Study of the Properties and Reliability of EMC Packaging Material

Hsien-Tang Chiu, Jung-Sheng Chung

Graduate School of Textile and Polymer Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Sec.4, Taipei, Taiwan 10672, Republic of China

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ABSTRACT: Thermoplastic nylon powder with a low melting point was added to Biphenyl Epoxy to serve as a forming stress release agent that is intended to reduce the stress resulting from Epoxy Molding Compound (EMC). The purpose of this study was to explore the physical impact and effect on the formed object after adding nylon powder to Biphenyl Epoxy. Mechanical properties were explored through the Izod impact test and the three-point bending test. Thermal Mechanical Analysis and Dynamic Mechanical Analysis were conducted to probe the coefficient of thermal expansion (CTE) and the glass transition temperature (T_g). The rate of water absorption was measured via a test of the pressure cook test (PCT), and insulation resistance was assessed through the insulating destruction experiment. The results indicate that adding nylon powder increases the fracture energy of the epoxy-formed material; however, mechanical properties decreased slightly. TMA showed that the CTE (α_1) decreased when nylon was added, and DMA revealed that heat resistance decreased slightly. The water absorption rate test and the PCT test showed that the rate of water absorption increased to a small extent, whereas the breakdown voltage (BDV) decreased slightly. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3928–3933, 2003

Key words: blending; nylon; thermoplastics; thermosets

INTRODUCTION

Epoxy resin is characterized by features of excellent adhesion, superb stability, small shrinkage, outstanding mechanical and electrical properties, and resistance against solvents, acids, alkalies, and water. Consequently, it is considered a good material for IC packaging. Nevertheless, brittleness resulting from high crosslinking leads to increased failure rate of IC elements. As IC devices are developing towards a highly intensive and small-scaled trend, requirements for low stress and brittleness resistance demanded for the packaging material become even stricter. As a result, elements like low moisture absorption, coefficient of thermal expansion, heat resistance, etc., will be critical to evaluate materials.

Recently, silicone rubber has been applied to improve tenacity and stress of packaging material[1,2] because it can maintain the original properties of heat resistance and thermal stress; however, silicone rubber is incompatible with epoxy resin from the thermodynamic perspective, and compatibility needs to be increased by other techniques like introducing phenyl to silicone rubber, combining silicone rubber with amino or epoxy substance with epoxy resin to form block copolymerization, adding polyether, etc.[3]

As thermoplastic epoxy resin has already laid a good foundation,[4–6] the approach of physical blending of a low melting point crystalline nylon powder was adopted in this study to serve as a tenacity and stress modifier. For the process of manufacturing EMC material, this method is not only convenient and quick, but also can increase the impact and fracture energy of the material, which modifies epoxy resin, reduces the inner stress, and maintains heat resistance of the material. As a result, the effect of adding nylon powder to epoxy-formed products is discussed in this research. For the experiment, Izod impact, the three-point bending, and the adhesive strength tests were utilized to explore mechanical properties. Morphology was observed through an electron microscope, and the impact of nylon epoxy resin was probed. The effect of the glass transition temperature (T_g) was evaluated by conducting Dynamic Mechanical Analysis (DMA). The effects of the coefficient of thermal expansion (CTE) as well as physical and chemical properties were explored through Thermal Mechanical Analysis (TMA), the pressure cook test (PCT), and the moisture absorption tests. Impact upon insulation resistance was assessed via the breakdown voltage experiment.

EXPERIMENTAL

Materials

The materials used herein included Biphenyl Epoxy, product name YX4000H (EEW 193), and Terpene Phe-

Correspondence to: H.-T Chiu (js.chung@msa.hinet.net).

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TABLE I
Table of Component Formulas

Component	Component formula (all compositions are in grams)				
	1	2	3	4	5
Epoxy	100	100	100	100	100
Hardner	83	83	83	83	83
Promoter	1	1	1	1	1
Silica	448	448	448	448	448
Flame retardant	6	6	6	6	6
Modifier	0	5	10	15	20
Coupling agent	1	1	1	1	1
Stearine	1	1	1	1	1

nol Hardner, product name MP402 (OH equivalent 175). Both were purchased from Yuka Shell Epoxy Co., Japan. TPP (Triphenylphosphine) was purchased from FERAK, Germany, and used as promoter. Nylon Powder from Toray Co., Japan, product name SP500, white powder with a particle size of 6.5 μm, m.p. 159°C. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide from Schill+Seilacher, Germany, was used as flame retardant. Fused silica was supplied from Fukusima Kiln Co., Japan. 3-Glycidyloxypropyltrimethoxysilane, $C_9H_{20}O_5Si$, from Tokyo Kasei Industrial Co., Ltd., was used as coupling agent. Stearine, $CH_3(CH_2)_{16}$ COOH, from FERAK, Germany, was used as a release agent.

Sample preparation

The components of the sample are shown in Table I.

Epoxy and the hardener of the same equivalent proportion of 1 : 1 was added to the aluminum container and then heated up to 120°C. After melting, it was evenly stirred with a mixer and kept until the temperature reduced to 80°C. TPP of 0.5 phr was added and stirred for 10 s. After cooling there was a break, which is the so-called B-stage. Then another TPP of 0.5 phr was added into the hardened epoxy and it was broken with a breaker, which leads to fine powder. Then, nylon powder of different contents was added to the broken epoxy.

On the other hand, the coupling agent and the deionizing water was stirred and mixed with a rate of 1 : 3. The filler was sprayed with an aerosol and then mixed with the filler with the broken epoxy sample and then refined with the two-roll mill at 90°C for 5 min. After cooling, the breaker was used to break the sample.

The sample was then filled into the hot pressed die and premelted at 90°C for 5 min. A working pressure of 2 MPa at 185°C for 30 min was applied prior to removing it from the die. Then it was sent to the oven for hardening for 7 h and then trimmed to the required size.

Measuring

For testing of flexural strength and flexural modulus, the test piece was trimmed to a size of 3 × 12.7 × 127 mm in accordance with ASTM D790 and the span interval was set as 50 mm through the three-point bending test. The test was conducted with a velocity of 1.2 mm/min at room temperature via a universal strength-testing machine. The acquired strength and the modulus can be calculated with a formula as follows:

$$\sigma = 3PL/2bd^2$$

$$E\ L^3/4bd^3 \times P/y$$

where σ is stress, E is the flexural modulus, l is the distance between the test pieces, P is the maximum destructive power, b is the width of the test piece, d is the thickness of the test piece, and y is the delfection of the load point.

For testing of the Izod Impact, conduct the test with a V-shaped test piece of 1/8 inch (3/2 mm) in thickness and of 2.54 mm in the gap depth of the notch at room temperature. The acquired destructive energy can be calculated via the following formula:

$$A = E/b(t - d) \times 1000$$

where A is the destructive power, E is the absorption power, b is the width of the test piece, t is the thickness of the test piece, and d is the depth of the V-shaped notch.

For testing of lap shear adhesive strength, place the powdered resin between two aluminum pieces of 25 × 10 mm and place it onto the hot press. The adhesion area will be controlled within 25 × 25 mm^2. Premelt it at 90°C for 3 min and then increase to 180°C to harden it for 7 h. Upon reducing to room temperature, conduct the test with a velocity of 50 mm/min via the universal strength testing machine. For testing of the dynamic mechanical analysis, apply DMA983 produced by Du Pont to the powdered resin of 3 × 40 × 10 mm that has been hot pressed but not added with filler under a resonance frequency of 1 Hz with an increasing temperature of 5°C/min. The range is from room temperature to 250°C. For testing of thermal mechanical analysis, conduct the test with the test piece trimmed into a size of 3 × 4 × 4 mm at a rising temperature of 2°C/min. The range is from room temperature to 250°C. For testing of thermal gravity analysis, we use the model ULVAC TGD 700RH of a thermal gravity analyzer (TGA) to conduct the test under nitrogen at an increasing temperature of 10°C/min. The range is from room temperature to 700°C. For testing of water absorption rate, trim the test piece to a size of 3 × 5 × 5 mm, place it in a dryer for 2 h,

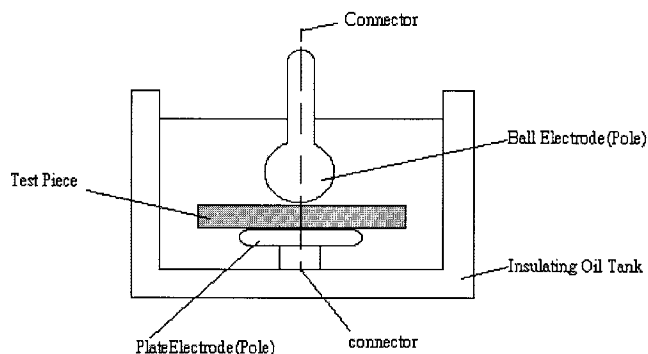

Figure 1 Layout of insulation destruction strength testing.

and remove it to weigh. Put it into an oven at constant temperature and moisture and set the temperature at 85°C and the relative humidity at 85%. Remove it to scale the weight after 100 h. Water absorption rate = [(weight after 100 h − weight removed from the dryer)/weight removed from the dryer] × 100. For testing of the pressure cooking test, trim the test piece to a size of 3 × 5 × 5 mm, place it in a dryer for 2 h, and remove it to weigh. Set the temperature at 130°C and the pressure at 2 atm. Remove it to scale the weight after 24 h. Water absorption rate = [(weight after 24 h − weight removed from the dryer)/weight removed from the dryer] × 100. For Breakdown voltage testing, trim the test piece to a size of 3 × 8 × 8 mm and conduct the test with an increasing voltage rate of 500 V/s until current penetrates. Layout of the breakdown voltage testing is shown in Figure 1.

RESULTS AND DISCUSSION

The material used for EMC has to be characterized with excellent mechanical strength, heat resistance, low water absorption rate, and adhesive strength. The impact upon physical properties, thermal resistance, and insulation by adding nylon powder is discussed as follows.

Dynamic impact imposed by nylon

The relationship between the flexural strength and the amount of nylon powder is shown in Figure 2. After adding nylon, the flexural strength decreases, which might be the result from a low density of crosslinking network compared with that of pure epoxy.[6] The strength decreases to a maximum extent between 5 and 10 phr. The relationship between the flexural modulus and the amount of nylon powder is shown in Figure 3. The modulus decreases as more nylon is added, which indicates that it is tougher than pure epoxy.

The relationship between the fracture energy in the Izod impact test and the amount of nylon powder is shown in Figure 4. The linking density of epoxy decreases as more nylon is added, which makes the material tough, ductile, and increases its fracture energy.

As nylon is added, the lap shear adhesive strength decreases as shown in Figure 5. As the molecular weight of nylon is greater, viscosity becomes greater after melting. As nylon is added, the wetting ability of

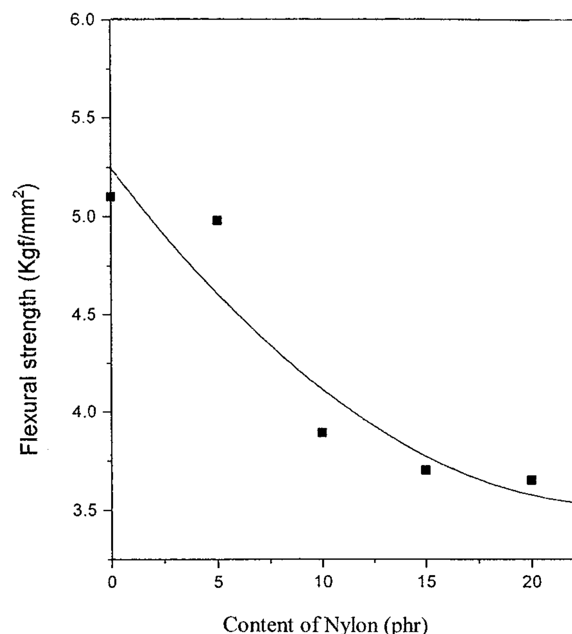

Figure 2 Relationship between flexural strength and different contents of nylon.

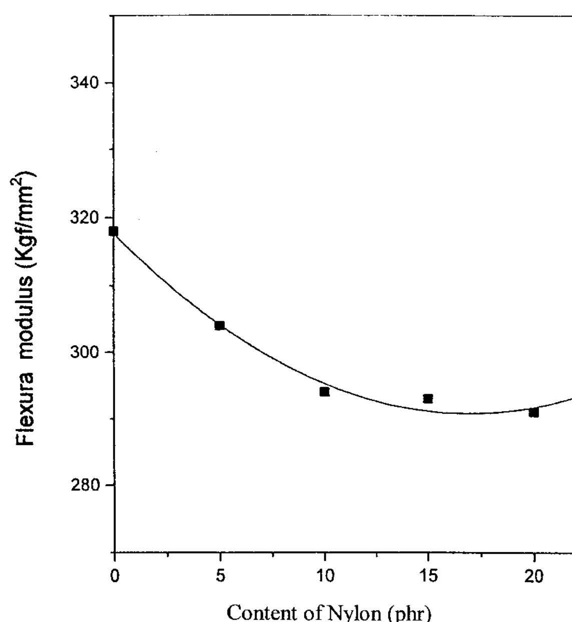

Figure 3 Relationship between flexural modulus and different contents of nylon.

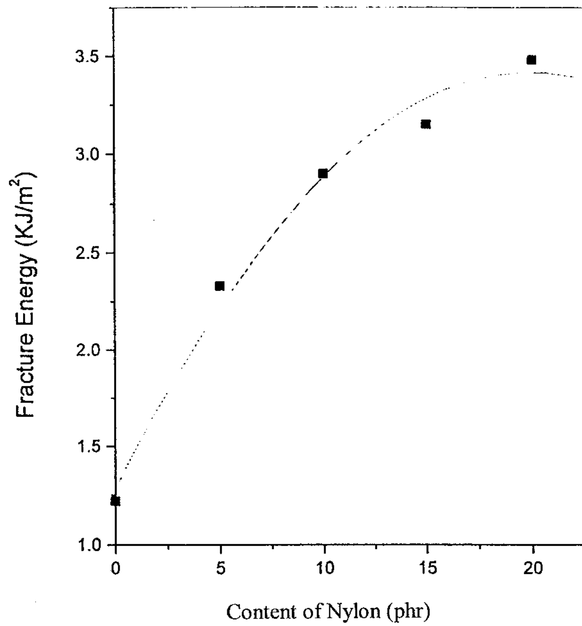

Figure 4 Relationship between Izod impact test and different contents of nylon.

material becomes worse and adhesion is reduced as well. In addition, as nylon has worse adhesion than epoxy, nylon dominant effect is revealed.

Glass transition temperature (T_g) effect imposed by nylon

The relationship between tan δ of DMA and the temperature is shown in Figure 6. The α, the transition

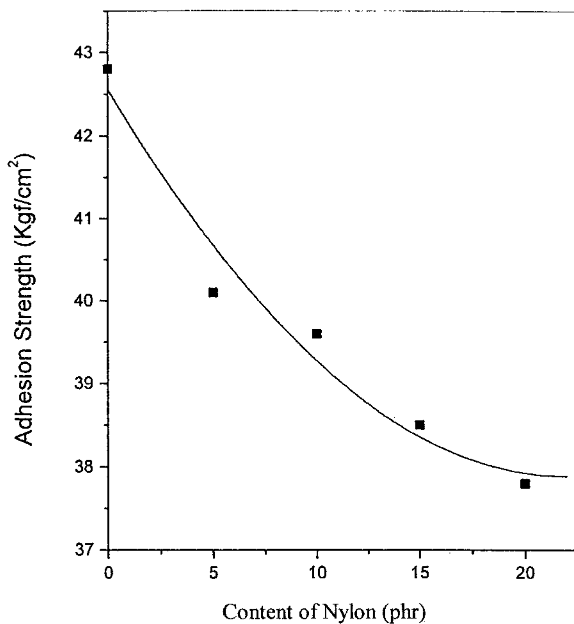

Figure 5 Relationship between adhesion strength and different contents of nylon.

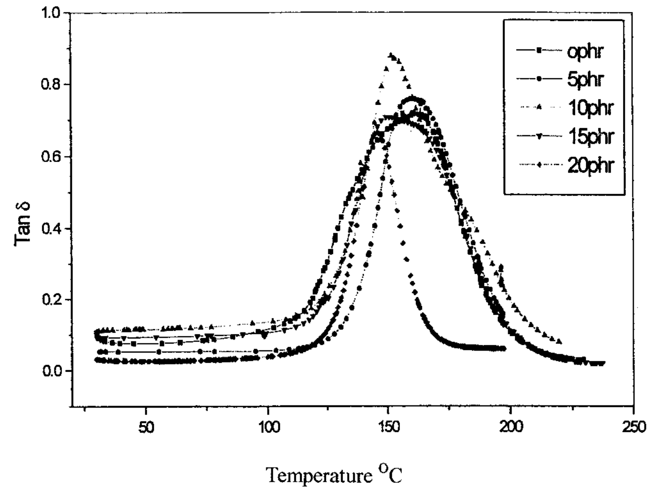

Figure 6 Analysis chart of dynamic viscoelasticity by adding different contents of nylon.

peak, in the figure refers to the glass transition point of integral epoxy (T_g). After adding nylon powder, T_g decreases slightly. As it reaches 20 phr, T_g decreases to 149.8°C. T_g of epoxy is affected by crosslink density after curing because it limits segmental mobility of polymer chains. As more nylon powder is added, a lower crosslink density results, which leads to reduction of T_g. Table 2 shows the T_g of different contents of nylon powder added.

Furthermore, polymer molecules begin to move as the temperature is increased, which causes linear volume expansion. The coefficient of thermal expansion is called α_1. When the temperature reaches the glass transition temperature, the material changes from the glassy state to the rubbery state, which makes the volume expand freely and rapidly. A turning point appears at this moment.[8] As the temperature keeps increasing, the material keeps on expanding and the coefficient of the thermal expansion is called α_2, which is greater than α_1. Results of the acquired T_g and coefficients of thermal expansion are shown in Table 3.

According to the TMA results, it is known that the T_g of the formed material reduces as nylon is added, which coincides with that of the DMA testing.

Impact upon physical properties imposed by nylon

Based on the results shown in Table 3, the coefficient of thermal expansion decreases as nylon powder is

TABLE II
T_g Data Acquired from DMA Testing

Component			5 phr	10 phr	15 phr	20 phr
Result	Nylon	Epoxy	nylon	nylon	nylon	nylon
T_g(°C)	55.6	161.3	159.9	153.8	153.1	149.8

TABLE III
T_g and Coefficient of Thermal Expansion Acquired from TMA Testing

Component / Result	0 phr nylon	5 phr nylon	10 phr nylon	15 phr nylon	20 phr nylon
T_g(°C)	128.5	123.5	118.7	115.5	106.4
$\alpha_1(1/°C) \times 10^{-6}$	37.9	26.9	25.9	25.5	23.7
$\alpha_2(1/°C) \times 10^{-6}$	85.6	96.0	86.6	88.9	82.3

added. However, when nylon powder with a greater coefficient of thermal expansion is used as a stress release agent, α_1 becomes smaller and smaller. As epoxy resin added with nylon powder varies in contracting level at the processing temperature and room temperature after cooling, a radial tensile stress[9] is produced on the interface between these two materials, which not only destroys the interface and forms cavitation, but also increases the local free volume between nylon and epoxy, and makes CTE become greater as more nylon powder is added. If filler with a low CTE is applied, the direction of the produced stress becomes contrary. The stress will decrease the local free volume[10] between resin matrix and silica filler. As more nylon powder is added, such phenomenon becomes even more significant, which leads to reduction of the CTE.

In addition, as nylon changes from a solid state to a liquid state during the hardening linking reaction process, the volume will expand; however, thermosetting resin produces contraction due to linking, whose stress offsets the expansion force produced by nylon exactly. Consequently, it is inferred that the contracting stress would be reduced after hardening nylon.

In Figure 7, when the temperature reaches 400°C,

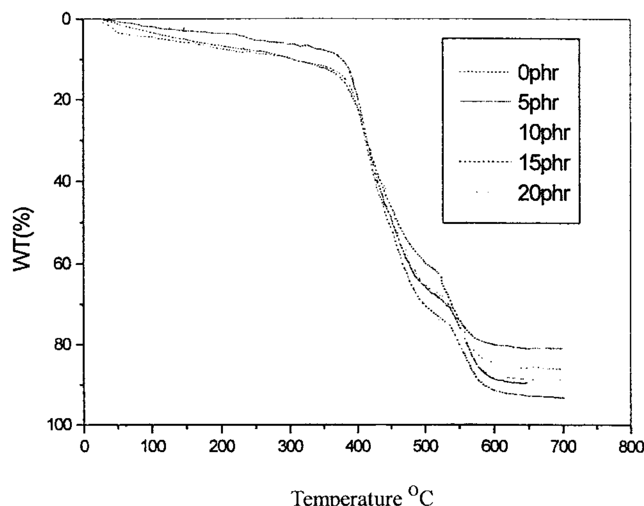

Figure 7 Analysis chart of thermogravity loss for materials with different contents of nylon.

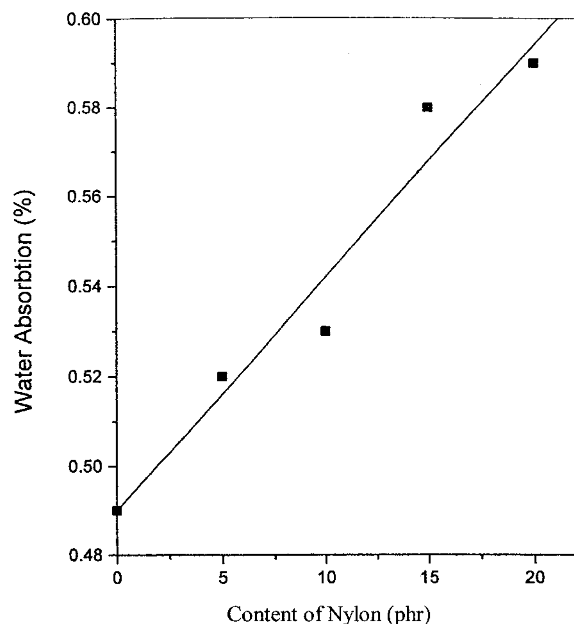

Figure 8 Water absorption rates of different contents of nylon at 85% of R.H., 85°C for 100 h.

weight loss is the greatest, which is the temperature of degradation (T_d) for resin. According to the TGA results, it is known that the material has good thermal properties.

The relationship between the water absorption rate and nylon content is shown in Figure 8. As the nylon content increases, the water absorption rate increases because NHCO, a functional group of nylon, can be integrated with water easily, which results in hydrogen bonding. The water absorption rate plays a critical part in creating a "popcorn effect" for IC elements. Nevertheless, as a limited quantity is added, the revealed effect is not great.

The relationship between the water absorption rate after PCT and nylon content is shown in Figure 9. The water absorption rate is affected by addition of nylon powder, and becomes even higher than the previous test, which is because water molecules can enter the empty spaces inside the material more easily under high pressure.

Impact upon insulation destruction imposed by nylon

Results of breakdown voltage are listed in Table IV.

Insulation of the material decreases along with the addition of nylon because nylon can absorb water easily and has a lower insulation property than epoxy resin. As a result, breakdown voltage reduces as nylon increases.

CONCLUSIONS

The advantages of using Biphenyl epoxy resin as EMC packaging material are low melting viscosity, high

wetting ability, and excellent lap shear adhesive strength. In addition, a large amount of fillers can be added to increase strength, decrease the coefficient of thermal expansion, and reduce the water absorption rate. Based on the results of 70 wt % of filler amount in this study, material fracture energy was increased by adding nylon; however, mechanical properties decreased slightly. According to the TMA results, the coefficient of thermal expansion (α_1) became lower as more nylon was added. The DMA experiment also revealed that heat resistance of the material was reduced to a small extent. The water absorption rate increased slightly in the water absorption test and PCT experiment. The insulation resistance test also indicated the breakdown voltage decreased slightly.

TABLE IV
Breakdown Voltage at the Voltage Increasing Rate of 500 V/s

Component Result	0 phr nylon	5 phr nylon	10 phr nylon	15 phr nylon	20 phr nylon
Breakdown voltage (kV/mm)	19.7	15.8	13.4	11.3	10.3

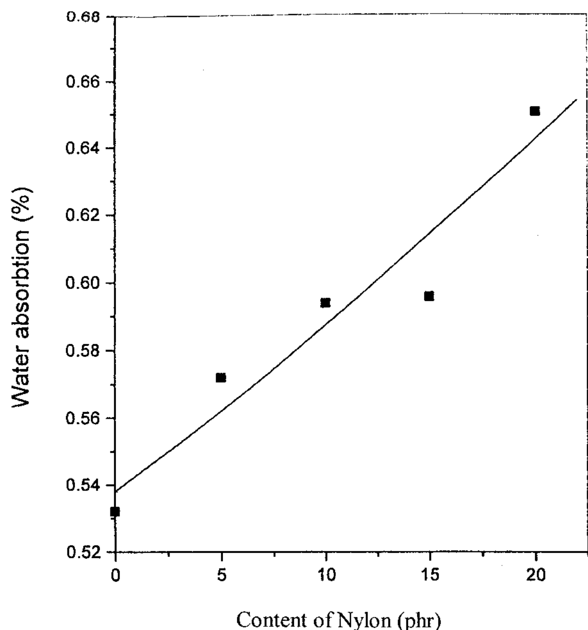

Figure 9 Water absorption rates of different contents of nylon at 2 atm, 130°C for 24 h.

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