

STUDY OF FORMULATION VARIABLES OF THERMOPLASTIC REFLECTING MATERIALS FOR TRAFFIC MARKING

ESTUDIO DE VARIABLES DE LA FORMULACION DE MATERIALES TERMOPLASTICOS PARA USO VIAL

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SUMMARY

Nine formulations of thermoplastic materials for traffic marking were prepared using a resin based on maleic anhydride modified with rosin in different proportions (18, 22 and 26%). As plasticizer a liquid coconut long oil alkyd resin (100% solids) was employed.

Hiding pigment was titanium dioxide; calcium carbonate and micronized talc were used as extenders. Coarse marble powder is used to facilitate the incorporation of glass beads. The operation was made employing a double Z mixer oil heated to obtain a mass temperature of 180-190 °C. The mixer was provided with two asynchronous arms rotating at 46 rpm.

Dry and wet abrasion tests were carried out and the obtained results indicated that wearing values are three times greater in the case of the wet test.

It is demonstrated that plasticization degree controls hardness variation as a function of temperature, determining a critical point which is the beginning of an abrupt reduction of hardness. Water absorption increases when plasticizer content increases. Matrix correlation of tests results was used to analyze the obtained numeric values.

Keywords: *thermoplastic materials, reflecting properties, agglutinant, dry abrasion test, wet abrasion test, bond strength, water elimination rate.*

INTRODUCTION

Frequently reflecting thermoplastics applied in city streets, roads or highways lost their efficiency due to the wearing or to the partial detachment of the used materials. The appearance and physical characteristics were modified.

The adequate life-time is a function of different variables [1], acting individually or as a whole: adhesion to the surface where they were applied on (asphalt or concrete), resistance to abrasion and weathering (moisture due to rain, dew remaining long time in contact with

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thermoplastic marks), high temperatures producing deformation or low temperatures diminishing elasticity and favouring checking or cracking of the coat.

An important aspect is related to the influence of traffic intensity and the rolling action of tires, specially the pressure when the tire takes contact with the line or the suction when rolling over them. A high quality result is related to the components of the formulation and to the adequate cleaning of the surface before application. A best performance was always obtained in asphalt pavements [2].

The objective of this research is to determine the influence of composition variables (pigment/binder ratio, resin content, plasticizer type and content, fillers employed, and PVC) on the adhesion or wearing resistance of the thermoplastic applied on a concrete surface.

EXPERIMENTAL

Nine samples of thermoplastics reflecting materials were formulated, containing as agglutinant a resin based on maleic anhydride and modified with rosin (A.I.= 14; melting point 114 °C). The modified resin was used in 18, 22 or 26% on the total formulation. As plasticizer a coconut oil alkyd resin was employed (without organic solvents) in a proportion between 2.7 and 6.5 per cent.

As hiding pigment titanium dioxide rutile type was employed, to obtain a white colour with high luminosity ($Y > 80$). Pigment formulation was completed using fillers as calcium carbonate and talc, which are of good wearing resistance. Samples formulation were indicated in **Table 1**.

TABLE 1

Composition of the thermoplastic materials*

Material	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC
Maleic resin	18.0	22.0	26.0	18.0	22.0	26.0	16.0	22.0	26.0
Alkyd resin	2.7	3.3	3.9	3.6	4.4	5.2	4.5	5.5	6.5
Titanium dioxide	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Glass beads	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Marble	22.4	20.3	18.2	22.0	19.8	17.6	21.6	19.3	17.0
Calcium carbonate	22.4	20.3	18.2	22.0	19.8	17.6	21.6	19.3	17.0
Talc	4.5	4.1	3.6	4.4	4.0	3.6	4.3	3.9	3.5

* g.100 g

A double Z mixer (**Fig. 1**) was used for the thermoplastic preparation, having the mixer two asynchronic arms, one of them rotating at 46 rpm. For heating a mineral thermic fluid which circulates in the heating jacket was employed (maximum temperature 300 °C).

Titanium dioxide, fillers and glass beads were incorporated at 180-190 °C. The operation at this temperature lasts 30 minutes. After that, the product obtained was casted in special molds.



Fig. 1.- Double Z mixer for test samples preparation.

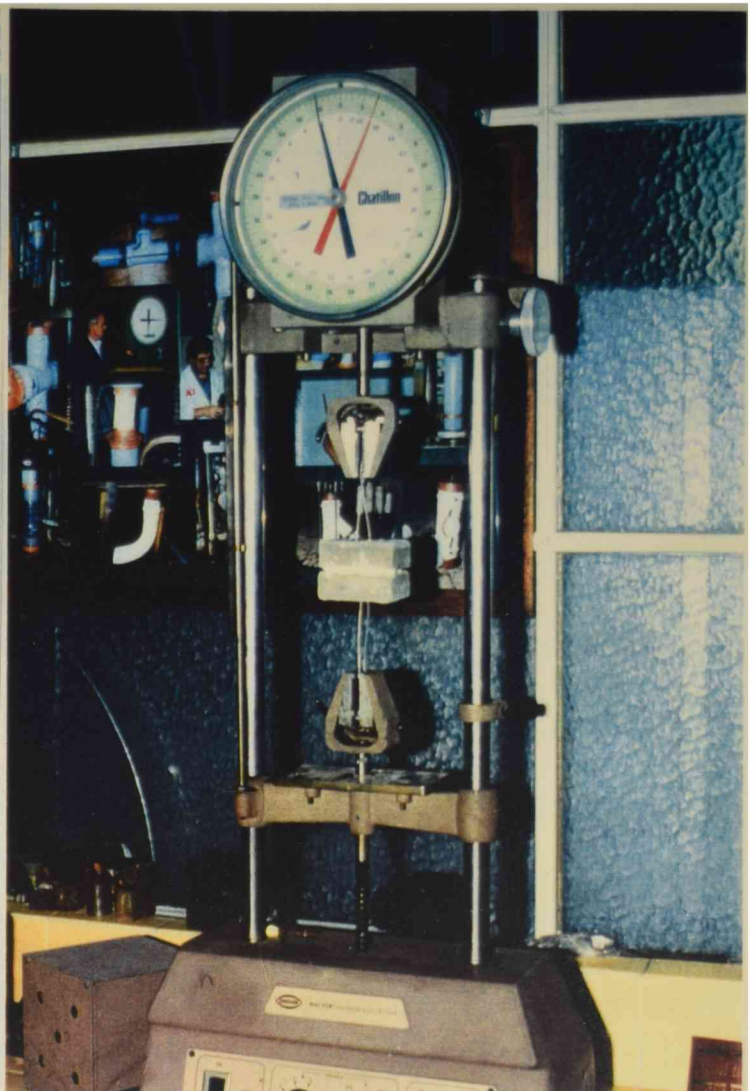


Fig. 2.- Adhesion-strength determination by CIDEPINT method.

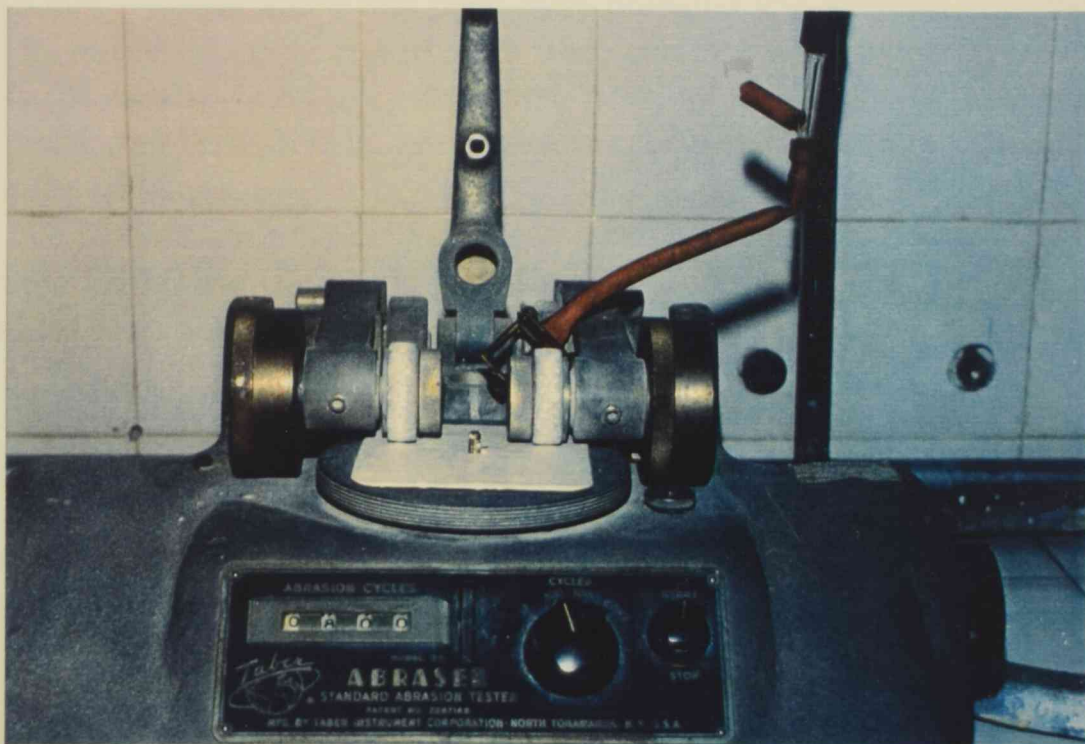


Fig. 3.- Wet and dry abrasion test equipment.

The samples tests were performed at different temperatures; wet and dry abrasion, Shore A hardness, adhesion-cohesion, water absorption and water elimination rate were determined.

For the **wet and dry abrasion test** [3], circular specimens were employed (80 mm diameter and 3 mm thick). After 24 hours samples were abraded using a Taber Abraser equipment, with a H-22 abrasive and 1000 g load (ASTM D 4060). The dust produced by the wearing operation was eliminated constantly by flowing pressurized air. When a track is formed as a consequence of wearing, the sample is weighed with an exactitude of 1 mg. After that, the wearing operation is continued along 100 revolutions of the equipment and newly weighed. The difference between the two values obtained is expressed as dry wearing (**Fig. 2**).

After finishing the previous test, distilled water is added to the track and the operation continued during 100 revolutions more. The sample is now conditioned for water elimination and weighed. The difference with the previous value is expressed as wet wearing.

Shore A hardness [4] at temperatures between 40 and 70 °C was determined each 5 °C, according to DIN 53505. In this case test plates are 50 mm diameter and 3 mm thick; the value was registered after 15 seconds. Samples were stabilized during 1 hour at test temperature before hardness determination.

To obtain adhesion and cohesion strength values a method developed at CIDEPINT was employed [5,6]. The melted material was put in the midst of concrete probes (3 mm thick), previously primed with an acrylic varnish and preheated at 40 °C. An iron flexible wire was inserted in test probes to allow the clamps of a dynamometer. The traction effort was performed at a velocity of 200 mm.min⁻¹ and at a temperature of 20 °C (**Fig. 3**).

For the determination of **water absorption and water elimination rates** [7,8,9], specimens of 50 mm diameter and 3 mm thick were prepared and weighed with the precision of 1 mg. Hung by means of a copper wire, they were completely submerged in distilled water at 20 ± 1 °C for 24 hours. After that, they were dried with filter paper and weighed; the operation was made after 48 and 72 h. **Absorption values** were obtained by difference with the initial weight of the samples .

Afterwards the probes were conditioned at 20 °C and 50 % HR. By weighing, **water elimination values** were obtained.

DISCUSSION

The maleic resin is the agglutinant used in the formulation of thermoplastic traffic materials. The modification of physical properties (reduction of melting point and adequate elasticity characteristics) by means of an alkyd resin improved the system wetting, facilitating the incorporation of the hiding pigment (TiO₂), fillers and glass beads. In those conditions a homogeneous distribution of glass beads was obtained. This is a very important aspect in field behaviour; in wearing, an adequate distribution of beads in the mass assures adequate night visibility, during a long period.

A certain correlation was observed between the thermoplastic traffic materials composition and the values of the obtained physical properties (**Table 2**).

TABLE 2

Correlation between materials composition variables and physical properties

	R	P	M	C	T	W ⁺	AS	D	Δ	PVC	W ⁻
R	1.00	0.58	-0.97	-0.93	-0.98	-0.92	0.98	-0.31	-0.89	-0.97	-0.90
P	0.58	1.00	-0.75	-0.77	-0.72	-0.71	0.43	-0.94	-0.73	-0.76	-0.75
M	-0.97	-0.75	1.00	0.97	0.99	0.95	-0.91	0.51	0.93	1.00	0.94
C	-0.93	-0.77	0.97	1.00	0.97	0.98	-0.85	0.55	0.93	0.97	0.98
T	-0.98	-0.72	0.99	0.97	1.00	0.95	-0.91	0.48	0.91	1.00	0.94
W ⁺	-0.92	-0.71	0.95	0.98	0.95	1.00	-0.87	0.50	0.84	0.95	1.00
AS	0.98	0.43	-0.91	-0.85	-0.91	-0.87	1.00	-0.15	-0.83	-0.91	-0.84
D	-0.31	-0.94	0.51	0.55	0.48	0.50	-0.15	1.00	0.46	0.52	0.55
Δ	-0.89	-0.73	0.93	0.93	0.91	0.84	-0.83	0.46	1.00	0.92	0.84
PVC	-0.97	-0.76	1.00	0.97	1.00	0.95	-0.91	0.52	0.92	1.00	0.95
W ⁻	-0.90	-0.75	0.94	0.98	0.94	1.00	-0.84	0.55	0.84	0.95	1.00

Key of the table

- | | | | |
|-----|-------------------|------------------|-------------------|
| R: | resin | P: | Plasticizer |
| M: | marble powder | C: | calcium carbonate |
| T: | micronized talc | W ⁺ : | water absorption |
| AS: | adhesion-strength | D: | hardness at 55°C |
| Δ: | abrasion | PVC: | PVC |
| | W: | | water elimination |

In the dry abrasion test the trend of wearing is determined by pigment volume concentration of the different samples. Two series of wearing values were obtained (Fig. 4).

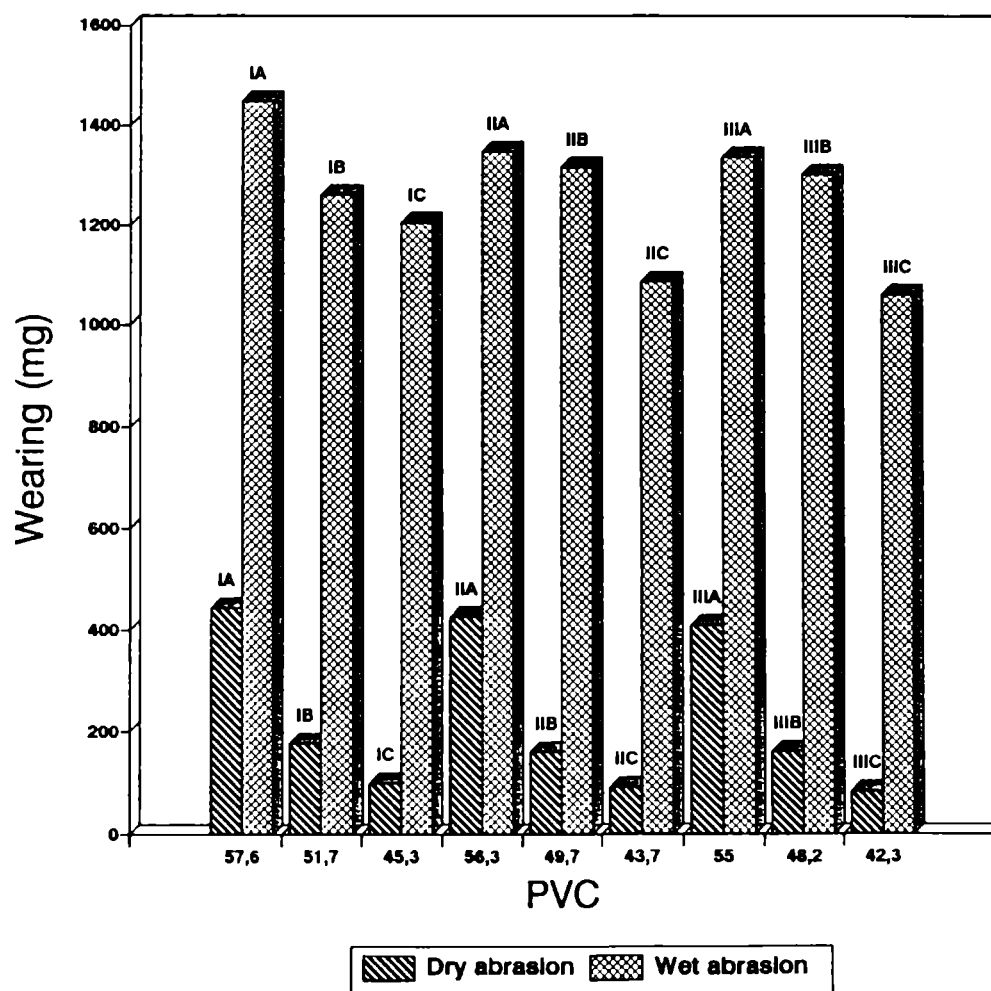


Fig. 4.- Comparative result of dry and wet abrasion test.

The wet abrasion test shows greater wearing values than those obtained in the dry abrasion test.

Results of hardness test, as a function of temperature, are related to the plasticization degree of the agglutinant resin. This is particularly observed over a temperature of 55 °C, which is considered critical; over this temperature value, hardness dismishes abruptly in practically all the samples. This characteristics is independent of plasticizer level and PVC values (Fig. 5).

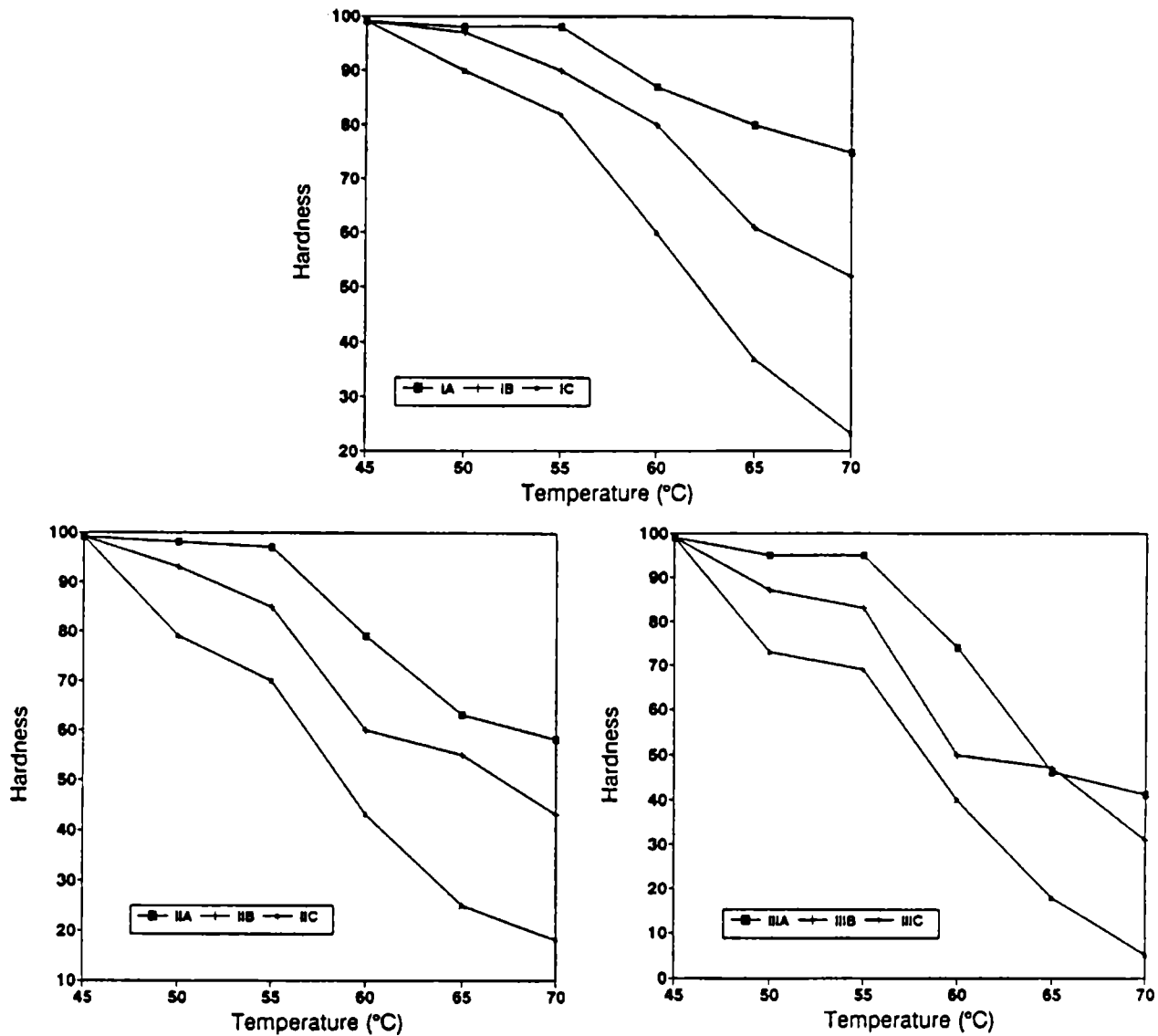


Fig. 5.- Variations of hardness as a function of the temperature.

The indicated critical temperature is a harmful interactive factor in the material application.

Adhesion-tension values are lineally dependent on the employed resin (Fig. 6) and not related with the plasticizer level; the obtained values expressed in kg.cm^{-2} are of the same order than those of the standards used to qualify this type of materials.

In the results of water absorption (Fig. 7) and water elimination (Fig. 8) tests, the increase of weight of the termoplastic mass during immersion is faster than the elimination value.

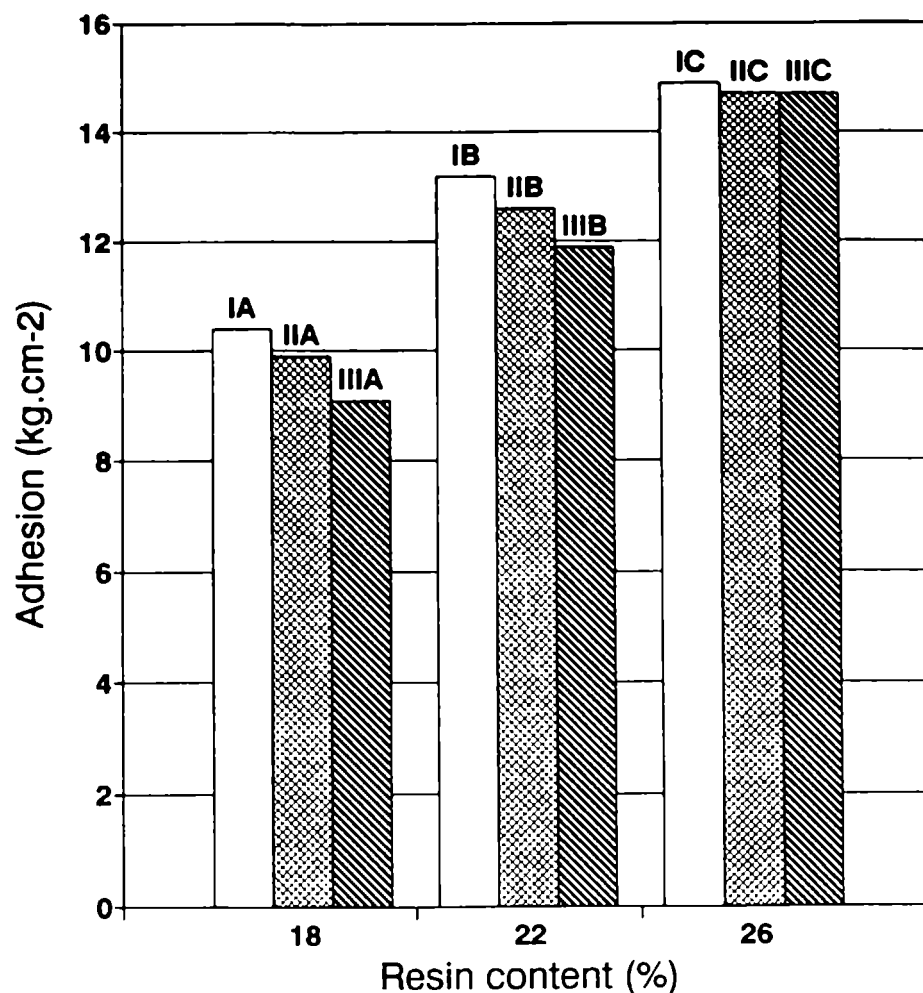


Fig. 6.- Variations in adhesion-strength as a function of resin content.

CONCLUSIONS

- 1.- The wet abrasion wearing values are higher than those obtained in the dry abrasion test. Wearing is directly dependent on the plasticizer level but independent of the maleic resin content.
- 2.- Plasticization degree has a high influence on hardness variation as a function of temperature. A critical point appears at 55 °C with a sudden reduction of hardness values.
- 3.- Adhesion strength is dependent on the resin content, a higher content increases adhesion strength. This parameter is independent of the plasticization degree.
- 4.- Water absorption decreases when plasticizer increases, independently of the resin content. Water elimination rate decreases too.
- 5.- The retained moisture of the thermoplastic traffic material after immersion must be considered as a harmful property in relation to the wearing resistance in service.

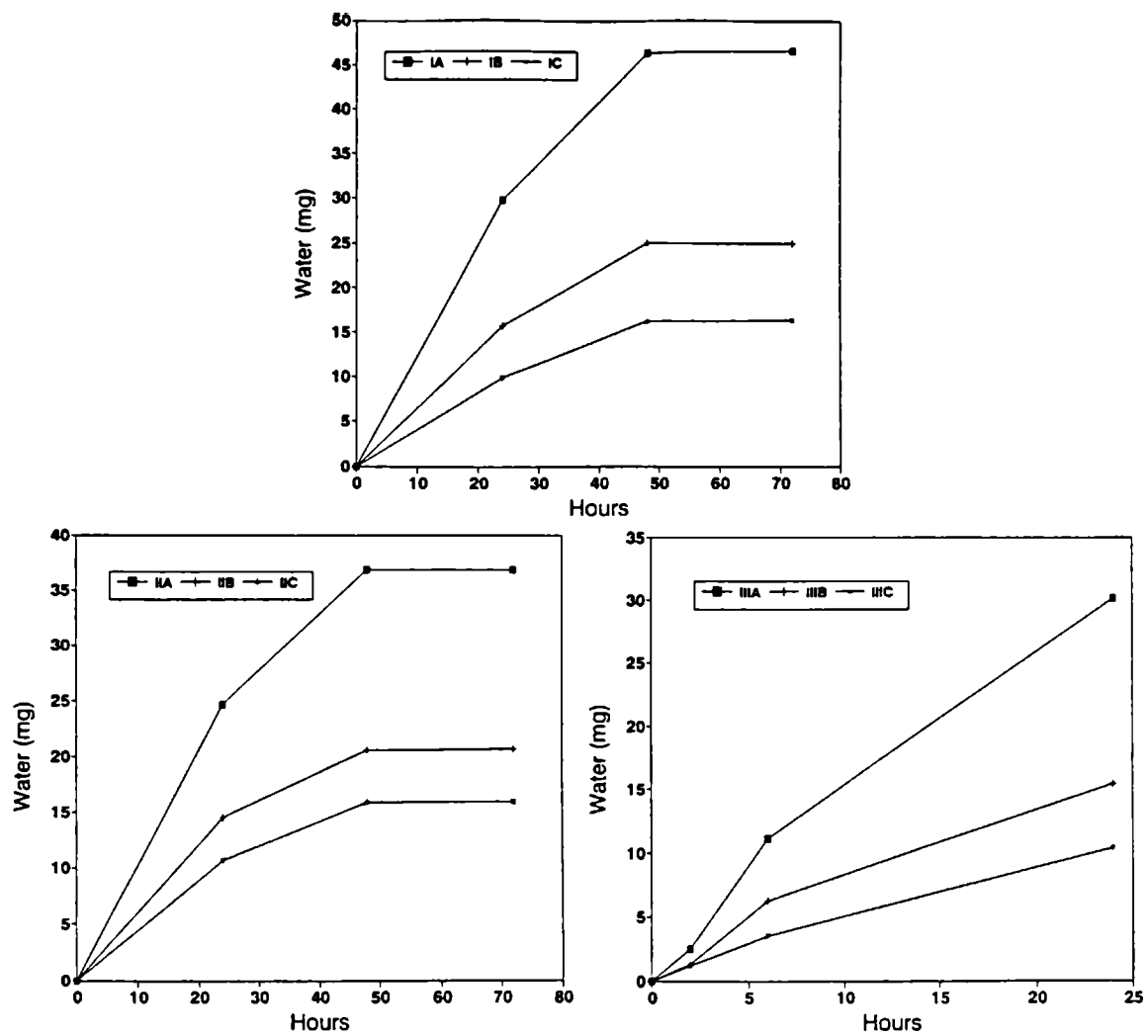


Fig. 7.- Water absorption values as a function of time.

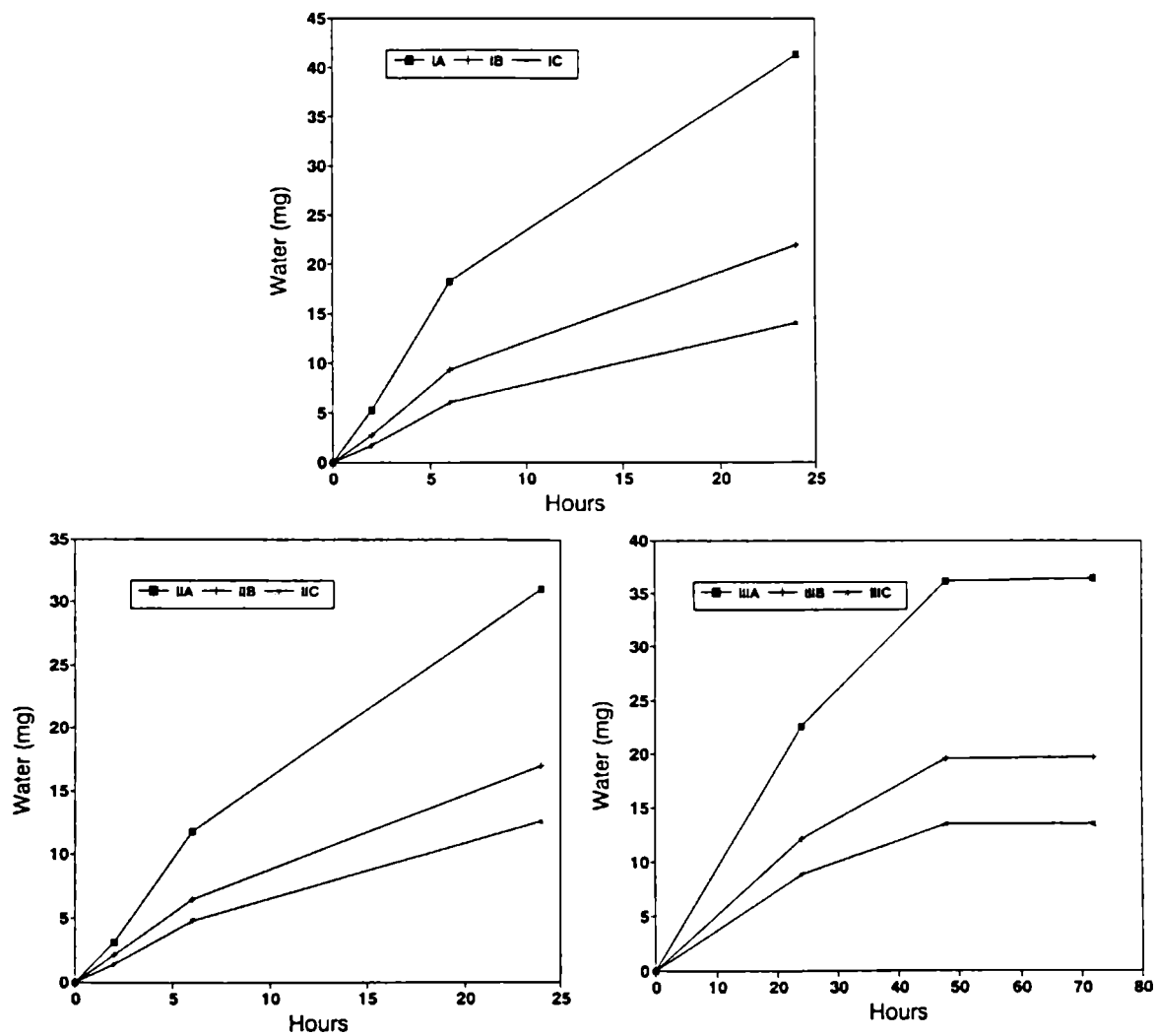


Fig. 8.- Water elimination values as a function of time.

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