Polymer-Insulating Material for Rated Electrical Applications

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ABSTRACT: Putty is an encapsulation polymer-insulating material that protects the windings of large motors, generators, and transformers from coronas, radiation, and heat. It is used as a barrier insulation in windings to make void-free and air-gap-free structures. A two-pack epoxy putty has been developed with inorganic-filler powder materials. The cured putty system has very high adhesion to substrates, and it is flexible enough to absorb the heating and cooling cycles of coils without cracking after long-time use. The mechanical and electrical properties of the putty have been determined with methods of the American Society for Testing and Materials. The temperature class of the putty is 203°C. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2310–2315, 2010

Key words: composites; crosslinking; dielectric properties; hardness; mechanical properties

INTRODUCTION

When insulation is required to have a higher electric strength than that of spacing insulation, it is called barrier insulation. Because the voltage gradient or field stress in this case exceeds the breakdown stress for gases, it is important to eliminate void spaces.[1] If such voids are present, organic insulation may be rapidly destroyed by partial discharges (coronas) within the voids.[2] Barrier insulations are usually formulated to incorporate materials that are resistant to the action of partial discharges and processed to minimize these spaces. Some inorganic materials such as talc, mica, iron oxide, and silica powders inherently have very high barrier strengths.[3] They are required as protective coatings for rotors, stators, and transformer cores, and polymers are materials that do the job. Epoxy, solvent-less polyester, and polyurethane resins are generally used for the preparation of putty for electrical applications. Putty, a mixture of a high percentage of fillers and resin, has a pastelike structure. When applied by hand or with a knife to the voids of coils and heat-cured, it produces a hard composite mass with a smooth surface. Because the inorganic particles in putty have inherent resistance to stresses, the performance of putty is solely dependent on the capacity of the polymer matrix to withstand mechanical, thermal, electrical, and chemical stresses.[4] An epoxy resin with an anhydride hardener is a very suitable candidate for putty formulations. It has very good adhesion to substrates and high mechanical properties.[5] However, an epoxy putty is very hard and develops cracks from the heating and cooling cycles of coils. On the other hand, a polyester putty system is quite flexible, but its electrical and mechanical properties deteriorate rapidly with the aging of coils.[6] To overcome this problem, an epoxy system has been developed with a long-chain dianhydride hardener that has much molecular freedom through two ester linkages (see the structure of the anhydride in Fig. 1). The mechanical, electrical, and chemical resistance properties of this epoxy putty have been thoroughly evaluated. It is also interesting that the cured polymer composite can survive severe heat and vibration with a humidity treatment over a long time, whereas other putties under the same conditions fail. The thermal class of the putty has been determined by International Electrotechnical Commission (IEC) method 60216 to be 203.03°C. This putty is recommended for applications in 200°C-rated motors, generators, and transformers.

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EXPERIMENTAL

Synthesis of the anhydride hardener

A mixture of 288 g (2 mol) of cyclohexane dimethanol and 768 g (4 mol) of trimellitic anhydride was reacted in a glass kettle (3 L) with stirring under a nitrogen purge. The temperature was gradually increased to 280°C for about 90 min. During this time, about 68 g of water evolved (72 g theoretically).

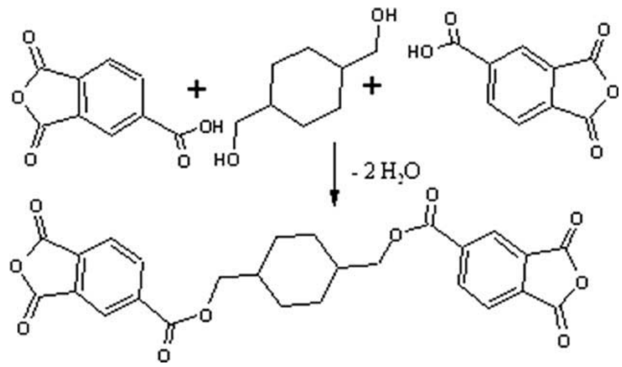

Figure 1 Structure of the dianhydride used as the hardener for the epoxy resin.

A vacuum of 7–8 mmHg was applied for 30 min at 260°C. The viscous mass was cooled to 120°C and poured into a tray to bring it to room temperature. The flakes of the anhydride were ground into a powder form.[7]

ANAL. Calcd. for the anhydride product: C, 63.42%; H, 4.09%; O, 32.49%. Found: C, 63.44%; H, 4.06%; O, 32.49%. Melting point: 110°C. Formula weight: 492.431.

Design of the putty

The epoxy putty was a two-pack system: one part was only virgin epoxy resin [diglycidyl ether of bisphenol A (DGEBA); GY 250, Ciba-Geigy, Mumbai, India; epoxy equivalent = 180–190 eq/kg, viscosity = 10,000 mPa s], and the other part was a mixture of anhydride, talc, alumina, iron oxide, cadmium sulfide, and *tert*-triethyl amine (see Table I). During its application, the two parts were thoroughly mixed to make a paste in a machine *in vacuo* such that entrapped air was removed. However, different putty compositions were made through changes in the filler/polymer ratio. With a very high percentage of the filler, it was very difficult to mix the composition homogeneously, and with a very low percentage of the filler, resin and anhydride oozed to the surface and flowed during elevated-temperature curing. As a result, the presented composition was selected as the optimum one (Table I). The paste was applied in a metal die to make test pieces for mechanical, electrical, and thermal experimentation. The putty was cured to a hard mass at 160°C for 10 h in an air-circulated oven. Special test samples were fabricated from this cured mass to measure the mechanical and electrical properties. Some of the test pieces were treated with boiling water, and then the dielectric properties of the samples were measured to monitor the moisture resistance of the putty compound. The accelerated thermal aging test of the flexural strength of the putty bar was done with 60 mm × 20 mm × 3 mm pieces.

Mechanical properties of the putty

Hardness has been variously defined as resistance to local penetration, scratching, machining, wear or abrasion, and yielding. Shore hardness is a measure of the resistance of a material to indentation by three spring-loaded indenters. A diamond-tipped hammer in a graduated glass tube is allowed to fall from a known height onto the specimen to be tested, and the hardness number depends on the height to which the hammer rebounds: the harder the material, the higher the rebound. Shore hardness is measured with an apparatus known as a durometer according to American Society for Testing and Materials (ASTM) method D 2240.[8] The hardness of the putty sample was measured at 25 and 200°C. Compressive properties describe the behavior of a material when it is subjected to a compressive load at a relatively low and uniform rate. The compressive strength of the putty sample (12.7 mm × 12.7 mm × 25.4 mm) was measured by the sample's placement between compressive plates parallel to its surface and then the application of a compression load (at a speed of 0.5 mm/min) according to ASTM method D 695.[9] The tensile strength, elongation at break, and modulus of elasticity of the putty were measured

TABLE I
Names and Sources of the Putty Ingredients

S.No	Name	Quantity (g)	Source
		Dianhydride	
1	Cyclohexane dimethanol	288	Eastman, Kingsport, TN
2	Trimellitic anhydride	768	Amoco, Chicago, Illinois
		Putty	
3	DGEBA (GY 250)	915	Ciba-Geigy, Mumbai, India
4	Dianhydride	726	
5	Talc	440	Degussa, Bennigsenplatz, Germany
6	Alumina	120	Degussa, Bennigsenplatz, Germany
7	Iron oxide	8.5	Bayer, Leverkusen, Germany
8	Cadmium sulfide	8.5	Sudarshan Chemicals, Pune, India
9	*tert*-Triethyl amine	5.3	Fluka, Mumbai, India

TABLE II
Mechanical Properties of the Putty

S.No	Property	Value
1	Shore D hardness	
	At 25°C	80
	At 200°C	76
2	Compressive strength	
	At 25°C	58 N/mm^2
	At 200°C	54 N/mm^2
3	Elongation at break	
	At 25°C	1.8%
	At 200°C	2.4%
4	Tensile strength	
	At 25°C	25 N/mm^2
	At 200°C	22 N/mm^2
5	Modulus of elasticity at 25°C	25,000 N/mm^2
6	Shear strength	
	At 25°C	4 N/mm^2
	At 200°C	3.6 N/mm^2
7	Flexural strength	
	At 25°C	48 N/mm^2
	At 200°C	46 N/mm^2
8	Abrasion resistance at 25°C	225 mg
9	Adhesive strength (Cu–Cu)	180 kg/cm
10	Heat deflection temperature	185°C

with an Instron model 3440 universal testing machine according to ASTM method D 3039.[10] The in-plane shear strength of the putty was calculated by the division of the maximum shear load by the product of the width of the specimen and the length of the failed area. The width, thickness, and length between the notches of the specimen were measured (79.5 mm × 12.7 mm × 6.6 mm). The specimen was placed in the fixture, and the bolts were tightened. The specimen was loaded to failure at 1.3 mm/min in an Instron universal testing machine. The sheared area was measured and used to calculate the shear strength (ASTM D 3846).[11] Test specimen disks were spun on a turntable and were abraded by a pair of abrading wheels for a specified number of cycles under a specified load. The mass change of a putty disk due to material loss from abrasion is called abrasion resistance (ASTM D 1044).[12] The flexural strength of the putty sample (60 mm × 20 mm × 3 mm) was measured with a universal testing machine according to ASTM method D 790.[13] All the experiments were also performed at 200°C in a special hot air chamber in which the sample holder of the Instron universal machine could move freely. All the aforementioned experiments were performed five times with five samples, and the average values are reported in Table II. The heat deflection temperature is the temperature at which a standard test bar deflects a specified distance under a load. It is used to determine the short-term heat resistance of a material that is able to sustain light loads at high temperatures and does not loose its rigidity over a narrow temperature range. Three rectangular strips (150 mm × 10 mm × 4 mm) were placed under the deflection measuring device. A load of 1.80 MPa was placed on each specimen. The specimens were then lowered into a silicone oil bath; the temperature was raised at 2°C/min until they deflected 0.25 mm (ASTM D 648),[14] and the average value of the heat deflection temperature experiment is reported.

Electrical properties of the putty

The dielectric strength of the putty was measured on a cured plate (120 mm × 120 mm × 1 mm) with a model HVO-35 instrument (35-kV alternating current and 75 mA; Sivanand Electronics, Mumbai, India) according to ASTM procedure D 149-97a.[15] The volume resistivity, dielectric constant, and dissipation factor were measured on these plates with a model EW188 instrument (Sivanand Electronics) according to ASTM methods D 257-07 and D 150.[16,17] Some of the plates were immersed into water, boiling water, and transformer oils for a few days (see Table III), dried at room temperature, and then tested for the electrical properties. All testing was done five times with five samples, and the average values are presented in Table III. The tracking resistance and arc resistance were measured on a cured putty plate (120 mm × 120 mm × 3 mm) according to ASTM methods D 3638-07 and D 495, respectively.[18,19] An electrically conductive solution of ammonium chloride (0.1*N* NH_4Cl) was dripped (1 drop/s) between two platinum electrodes placed on cured plates (3 mm thick) of the putty. The electrodes were positioned at a distance of 4 ± 0.1 mm and at an angle of 60° to the horizontal. The maximum alternating current voltage (60 Hz) with 50 drops of a solution when the overcurrent of relay tripping first occurs is called the comparative tracking index. For arc resistance, two carbon electrodes were placed on the sample surface at a distance of 1 mm and at an angle of 60° to the horizontal. The arc intensity was doubled every 30 s with an applied voltage of 220 V. The time in seconds that the insulating surface survived against the arc is called the arc resistance.

Determination of the thermal class of the putty

Sixty test pieces of the cured putty (60 mm × 20 mm × 3 mm) were placed separately in three ovens at 210, 230, and 250°C.[20] The aging cycles were 49 days at 210°C, 14 days at 230°C, and 4 days at 250°C.[21,22] After each cycle of temperature and time aging, five samples were taken out of the oven and allowed to cool to room temperature. Flexural strengths were measured for these samples, and the average values were recorded (see Table IV). The experiments were carried out until a 50% loss of the initial flexural strength occurred (see IEC 60216, parts 1 and 2). The

TABLE III
Electrical Properties of the Putty

S.No	Properties	Value
1	Volume resistivity in air at 25°C	2.8×10^{15} Ω cm
	After immersion in water for 7 days	1.8×10^{14} Ω cm
	After immersion in boiling water for 1 day	1.2×10^{12} Ω cm
	After immersion in transformer oil for 7 days	2.8×10^{15} Ω cm
2	Dielectric strength in air at 25°C	25 kV/mm
	After immersion in water for 7 days	23 kV/mm
	After immersion in boiling water for 1 day	18 kV/mm
	After immersion in transformer oil for 7 days	24 kV/mm
3	Dielectric constant in air at 25°C	2.8
	After immersion in water for 7 days	3.4
	After immersion in boiling water for 1 day	4.8
	After immersion in transformer oil for 7 days	3
4	Dissipation factor in air at 25°C	0.03
	After immersion in water for 7 days	0.18
	After immersion in boiling water for 1 day	0.5
	After immersion in transformer oil for 7 days	0.08
5	Tracking resistance	160
6	Arc resistance	120 s

time in days to the 50% loss of flexural strength (see Fig. 2) was converted to hours, and then the logarithm of time versus the inverse of the absolute temperature was plotted. The extrapolation of the straight line to the logarithm of the 20,000-h line gave the temperature index of the cured putty (Fig. 3).

RESULTS AND DISCUSSION

Structure of the putty

The epoxy putty is an epoxy resin with an extremely high viscosity based on bisphenol A that contains inorganic fillers and an anhydride hardener. It is a two-component epoxy resin system designed specifically for a patching system. When applied by hand or with a steel trowel, it seals air voids, cracks, and gaps in horizontal, vertical, and overhead surfaces of coils in motor and transformer windings. The dianhydride has four reactive groups that react with four epoxy groups of DGEBA, and it makes a three-dimensional network structure. Tertiary triethyl amine is used as a catalyst of the curing reaction and increases the speed of the curing reaction. Without the amine, the curing reaction takes a lot of time to cure, and putty oozes from the place of application. The cured polymer is a saturated polyester polymer with two hydroxyl groups per DGEBA segment. This hanging hydroxyl group produces adhesion of the resin to the inorganic fillers and substrates. On the other hand, the anhydride structure is quite flexible because of two ester linkages, and this provides more advantage than the other anhydride-curing putty. This putty does not develop cracks from the heating and cooling cycles of heavy-duty motors and transformers.

The fillers used in the putty have different functions. The alumina used in the putty has crystalline

TABLE IV
Flexural Strength of the Putty After Heat Aging

	Flexural strength (N/mm^2)		
Cycles completed	At 210°C	At 230°C	At 250°C
Initial	48	48	48
1	45.2	44.5	43
2	42.5	41.3	38
3	40	37.2	34
4	37.1	34.5	29
5	34.7	30	24
6	32	27.5	19.5
7	29	24	
8	26	20	
9	23.5		
10	21		

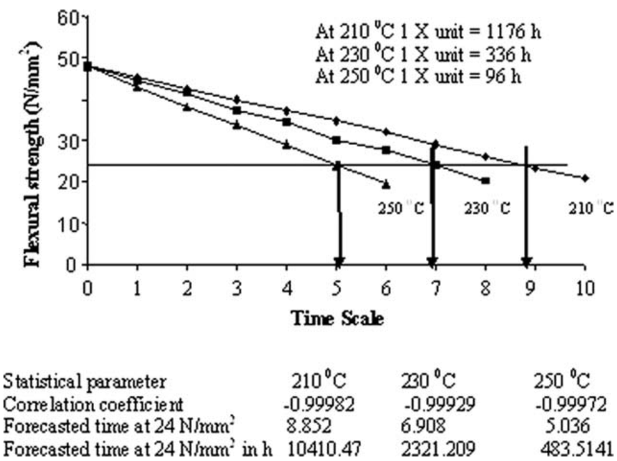

Figure 2 Determination of the aging time up to a 50% loss of the flexural strength at 210, 230, and 250°C.

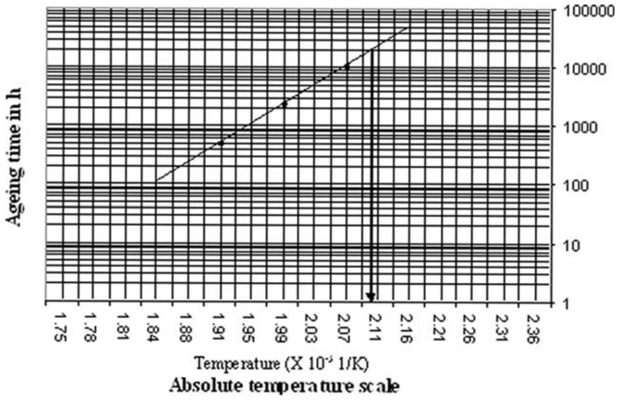

Figure 3 Thermal endurance curve for the epoxy putty: the logarithm of time versus the reciprocal of the temperature. The extrapolation of the Arrhenius plot to 20,000 h meets the *x* axis at 2.101.

water, which is easily released, absorbs heat, and is recaptured on cooling. The red iron oxide and cadmium sulfide are semiconducting materials that resist the formation of tracking paths in putty. Talc is used for its very low dielectric constant and low cost. On curing, the final structure is a hard mass with a resin-rich surface.

Properties of the putty

The mechanical properties of the putty compound were thoroughly evaluated because it could be used as a structural material in rated motors and transformers. The hardness, bond strength, and compression strength of the putty are good enough (see Table II) to withstand mechanical loads such as the vibrations and centrifugal force of electrical equipment. The putty, sandwiched (1 mm thick) and cured between two copper plates, was treated with boiling water, a mild acid (0.01*N* HCl), and an alkali solution (0.01*N* KOH) for 7 days separately, and the adhesive strength was measured. It was affected very little. The flexural strength and abrasion resistance of the putty are very high, and it can withstand sudden jerks. The heat deflection temperature of the cured putty is 185°C, and the mechanical properties are affected very little up to this temperature. After each aging cycle at 200°C for 49 days, five putty test specimens were fixed in a vibration bed of $\pm 7g$ intensity for 1 h. They were then placed in a humidity chamber (100% relative humidity at 40°C) for 48 h. The goal was to determine how the humidity would affect the core putty structure by entering through cracks (if any) produced by the vibration treatment. After each aging cycle, which was followed by vibration and humidity conditioning, each test specimen was immediately subjected to a flexural strength test. The flexural strength remained unaltered after six cycles (see Table V). Because the inner structure of the putty is much more flexible on account of its large dianhydride content, the putty was expected to survive the vibration treatments. Both peroxide-cured polyester-based and monoanhydride-cured epoxy putties (generally used in traction motors and generators) survived only a few cycles.

Because this putty compound was designed solely for application in electrical equipment, its electrical properties were also thoroughly evaluated. The volume resistivity, dielectric strength, dielectric constant, and dissipation factor of the putty were determined at 25°C and after treatment with boiling water and transformer oil (see Table III). The dielectric properties were affected very little by the boiling-water treatment. All these dielectric properties are good indications of the putty as an insulating material.[23]

The temperature class of the putty compound is 203°C. The heat-aging data for the flexural strength were statistically calculated for the correlation coefficient and for the forecast temperature at 20,000 h. The correlation coefficient and temperature rating of the putty were 0.999 and 203.03°C, respectively, and this also showed consistency in experimentation (Fig. 3). This putty is highly recommended for use in 200°C-rated motors and transformers.

CONCLUSIONS

A putty compound was designed with a conventional DEGBA resin and a tetra-acid dianhydride containing inorganic fillers. The cured structure of the putty is a crosslinked polyester matrix, and fillers are embedded in it. The anhydride was synthesized for more flexibility in the structure as a putty cured with a conventional anhydride developed

TABLE V
Comparison of the Flexural Strength After Heat Aging, Vibration, and Humidity Treatment of the Studied Putty and Standard Putty Products

	Flexural strength (N/mm^2)		
Cycles completed	Modified-dianhydride-cured epoxy putty	Monoanhydride-cured epoxy putty	Peroxide-cured polyester putty
1	46	40	32
2	45.2	32	24
3	45.2	28	16
4	45	20	8
5	45.2	12	8
6	45.2	12	8
7	40	12	8
8	38	12	8
9	35	10	8

One cycle consisted of 49 days at 200°C, treatment with $\pm 7g$ vibration for 1 h, and treatment with humidity (100% relative humidity at 40°C) for 48 h.

cracks after longtime use because of its inherent hardness. The heat deflection temperature and mechanical and electrical properties were evaluated. The cured putty is expected to prevent the formation of cracks, electrical treeing, and tracking paths in the structure when it is exposed to the heating and cooling cycles of coils and vibration, electrical, and environmental stresses. Furthermore, the temperature class of the putty is 203°C, and it can be used in heavy-duty motors, transformers, and other electrical equipment.

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