

MICROEMULSION COPOLYMERS FOR RETANNING APPLICATIONS ON LEATHERS

by

G.V.RAMANA REDDY^{1*}, P.SARAVANAN¹, D.PREMKUMAR² AND R.W.SUGUMAR²

¹*Central Leather Research Institute, Adyar, Chennai-600 020, India.*

²*Department of Chemistry, Madras Christian College,*

TAMBARAM, CHENNAI-600 059, INDIA.

ABSTRACT

The microemulsion polymerization method is used to synthesize tercopolymers of styrene, methyl methacrylate and methacrylic acid with finer particle dispersions. Four compositions of the monomers mixture are used in these syntheses. The copolymerization reactions are carried out at 70°C with potassium persulphate (KPS) as the initiator. Sodium lauryl sulphate (SLS) and n-heptanol (HA) are being used as the surfactant and cosurfactant combinations, respectively, in these reaction media. These experimental products are employed in retanning wet blue goat skins along with the fatliquoring agent, Balmol SXE. The offer of the experimental products are varied in the retanning experiments and the effects of these products on retanned goat skins are observed by measuring tensile strength, tearing strength and bursting strength. The copolymer products II and III containing 5 and 7.5 weight percents of methacrylic acid as comonomer units, respectively, in the copolymers show considerable improvement in these properties. Product I containing no methacrylic acid groups in the copolymer shows improvement in tensile strength and fall in other properties. Product IV containing 10 (%wt) of methacrylic acid groups in the copolymer does not show considerable improvement in these physical properties, the tensile strength decreases with the offer of the product, no uniform variation of tear strength with the offer level and the grain bursting strength increases with the offer of the product. Scanning electron micrographs (SEM) are obtained for the leathers retanned with product I and these SEM analyses reveal good filling of the product I in the leather matrix.

RESUMEN

El método de polimerización de micro emulsiones se utiliza para sintetizar tercopolímeros [involucran más de dos monómeros] de estireno, metil meta acrilato y ácido meta acrílico para obtener dispersiones de partícula más fina. Cuatro composiciones de mezcla de monómeros se utilizan en estas síntesis. Las reacciones de copolimerización son efectuadas a 70°C con persulfato de potasio (KPS) como iniciador. Lauril-sulfato sódico (SLS) y n-heptanol (HA) se emplean en combinaciones como agente y coagente de superficie, respectivamente, en estos medios de reacción. Estos productos experimentales se emplean en recurtición de pieles caprinas curtidas al cromo conjuntamente con el agente de engrase, Balmol SXE. La oferta de los productos experimentales son variados en ensayos de recurtidos y los efectos de estos productos sobre las pieles caprinas en el recurtido fueron observados al determinar la resistencia a la tracción, la resistencia al rasgado y las resistencias en el lastómetro [estallido de flor y distensión]. Los productos copoliméricos II y III conteniendo 5 y 7,5 por ciento por peso del ácido meta acrílico como una de las unidades comonoméricas, respectivamente, en los copolímeros, demuestra considerable mejoría en estas propiedades. El producto I que no contiene grupos de ácido meta acrílico en el copolímero, demuestra una mejoría en la resistencia a la tracción y empeoramiento de las otras propiedades. El producto IV conteniendo 10 (% por peso) de grupos de ácido meta acrílico en el copolímero no demuestra significativa mejoría en estas propiedades físicas, y la resistencia a la tracción disminuye con la oferta del producto, ninguna variación uniforme en la resistencia al rasgado con el nivel de oferta [es evidente] y la resistencia al estallido de flor [en el lastómetro] aumenta con la oferta del producto. Microscopía por barrido electrónico (SEM) obtenidos para los cueros recurtidos con el producto I; los análisis por SEM demuestran buena acción de relleno del producto I en la matriz del cuero.

*Corresponding author E-mail: gvrr2004@yahoo.com

Manuscript received April 14, 2007, and accepted for publication November 3, 2007

TABLE I
Microemulsion copolymers of styrene, methyl methacrylate and methacrylic acid

Product	Composition of comonomer in the initial reaction mixture (%W)	Estimated Tg's (°K)	Solid Content (%W)	pH of M E copolymer solution
I	50.0% STY 50.0% MMA 0% MAA	375.48	13.40	3.5
II	50.0% STY 45.0% MMA 5.0% MAA	380.12	14.00	3.0
III	50.0% STY 42.5% MMA 7.5% MAA	382.48	12.92	3.0
IV	50.0% STY 40.0% MMA 10.0% MAA	384.87	13.60	2.5

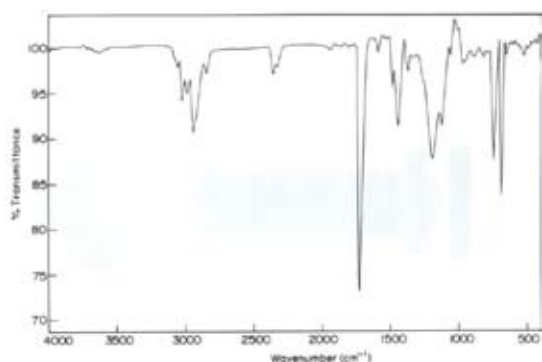


Fig. 1. FTIR spectrum of copolymer sample II.

Figure 1

INTRODUCTION

Acrylics due to their ability to form higher molecular weight compounds have been very useful in the manufacture of better quality leathers. Acrylic syntans are superior compared to auxiliary synthetic tanning agents. Acrylic syntans enhance fullness and roundness of the leather not merely by physical filling of voids in the leather matrix, but they form chemical linkages with reactive sites of protein, thereby enhance the physical characteristics of the leather. The excellent stability of acrylic family as a whole endows the acrylic syntan treated leather with superior fastness to light, perspiration resistance and stability to pH changes. Yet another advantage of acrylic syntans is that they facilitate level dyeing and render uniform color even for pastel shades^{1,2}.

Certain acrylic compositions are known to render full and tight leathers. It has been shown that polymethacrylic acid can be considered as a proton donor for complexing either with the polypeptide chain of collagen or the chrome of chrome tanned leather to bring about tanning reactions. By modifying the backbone composition, molecular weight and attached functional group polymers can be designed to give specific performance characteristics to leathers³. The work on acrylic syntans has been reported by different coworkers in the literature⁴⁻⁷.

Microemulsion copolymers of acrylics as retanning agents show better filling due to the lesser particle sizes of microemulsions reflected in the increase of strength properties of the leathers^{8,9}. The microemulsion copolymers based on styrene (STY), methyl methacrylate (MMA) and methacrylic acid (MAA) are synthesized with four different compositions in the copolymers and applied as retanning agents on wet blue goat skins.

EXPERIMENTAL

Materials

The monomers, styrene (STY) (laboratory reagent), methyl methacrylate (MMA) (laboratory reagent) and methacrylic acid (MAA) (Commercial grade) were used in this study.

Potassium persulphate (KPS) (laboratory reagent), sodium lauryl sulphate (SLS) (Commercial grade), n-heptanol (HA) (laboratory reagent), acetone (analytical reagent), Chloroform (analytical reagent), tetrahydrofuran (HPLC grade), dehydrated alcohol (99.9% pure) and deuterated chloroform (Aldrich) were used as supplied without further purification. The synthetic fat liquoring agent, Balmol SXE (Commercial grade) was employed in the retanning baths in this study.

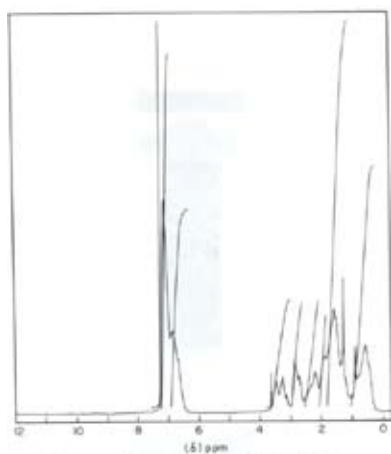


Fig. 2: Proton NMR spectrum of copolymer sample III.

Figure 2

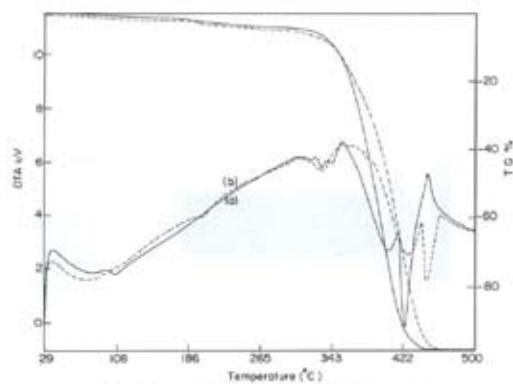


Fig. 3 TG/DTA analysis of the copolymers (a) sample I and (b) sample IV.

Figure 3

Methods

Microemulsion copolymerization

The microemulsion (ME) solution of monomers mixture was prepared by dissolving completely the monomers mixture (30 gms) of STY, MMA and MAA in the aqueous solution of SLS (40.5 gms) with 400 ml of water contained in a 500 ml reaction flask. The HA, used as co-surfactant, was also added (9.85 gms) along with the monomers mixture to this aqueous solution. This reaction mixture was stirred with the help of a glass stirrer for 20-30 minutes or until the monomers were completely solubilized in the SLS solution. To this reaction mixture at 70°C, 0.15 gms of potassium persulphate in 50 ml of water was added in 5 minutes while stirring the reaction mixture gently with the glass stirrer. The ME copolymerization reaction was carried out for complete conversion in one and half hours time. Four compositions of monomers mixtures were employed in preparing these ME copolymers (Table 1).

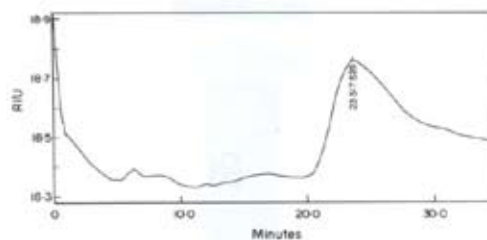


Fig. 4: GPC analysis for the determination of molecular weight of copolymer sample I.

Figure 4

The copolymers were isolated from the aliquots of these M.E. polymer solutions by precipitation with acetone and these precipitated copolymers were washed with ethanol/water mixtures. The washed monomers were dried in a vacuum oven at 60°C.

The infrared spectra (IR) of these copolymers were recorded with the use of NICOLET Impact Fourier Transform Infrared Spectrophotometer (USA) by casting thin films of the copolymers from chloroform solutions between KBr windows of size 2.5 x 4 mm (Fig. 1).

The nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature (25°C) with the use of JEOL ECR 500-MHZ high resolution NMR spectrometer and chloroform-d (CDCl_3) as solvent under the following conditions: number of scans 16, receiver gain 66, spectral width 10 KHz, relaxation delay 4 s, and by using 45° pulse width as 6.15 μs (Fig. 2). The thermogravimetry and differential thermal analysis (TG/DTA) of the copolymers were carried out with Seiko TG/DTA 200 instrument in the temperature region 30–600°C at a heating rate of 20°C and with a nitrogen gas flow of 100 ml/min. α -Alumina was used as the reference in platinum pans (Fig. 3).

The gel permeation chromatographic (GPC) analysis of the copolymer sample containing no MAA units was done to evaluate its molecular weight. A molecular weight calibration curve was obtained with polystyrene standards in the molecular weight range 2.3×10^3 to 3.1×10^6 (Polymer Laboratories, Church Stretton, Shropshire, UK). THF at a flow rate of 1 ml/min was used as the eluent (Fig. 4).

Application of M.E. copolymer solutions in retanning chrome tanned goat skins

Wet blue goatskins were chosen as starting materials for the application experiments and the process of retanning was carried out in drums. The wet blue was cut along the backbone into two halves. The right halves were processed according to a standard process of acid washing, rechroming, neutralization and fat liquoring. The left halves of the leathers were treated similarly and the experimental products were employed along with fat liquoring agent, Balmol SXE, in the final steps of these processes. After processing, all the leathers were jammed and toggle to dry. The right halves of the cut pieces of wet blue goatskins were used for the processing of the control leather test samples and the processing was carried out without

TABLE II
Process details for retanning application of experimental products on wet blue goatskins.
(All percentages are based on the shaved wet blue weight)

Unit process/ operation	Chemical/auxiliary	Percentage (%)	Running time (min)	Other instructions
Acid washing	Water	100		pH is adjusted to 3 - 3.5, drained
	Acetic acid	0.75	15	
Rechroming	Basic chromium sulphate	5		Data 5
	Water	100	40	
	Sodium formate	1	15	
	Sodium bicarbonate	1	3x15+30(3 feeds at 15 mins. interval and run 30 mins. after final feed)	
Washing Neutralization	Water	200	20	pH is adjusted to 4.0, drained Drained
	Water	100		
	Sodium formate	1	15	
	Sodium bicarbonate	1	3x15+30(3 feeds at 15 mins. interval and run 30 mins. after final feed)	
Washing Retanning and fatliquoring	Water	200	20	pH is adjusted to 5 - 5.5, drained. Drained
	Water	100		
	Synthetic fatliquor (Balmol SXE)	2	30	
	Experimental product	X	40	
Fixing	Formic acid (diluted 10 times with water)	1	3x10+40(3 feeds at 10 mins. interval and run 40 mins after final feed)	Drained, washed, piled overnight, next day hooked to dry and staked.

The experimental product is offered along with Balmol SXE in to the retanning drum in five different quantities as 0.5, 1.0, 2.0, 4.0 and 8.0% in the floats.

administering the experimental product in retanning of wet blue goatskins (Table 2).

These retanned skins were visually assessed for organo-leptic properties and compared with the standard test samples (control) made with the second half of the skin. The visual assessment for fullness, softness, smoothness and grain tightness for which no objective test methods available was done by the four experts in the leather manufacturing. The assessment was done by assigning 10 point rating (1 to 10) in the ascending order of the degree of each promotion and the mean values are presented in Table 3.

The physical testing of these retanned leather test samples were made by cutting the samples from official portions of experimental leathers with the use of metal dies and these cut samples were conditioned for about 48 hours at temperature 20°C and 65% relative humidity. These conditioned samples

were tested for tensile strength and tear strength on Instron 4501 (UK) with initial gauze length of 50 mm and cross head speed of 100 mm/minute, and the grain bursting strength was evaluated with the use of SATRA Test Equipment, Lastometer STD 104 (UK) (Table 4). The samples were cut from the official portions of the dry retanned and control leather test samples obtained by the application of product I, and the scanning electron microscopy (SEM) studies were carried by coating these pieces with gold in a sputter coater and by viewing in the SEM by the secondary electron mode (Jeol, JSM) (Figs. 5 and 6).

RESULTS AND DISCUSSION

The IR spectra show characteristic absorption bands due to various chemical groups in the copolymers (Fig. 1) and the NMR spectra show the chemical shifts due to various groups in the copolymers (Fig. 2) and the resonance peaks due to carboxyl protons are not observed in the NMR spectra. The GPC

TABLE III
Visual assessment of retanned leathers

Experimental product	% Offer	Fullness		Smoothness		Softness		Tightness	
		C	Ex	C	Ex	C	Ex	C	Ex
I	0.5	6	5	7	6	6	5	6	7
	1.0	4	5	5	6	4	5	6	6
	2.0	6	7	5	6	5	6	7	7
	4.0	5	7	4	5	6	6	5	6
	8.0	7	9	7	8	7	7	7	6
II	0.5	4	4	5	5	4	4	5	5
	1.0	4	4	5	6	4	5	5	6
	2.0	4	4	5	6	4	4	6	5
	4.0	4	6	6	7	4	5	4	6
	8.0	4	5	6	7	4	5	6	7
III	0.5	4	6	4	5	6	5	4	7
	1.0	4	7	4	5	5	5	5	7
	2.0	5	8	5	5	6	4	5	8
	4.0	5	9	5	4	7	5	5	8
	8.0	4	9	6	5	7	5	6	9
IV	0.5	5	6	5	5	6	5	5	7
	1.0	5	7	5	4	6	6	6	8
	2.0	5	7	5	5	7	5	6	8
	4.0	6	9	6	5	7	6	7	8
	8.0	5	9	7	5	8	5	6	9

The results are rating of 1 to 10 (10 being the best) and the average of assessments carried out by four experts.

analysis of the copolymer sample I containing 0% acid groups gives the retention time 23.537 minutes corresponding to the molecular weight (M_n) 1.0458×10^4 (Fig. 4). The TG/DTA analysis of the copolymer samples I and IV in the temperature region 30-500°C show endothermic decompositions in the region 306-463°C (Fig. 3).

Application studies of experimental products in retanning chrome tanned goat skins

The control and experimental leathers were produced (the process details are given in Table 2). The products were assessed for organo-leptic properties (Table 3) and tested for physical characteristics (Table 4).

It can be seen from the results of the organo-leptic property assessment of product I (Table 3) that there is no marked difference in the characteristics except the fullness and smoothness which are better in the case of leathers treated with product I. In the case of product II (Table 3) the smoothness and grain tightness are better for the experimental product. But no concrete conclusion can be arrived from this data as there is no trend observed in the characteristics with respect to the variation in offer of the polymeric formulation. The results with respect to product III (Table 3) show by and large a trend, where the fullness and grain tightness are increasing with the offer levels, the smoothness is almost unaltered and the softness

decreases with the increase in offer of the experimental product. Product IV shows (Table 3) a clear trend that the characteristics namely the fullness and grain tightness are increasing with the increase in offer level. The properties such as softness and smoothness decrease with the increase in offer level.

The physical properties such as tensile strength, tear strength and grain bursting strength are tested for all the five experiments (different offerings) of four formulations, and the results are tabulated in Table 4. Among the measures of both retanning and lubricating ability for any product, strength properties are considered important³. The results presented are the mean values of two sets of experiments and all the values are found to be within $\pm 2.9\sigma$. It could be inferred from the results of the physical testing of the leathers treated with product I (Table 4) that the tensile strength increases with the increase in the offer level but the increase is not in proportion with the offer level. The tear strength and the grain bursting strength decrease with the increase in offer level. These results indicate that the product I is capable of filling the leather significantly. The loading of leather may be the cause of the effect of decrease in the bursting strength and tear strength. However, the offer level 2% is found to be optimum where there is no significant decrease in these properties but the tensile strength increases significantly. The inferences are further substantiated with the scanning electron micrographs of the leather (Figs. 5 and 6).

TABLE IV
Physical Testing of retanned leathers

Experimental product	% Offer	Tensile Strength (Kg/cm ²)			Tear Strength (Kg/cm)			Grain Bursting (Kg)		
		C	Ex	Δ (%)	C	Ex	Δ (%)	C	Ex	Δ (%)
I	0.5	173.70	168.40	-3.1	31.58	30.18	-4.4	20.0	16.0	-20
	1.0	132.39	186.42	40.8	52.62	42.70	-18.9	22.0	24.0	9.0
	2.0	137.61	201.55	46.5	45.08	39.50	-12.4	20.0	28.0	40.0
	4.0	212.12	225.70	6.4	45.63	52.30	14.6	32.0	28.0	-12.5
	8.0	210.35	243.91	16.0	56.30	38.30	-31.9	30.0	28.0	-6.6
II	0.5	76.97	81.78	6.3	23.89	25.67	7.45	23.0	24.0	4.3
	1.0	81.83	107.74	31.7	23.45	30.50	30.0	16.5	14.0	-15.2
	2.0	68.63	70.31	2.5	24.11	26.78	11.1	9.5	11.0	15.8
	4.0	162.00	174.23	7.5	30.82	33.23	7.8	25.0	32.0	28.0
	8.0	137.34	149.50	8.9	31.22	34.23	9.6	13.0	15.0	15.4
III	0.5	80.74	113.92	41.1	22.51	26.10	15.9	9.0	12.5	38.9
	1.0	86.32	115.48	33.8	23.47	27.87	18.7	10.0	13.0	30.0
	2.0	82.20	118.94	44.7	25.67	30.18	7.4	9.0	11.0	22.2
	4.0	89.12	162.85	82.7	26.90	31.04	15.4	14.0	15.5	10.7
	8.0	108.80	136.02	25.0	32.31	27.98	-13.4	19.0	32.0	68.4
IV	0.5	194.81	176.72	-9.3	61.60	55.03	-10.7	24.0	27.0	12.5
	1.0	256.27	230.54	-10.0	65.05	63.38	-2.6	22.0	36.0	63.6
	2.0	292.12	224.02	-23.3	54.27	69.34	27.8	25.0	28.0	12.0
	4.0	196.02	161.31	-16.7	49.17	73.12	48.7	21.0	25.0	19.0
	8.0	187.36	140.96	-24.8	49.63	43.62	-12.1	15.0	21.0	40.0

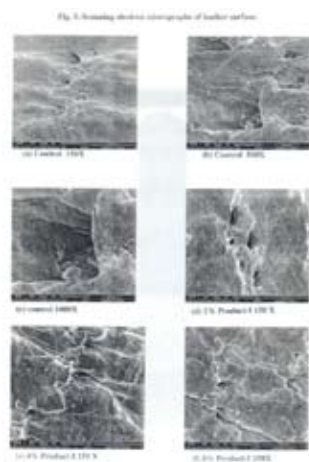


Figure 5

Large quantities of the surfactant exists in the experimental product which may cause to some extent denaturing of the leather¹⁰, this in turn reflects on the strength properties of the retanned leathers.

In the case of the physical testing results of leathers treated with product II (Table 4), all the physical properties are increasing with the increase in the offer levels. This indicate that the product is capable of forming cross links more than loading

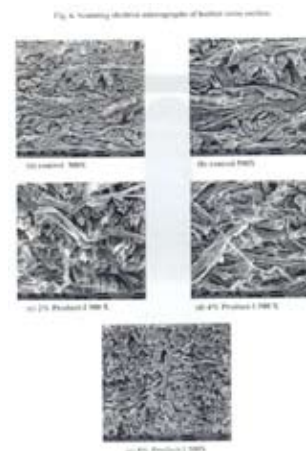


Figure 6

the leather, which is the conclusion drawn from organoleptic assessment (Table 3) where the fullness/ loading is not very significant.

The results of physical testing with respect to product III are presented in Table 4. The results show that physical properties are better when the offer of the product increases. There is no decrease in the grain bursting strength property when the offer of the product level is increased. So it can be inferred that

the product is not loaded on the grain but may be penetrated to the inner side of the leather. However, the increase in the properties is not proportional with the offer level. The results of the physical testing, with respect to product IV, show that the tensile strength is reduced by the offer of the product (Table 4). The tear strength increases beyond the offer level 2%. The grain bursting strength increases with the increase in the offer level of the product. It can be inferred that the product is capable of loading the leather very significantly which is reflected as improvement in fullness and decrease in tensile strength. As there is no decrease in grain bursting strength with the increase in the offer level it could be understood that the loading has not taken place selectively layer wise. In other words loading of entire leather is brought about but not selective loading of any particular layer or portion.

CONCLUSIONS

The visual assessment of the retanned skins reveals better performance by the experimental products compared to control leather test samples, much is reflected in properties like fullness and tightness. The physical testing results reveal that the application of product I on wet blue goat skins increases the tensile strength, and decreases the tear strength and grain bursting strength, assumed to be due to good filling of the experimental product, which is substantiated from the SEM analyses. The applications of products II and III in retanning wet blue goat skins show improvement in all physical properties studied with retanned skins, which is considered to be due to the cross linking of the experimental product with

the collagen fibrils in the leather. The physical testing results confined to the retanned leathers with product III reveal that the loading of the product is better in the inner sides rather than the grain side of the leather. Whereas the product IV shows the reverse effect, the tensile strength decreases with the offer of the product, no uniform variation of tear strength with the offer level and the grain bursting strength increases with the offer of the product. This is presumed that the loading of entire leather is brought about but not selective loading of any particular layer or portion.

REFERENCES

1. Traeubel, H. and Rogge, K.H.; *JALCA* **83**, 193, 1988.
2. Prentiss, W.C. and Ward, G.J.; *JALCA* **82**, 96, 1987.
3. El'Amma, A.G., Hodder, J.J. and Ward, G.J.; *JALCA* **91**, 237, 1996.
4. Prentiss, W.C. and Sigafos, C.R.; *JALCA* **70**, 481, 1975.
5. Danisch, P. and Kneip, M.; *JALCA* **91**, 120, 1996.
6. Lakshminarayana, Y., Parthasarathi, K. and Srinivasan, K.S.V., *JALCA* **85**, 22(1990)
7. Vijayalakshmi, L., Saravanan, P. and Srinivasan, K.S.V.; Proceedings of the XXIII ULTCS Congress, Germany, 1995.
8. Ramana Reddy, G.V., Saravanan, P. and Srinivasan, K.S.V.; *JALCA* **95**, 333, 2000.
9. Mallikarjana, G., Saravanan, P. and Ramana Reddy, G.V.; *JALCA* **97**, 215, 2002.
10. Kihira, Y. and Yamamura, H.; *Proc. Jpn. Congr. Mater. Res.* **28**, 213, 1985.