydrogen or an alkyl having 1 to 3 carbons.

2. The copolymer of claim 1, wherein the first monomer has the structure of Formula IA



Formula IA.

3. The copolymer of claim 1, wherein the first monomer has the structure of Formula IB



Formula IB.

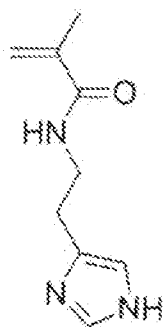
4. The copolymer of claim 1, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof.
5. The copolymer of claim 1, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, or combinations thereof.

6. The copolymer of claim 1, wherein the first monomer is present at about 3-28 mol %.
7. The copolymer of claim 1, wherein the second comonomer is present at about 72-97 mol % by weight of the total copolymer.
8. The copolymer of claim 1, wherein the copolymer is a random copolymer or a block copolymer.
9. An adhesive composition comprising the copolymer of claim 1.
10. The adhesive composition of claim 9, wherein the first monomer has the structure of Formula IA



Formula IA

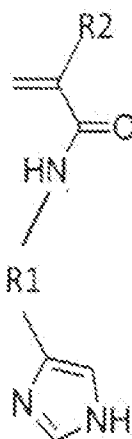
or Formula IB



Formula IB

or a combination thereof.

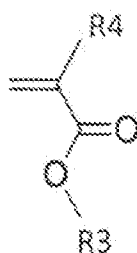
11. The adhesive of claim 9, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof.
12. The adhesive of claim 9, wherein the copolymer is a random or block copolymer.
13. The adhesive of claim 9, wherein the first monomer is present at about 3-28 mol % by weight of the total copolymer, and the second monomer is present at about 72-97 mol % by weight of the total copolymer.
14. A method for making an adhesive comprising the step of copolymerizing a first comonomer having a structure of Formula I



Formula I

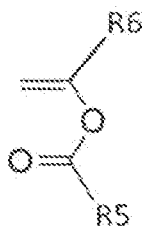
wherein R1 is alkylene having 1 to 3 carbons; and R2 is hydrogen or an alkyl having 1 to 2 carbons; and

a second comonomer having a structure of Formula II, III or IV, or combinations thereof



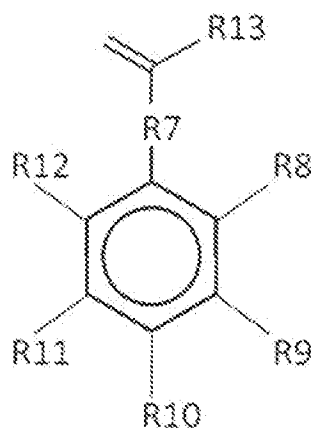
Formula II

wherein R3 is an alkyl having 1 to 16 carbons or alcohol or acids thereof; and R4 is hydrogen or an alkyl having 1 to 3 carbons;



Formula III

wherein R5 is an alkyl having 1 to 12 carbons or alcohols or acids thereof; and R6 is hydrogen or an alkyl having 1 to 3 carbons;



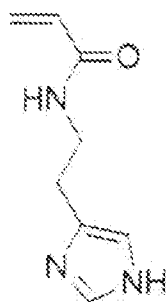
Formula IV

wherein R7 is an alkylene having 0 to 2 carbons; each of R8 to R12 is independently hydrogen, a halogen, or an alkyl having 1 to 3 carbons; and R13 is hydrogen or an alkyl having 1 to 3 carbons.

15. The method of claim 15, wherein the copolymerizing step occurs in a solvent and an initiator.
16. The method of claim 16, wherein the solvent is dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol, or combinations thereof.
17. The method of claim 16, wherein the initiator is azobisisobutyronitrile (AIBN), 4,4'-azobis(4-cyanovaleric acid), organic peroxides, or combinations thereof.

18. The method of claim 15, wherein the reaction is carried out at about 60-70°C for about 18-30 hours under inert gas.

19. The method of claim 15, wherein the first monomer has the structure of Formula IA.



Formula IA

or Formula IB



Formula IB

or a combination thereof

20. The method of claim 1, wherein the second monomer is n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof.

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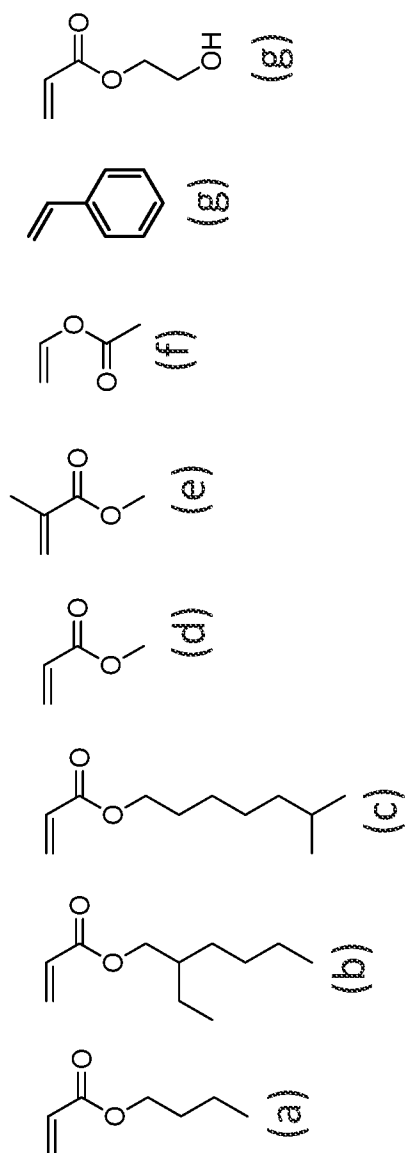


FIGURE 1

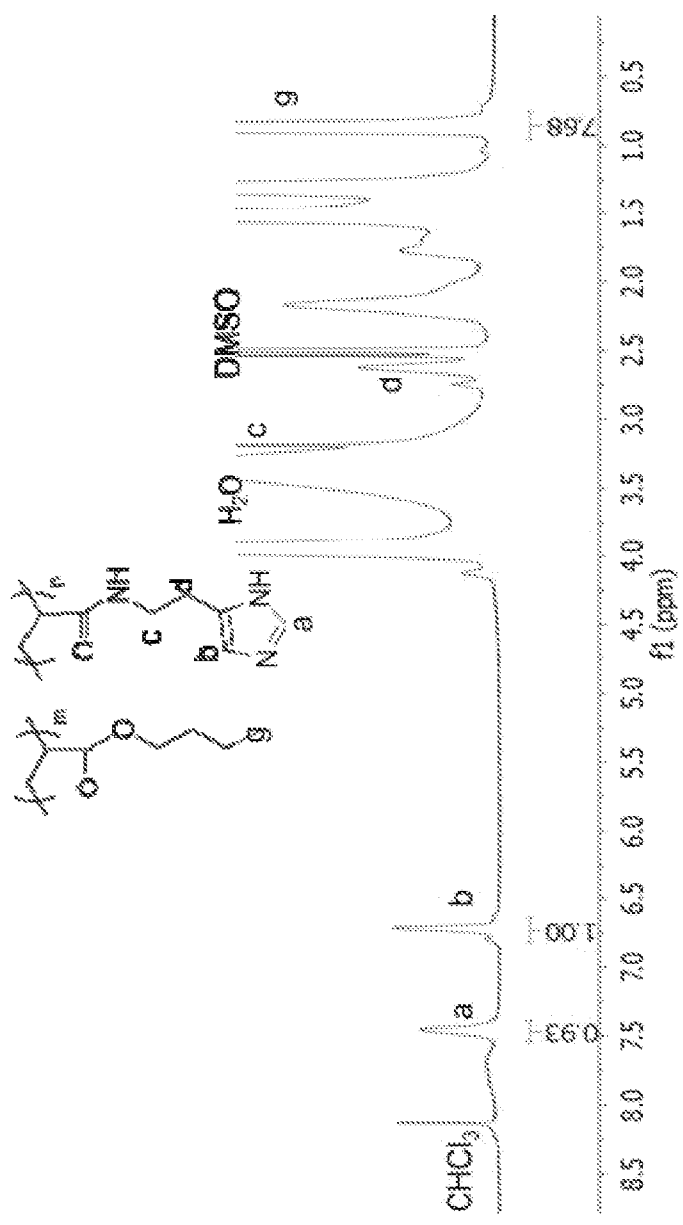


FIGURE 2

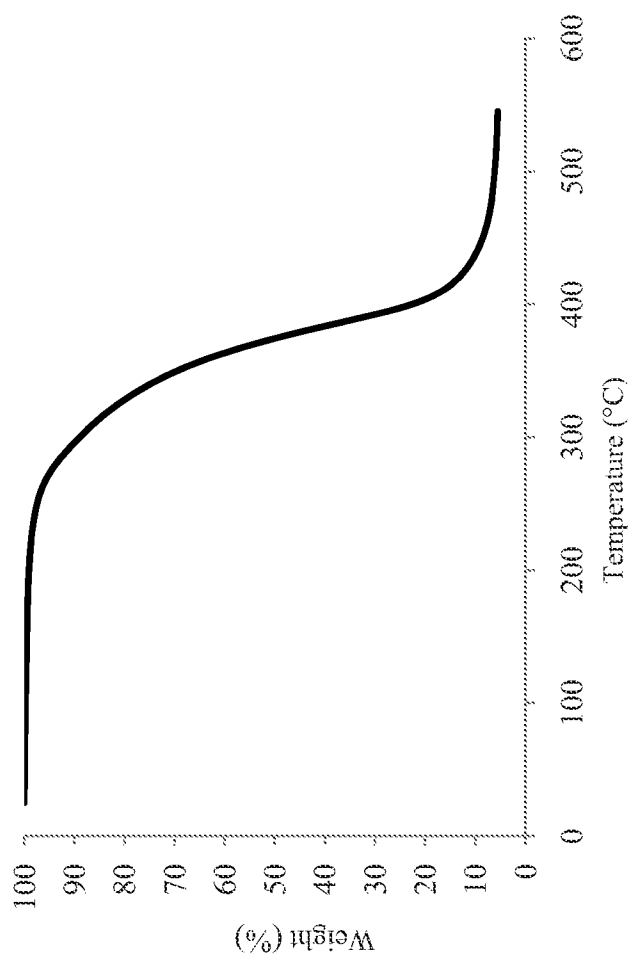


FIGURE 3

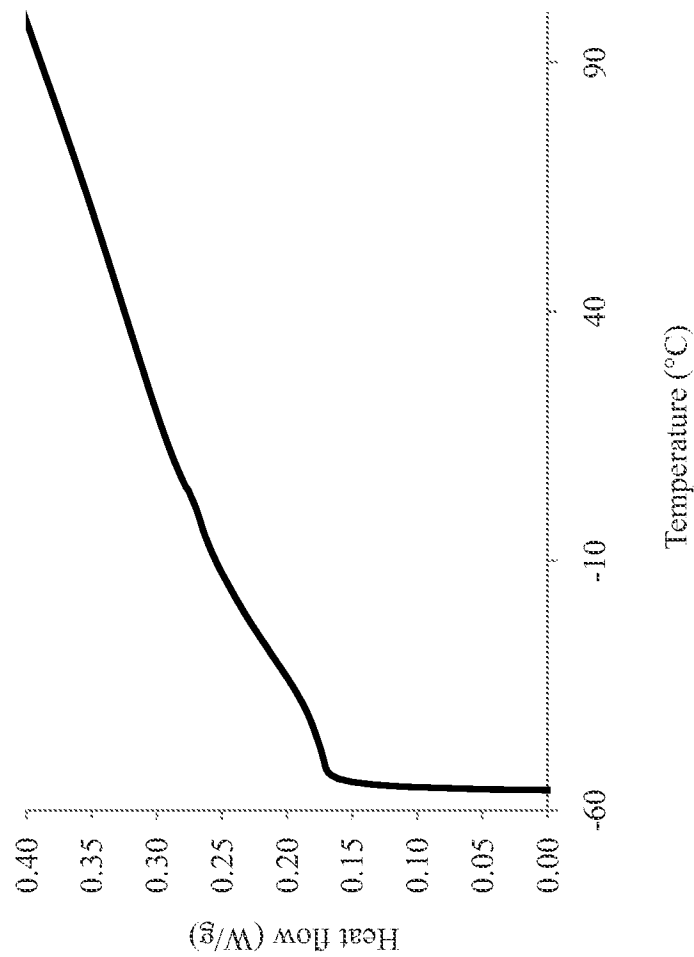


FIGURE 4

HA in polymer (mol%)	11%
HA in polymer (wt%)	13%
M _n	49k
M _w	101k
PDI	2.07
DP	371

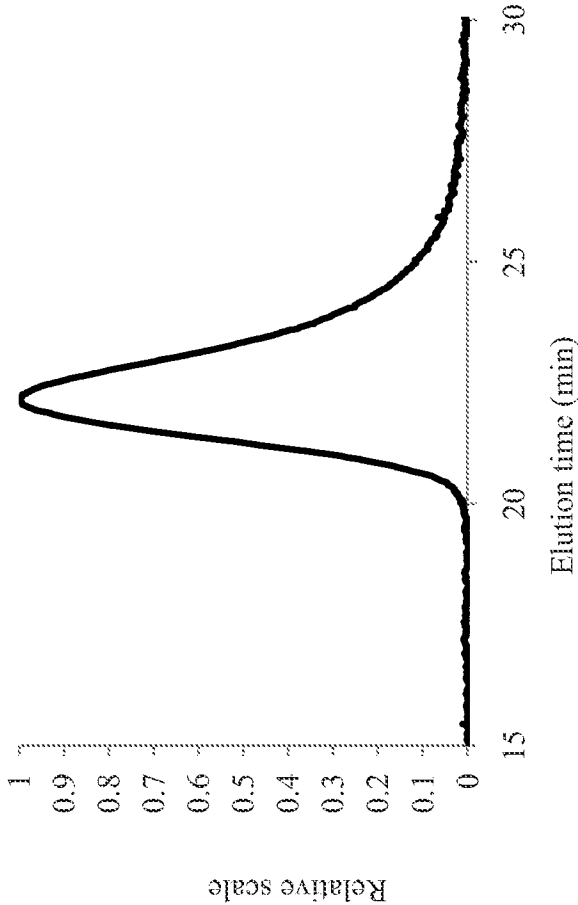


FIGURE 5

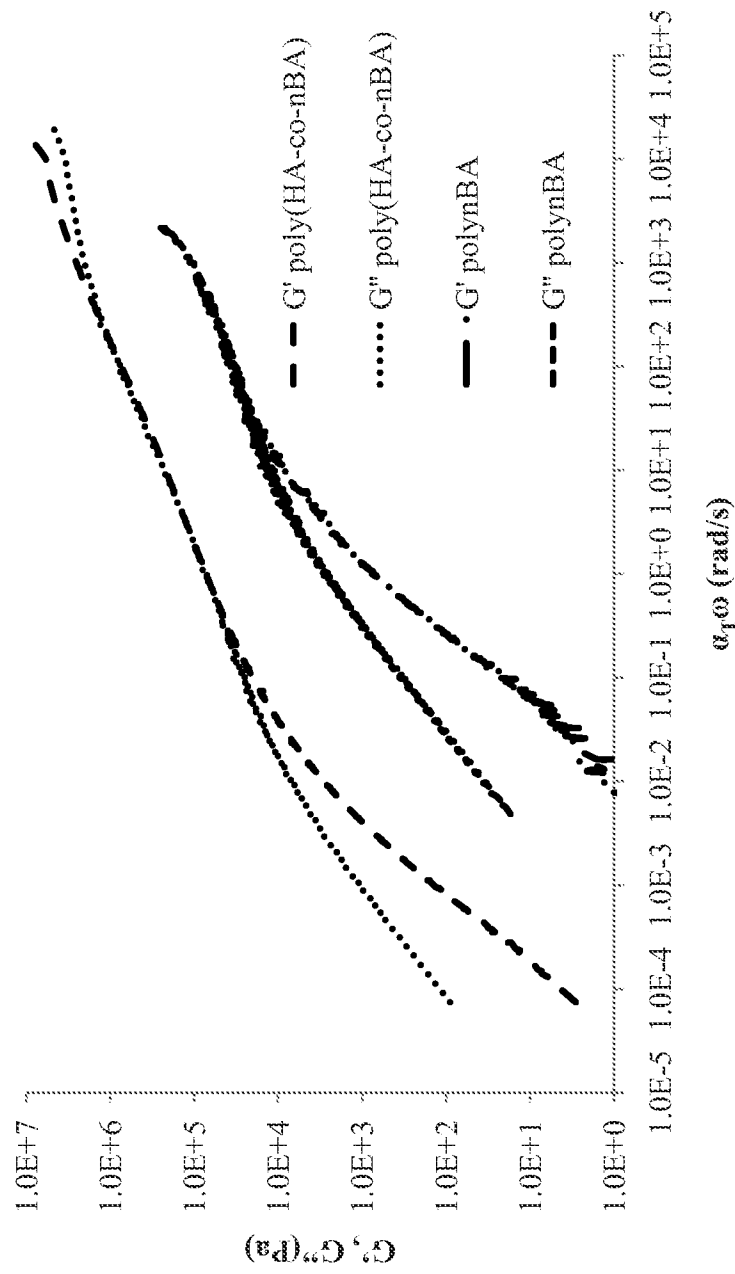


FIGURE 6

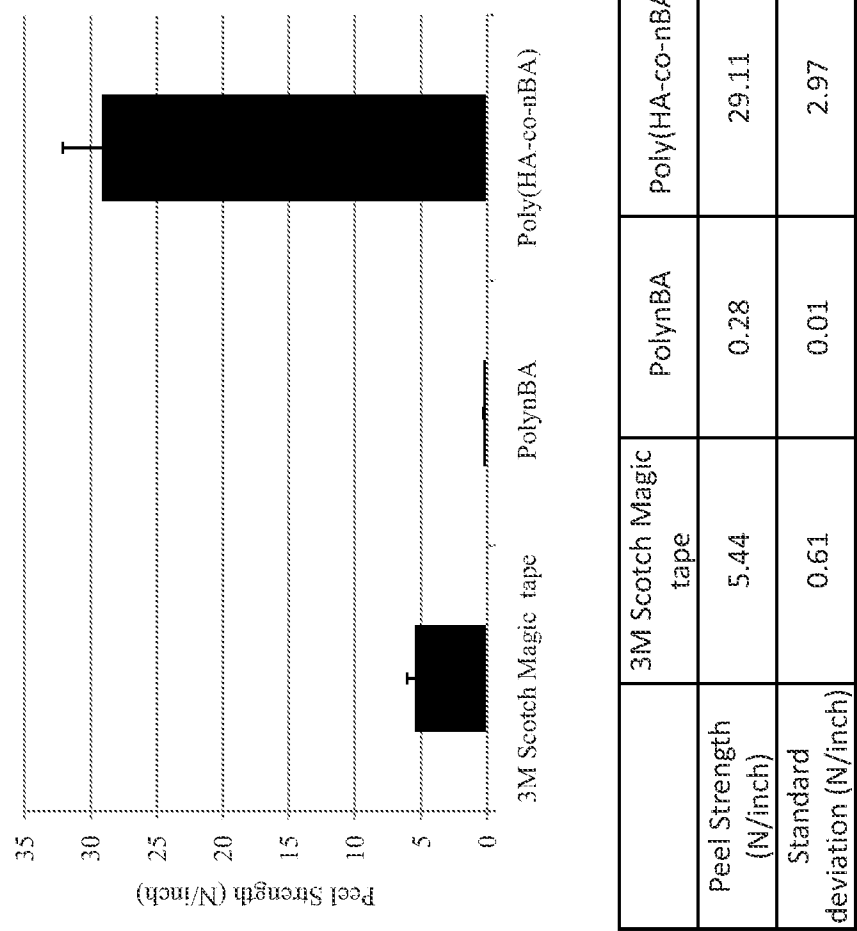


FIGURE 7

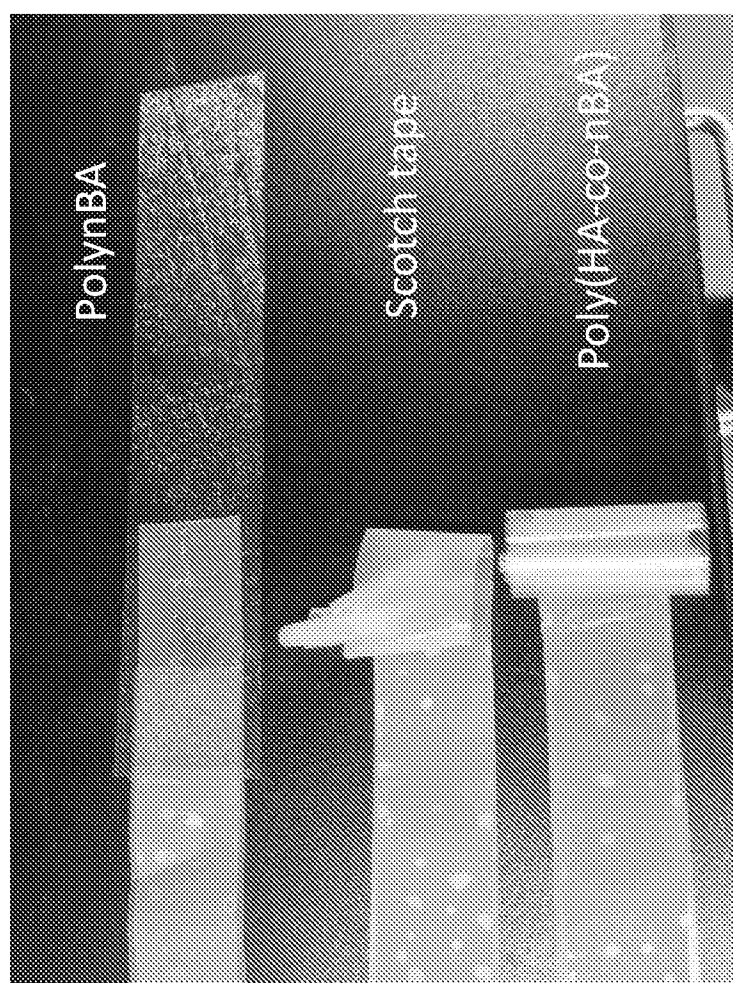


FIGURE 8

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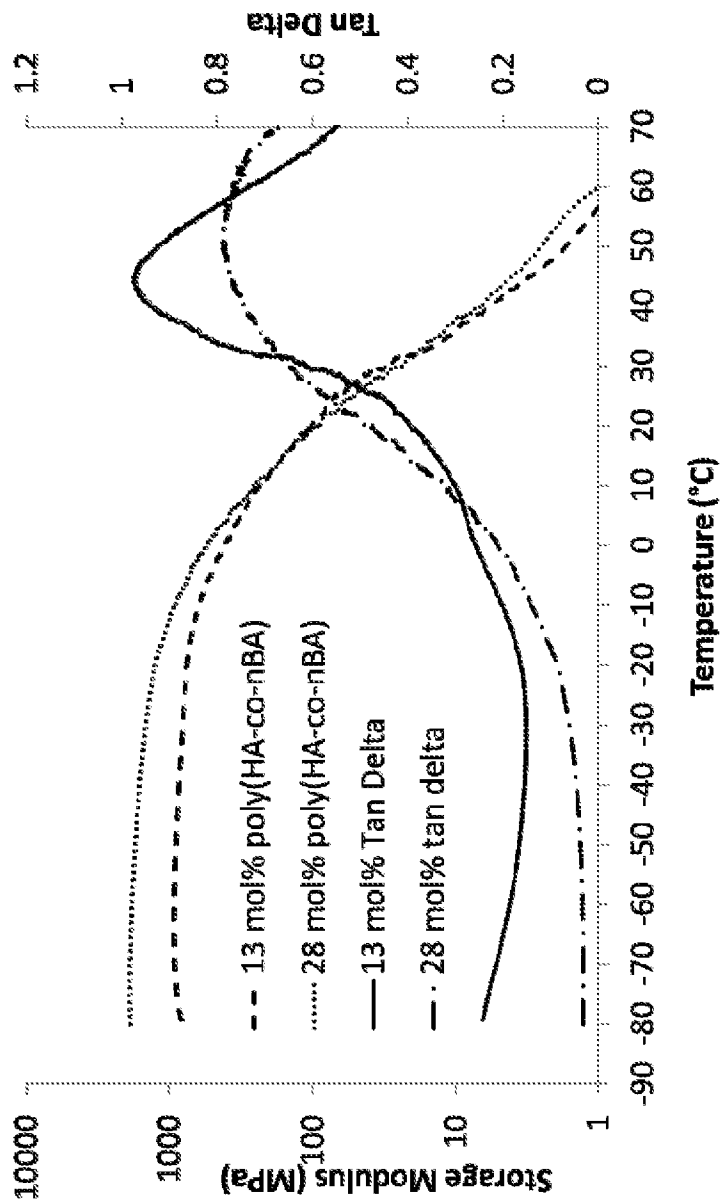


FIGURE 9



FIGURE 10