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COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
WORKING PARTY ON STRUCTURE AND PROPERTIES
OF COMMERCIAL POLYMERS*

PROPERTIES OF EDAM COPOLYMERS AS
POLYPROPYLENE RESIN MODIFIER

(Technical Report)

Prepared for publication by

RENYUAN QIAN¹, YUANZE XU¹, YIHONG CHEN¹, DEYAN SHEN¹, XIGAO JIN¹, LIUSHENG CHEN¹,
TADAYUKI OHMAE², SATORU HOSODA², HISAO TANAKA², TOSHIRO MASUDA³, AKIO NAKAJIMA⁴

¹Institute of Chemistry, Academia Sinica, Beijing 100080, China

²Chiba Research Laboratory, Sumitomo Chemical Co. Ltd., Chiba-ken 299-02, Japan

³Department of Materials Chemistry, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

⁴Osaka Institute of Technology, Osaka 535, Japan

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Properties of EDAM copolymers as polypropylene resin modifier (Technical Report)

Synopsis: The use of a copolymer of ethylene and N,N'-diethylaminoethyl methacrylate (EDAM) when melt blended into polypropylene (PP) to improve the dyeing properties of propylene fibres has been studied. It has been shown that when EDAM was heated in air, the oxygen in air accelerates the thermal decomposition of the DAM moiety of EDAM at 150°C, leaving polyethylene as the residue. However this heterogeneous reaction was not serious for the melt in extruder, in a capillary rheometer or in fibre spinning of PP/EDAM blends. Steady state viscosities of PP, PP/EDAM blends and EDAM under shear rates 10^0 - 10^4 s⁻¹ at 200°C and first normal stress differences under shear stresses of $3 \cdot 10^2$ - 10^4 Pa at 200°C were measured. Characteristics of the entrance flow to an orifice was measured using a die of length to diameter ratio $L/D=0$ in a capillary rheometer to estimate the elongational flow effects of these melts. The rheological behavior of PP/EDAM blends up to 20% EDAM resembles PP, while the PP/EDAM 50/50 blend resembles EDAM. Transmission electron microscopy of microtomed sections of the capillary extrudates of the PP/EDAM 80/20 blend and 50/50 blend showed clearly that the former has the morphology of EDAM islands in a PP sea while the latter the morphology of PP islands in an EDAM sea. For practical applications of EDAM modified PP fibres the EDAM content is less than 10%, such melt blends showed only a slight increase of viscosity. The dyeing behavior of EDAM modified PP fibres has also been studied. Two key chemicals which improve the dyeing properties of the EDAM modified PP fibres were found. One of them is sodium stearate. When it is added to the PP/EDAM blends for spinning, it accelerates the penetration of dyestuff into the fibre. The other is potassium salt of an alkylphosphate to be used as a dyebath auxiliary which improves color fastness and shows an antistatic finishing effect to the dyed fibre.

INTRODUCTION

Among various ways to overcoming the lack of dyeability of polypropylene (PP) fibres the most desirable one is surely to melt-blend a suitable amount of a copolymer of ethylene and N,N'-diethylaminoethyl methacrylate (EDAM) into PP base resin before melt spinning process^[1-6]. The diethylamino groups of EDAM enable the resulting modified PP fibres to be dyed freely into any color shade with a proper combination of acid dyes or premetallized type dyestuffs commonly used in Nylon or wool textile industry. The polyethylene moiety of EDAM copolymer performs good dispersion into PP when blended, leading to a smooth melt spinning of the fibre. Consequently the rheological behavior of PP/EDAM blends is of importance to industrial applications. In this paper 1) the rheological behavior of PP, PP/EDAM blends and EDAM and 2) EDAM as a dyeable modifier for PP fibres will be presented and discussed.

RHEOLOGICAL PROPERETIES OF EDAM AND PP/EDAM BLENDS

EXPERIMENTAL

The EDAM copolymer used was DA1701 of 27wt% DAM content having a MFI of 94g/10min at 190°C produced by Sumitomo Chemical Co., Japan. PP resin used was PP 70218 produced by Liaoyang Petrochemical Co., China which had a MFI of 18.1g/10min at 230°C and a viscosity average molar mass of $17.1 \cdot 10^4$. Three series of PP/EDAM blends were prepared. Samples of the series A PP/EDAM blends of 0,

5, 10, 20, 50 and 100% EDAM were prepared on a Brabender mixer at 200°C under N₂ atmosphere. Z-shaped rotor blade was used, rotating at 30rpm. Samples of the series B PP/EDAM blends were compounded with 0.2phr Irganox^R 1010, 0.2phr distearyl 3,3'-thiodipropionate (TPS) and 0.05phr calcium stearate and mixed at 200°C on a Labo Plastomill 65C made by Toyo Seiki Mfg. Co. according to the following procedure: premixing at 20rpm for 3min, then the rotor being stopped and preheating the sample for 2min and finally mixing at 50rpm for 5min. A roller type blade rotor was used. Samples of the series C PP/EDAM blends were prepared in the same way as the series B but without the incorporation of the stabilizers.

Dynamic viscoelastic properties were measured on Rheometrics RMS 605 instrument with a cone and plate rheometer, 25mm diameter and a cone angle of 0.1rad.

Steady state viscosity measurements were done on Rheometrics RMS 605 instrument with a cone and plate rheometer of 25mm diameter and a cone angle of 0.1rad for low shear rates (Beijing and Chiba). For higher shear rates a capillary extrusion rheometer, Instron 3211 with a capillary diameter of 0.76mm and capillary length-to-diameter ratio L/D of 100 (Beijing) and a Toyo Seiki Capirograph Rheometer with a capillary diameter of 0.76mm and L/D of 66.8 (Chiba) were used. Smooth joining of data from the cone and plate and the capillary rheometers was observed.

Infra-red spectra for EDAM were recorded on Bruker IFS 113V FTIR spectrometer at 2cm⁻¹ resolution. Powdered sample in KBr compact was used. The morphology of the PP/EDAM blends was observed by transmission electron microscopy (TEM) on Hitachi H500 electron microscope. The specimens for TEM were microtomed to 50nm thickness with a glass edged knife at liquid nitrogen temperature from the extrudate of a Capirograph Rheometer. The specimen was put on Cu support grids for electron microscopy after stained with 10% phosphowolframic acid solution at 60°C for 30min. EDAM regions were stained.

For the understanding of structural changes occurring during heating in air of EDAM copolymer the DA1701 pellet sample was heated in an oven at 150°C for 30min. After cooling to room temperature the sample was extracted with boiling CHCl₃ or ethylacetate in a Soxhlet apparatus, the insoluble gel part left on an analytical filter paper cone was weighed. Both the original EDAM sample and the gel part after heating were subjected to pyrolysis gas chromatography in conjunction with mass spectrometry (GC-MS). The pyrolysis GC-MS was performed with a CDS 1000 Pyroprobe made by CDS Instruments Co. connected to an on-line Hewlett-Packard HP 5890 gas chromatograph and a HP 5989 mass spectrometer system. About 0.1mg sample was pyrolysed at 600°C for 5s. The GC column used was a high resolution fused silica capillary column HP-5 of 0.25mm inside diameter, 25m long, coated with polymethylphenylsiloxane of 0.25µm thickness. The column temperature was maintained at 50°C for 8min and then programmed to 300°C at 10°C/min. Helium gas was used as the carrier gas flowing through the column at 50mL/min, being split at a ratio of 50:1. The pyrolysate was collected at every second. For MS a quadrupole mass spectrometer with an EI ionization source was used at 70ev at 250°C.

RESULTS AND DISCUSSION

Dynamic viscoelastic properties of EDAM and the effect of heating. Dynamic shear viscoelastic measurements were made for the sample DA1701 in the frequency range of 10⁻¹-10² rad/s, shear amplitude 0.10 and in the temperature range of 100-150°C under nitrogen atmosphere (Fig.1). Time-temperature superposition of the viscoelastic properties was found to be applicable to give

$$\log a_T = 2.63 \cdot 10^3 (1/T - 1/T_r), \quad T_r = 393\text{K} (120^\circ\text{C})$$

and an activation energy of 50.4kJ/mol. The rheological properties of EDAM were found to be independent of the shear amplitude in the range of 0.05-0.90 covered in the experiments. When measurements were conducted in ambient atmosphere some irreversible changes occurred above 150°C in the viscoelastic properties at very low shear rates resulting in pronounced increases of G' and G'' with decreasing shear rates. A search for the origin of the changes was carried out.

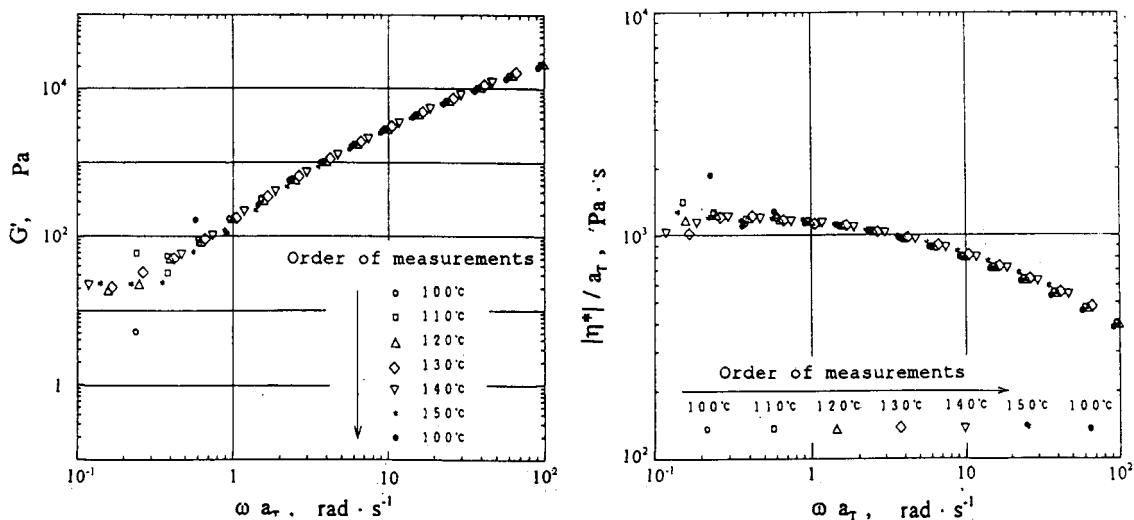


Fig. 1. (a) Dynamic storage modulus G' and (b) reduced complex dynamic viscosity $|\eta^*|/a_T$ of EDAM sample DA1701 as a function of reduced frequency ωa_T at temperatures from 100°C to 150°C measured under nitrogen atmosphere, $T_r=393\text{K}$

The polyethylene moiety of EDAM (DA1701) is crystalline to 28% in the as-received sample^[7]. Comparison of the IR spectra of the sample as received and after being heated at 150°C for 30min in ambient air and then freely cooled to room temperature shows that no major structural changes could be detected but the melting of the crystalline region of the polyethylene moiety. The crystalline bands at both 730cm^{-1} (CH_2 bending) and 1474cm^{-1} (CH_2 rocking) almost vanished as compared to the remaining amorphous bands at 719 and 1463cm^{-1} . The sample of DA1701 pellets after being heated at 150°C for 30min seemed remaining soluble in CHCl_3 at 60°C. On extracting the heated sample (8g) in an analytical filter paper cone with boiling CHCl_3 for 8h and then dried at 45°C for 24h left an insoluble residue amounting to 0.12% as compared to 0.05% insoluble residue for the unheated sample. Almost identical results were obtained by extracting with boiling ethylacetate. Careful examination by pyrolysis GC-MS of the insoluble residue left after ethylacetate extraction of the heated sample showed that the residue contained polyethylene moiety only as shown in Fig. 2. Apparently the

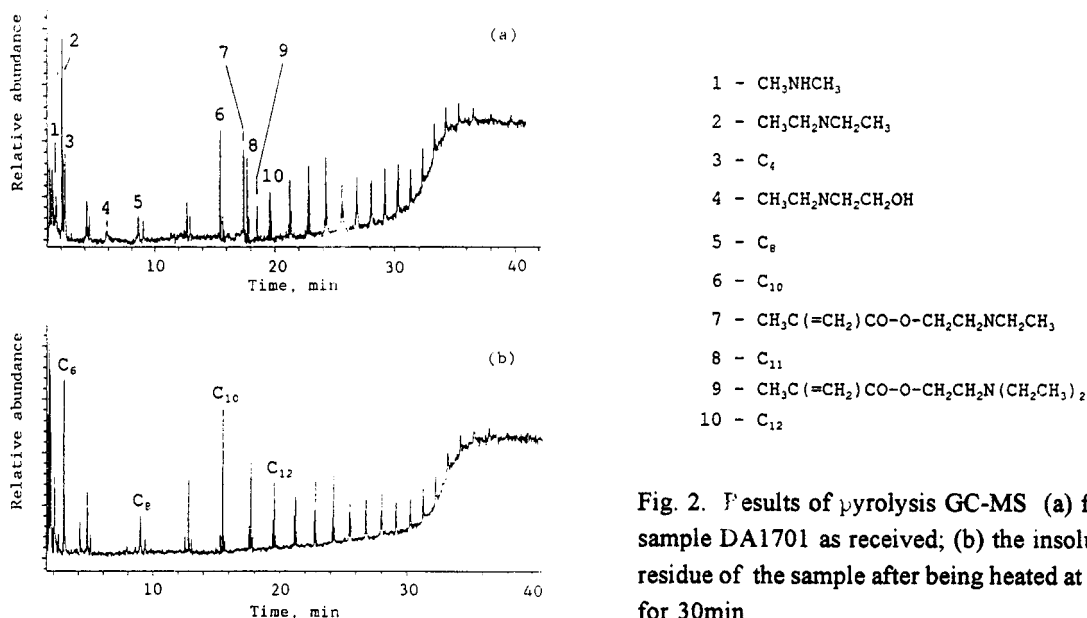


Fig. 2. Results of pyrolysis GC-MS (a) for the sample DA1701 as received; (b) the insoluble residue of the sample after being heated at 150°C for 30min

diethylaminoethyl methacrylate moiety of EDAM was decomposed in air at 150°C. This is in agreement with the thermogravimetric result of EDAM^[7] under nitrogen, where the thermal degradation occurred in two steps, 250-440°C and 440-500°C. Obviously the presence of oxygen in air accelerated the degradation to start at 150°C. As the oxidative degradation in air is a gas-solid heterogeneous reaction the extent of reaction will depend upon the heating duration and the conditions of air-polymer contact. In the case of a thin polymer melt layer as being measured in a cone and plate rheometer in ambient atmosphere erroneous results were observed due to the thermal degradation of EDAM. Comparison of the experimental results of cone and plate rheometry carried out in nitrogen and in air shows clearly that the thermal degradation of EDAM in air resulted in a pronounced increase of complex viscosity, storage and loss moduli at very low frequencies only, resembling the dynamic viscoelastic behavior of a rubber particles filled polymeric fluid^[8]. Presumably the polyethylene produced from thermal degradation of EDAM dispersed in the undecomposed EDAM melt acts as the rubber particles. However in pellet form or the melt in an extruder or in a capillary rheometer and in the fibre spinning of PP/EDAM blends no appreciable effects of the thermal oxidative degradation of EDAM will result.

Steady state shear flow of EDAM. Experimental data for the steady state shear viscosities of 100% EDAM of the series B samples (with stabilizers) and the series C samples (without stabilizers) at 200°C from capillary extrusion and cone and plate rheometers covering the shear rates from 10^0 - 10^4 s⁻¹ are shown in Fig. 3. Good agreement of the experimental data obtained in Chiba and in Beijing is observed for shear rates greater than 10s⁻¹. Some discrepancies in the viscosities at lower shear rates obtained by the two laboratories seem likely to be an effect of thermal degradation of EDAM. The viscosity behavior of the samples of series B and of series C appears nearly identical at shear rates above 10s⁻¹.

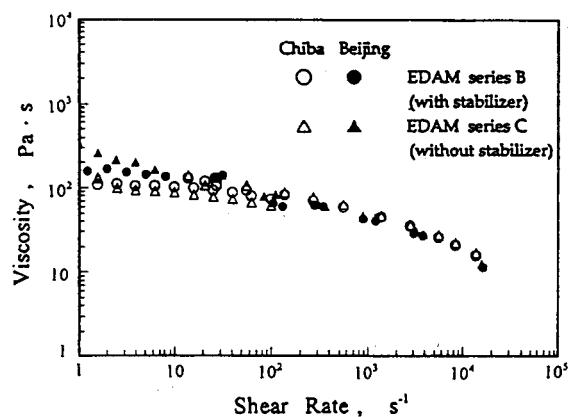


Fig. 3. Steady state viscosities as a function of shear rate of 100% EDAM from the series B and series C samples at 200°C

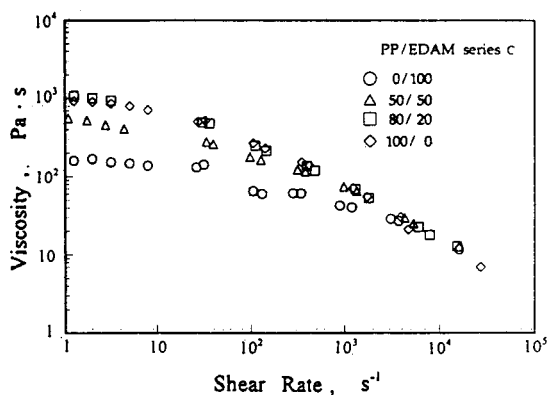


Fig. 4. Steady state viscosities as a function of shear rate of the series C samples of PP/EDAM blends at 200°C

Viscosities of PP/EDAM blends. As the effect of stabilizers on the viscosity behavior of EDAM is slight, only the experimental data of PP/EDAM blends of the series C with 0, 20, 50 and 100% EDAM are shown in Fig. 4. For the viscosities at 200°C under shear rates 10^0 - 10^4 s⁻¹, the viscosity behavior of the four samples falls into two categories. The PP/EDAM 80/20 blend resembles PP while the 50/50 blend and EDAM have much lower viscosities. TEM observation of the microtomed sections of the capillary extrudates showed that the PP/EDAM 80/20 blend had the morphology of EDAM islands in a PP sea, while the 50/50 blend had the morphology of PP islands in an EDAM sea as shown in Fig. 5. Consequently it is understandable that the PP/EDAM 80/20 blend has flow characteristics like PP while the 50/50 blend has flow characteristics like EDAM as further displayed in the entrance flow characteristics (*vide infra*).

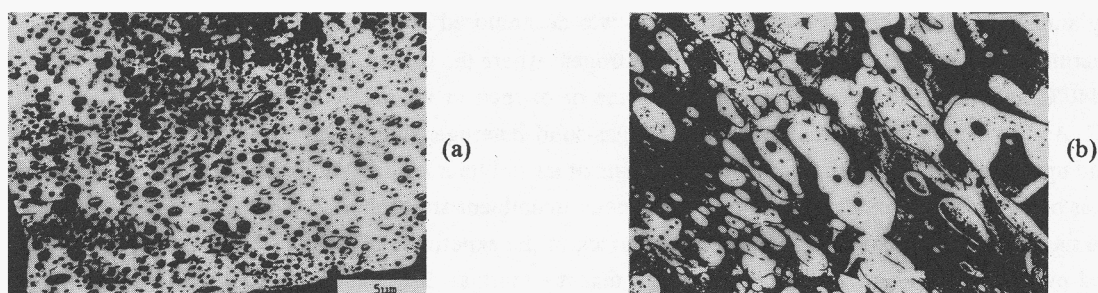


Fig. 5. Transmission electronmicrographs of the melt extruded blends (a) PP/EDAM 80/20; (b) PP/EDAM 50/50

For practical applications of EDAM as a dyeing improver for PP fibres the amount of EDAM used is usually small. The changes of viscosity at 200°C with PP/EDAM composition for the series A samples are shown in Fig. 6 at capillary wall stresses of (0.4-150)kPa. For a PP/EDAM 95/05 blend at wall stresses smaller than 10⁵kPa the activation energy found from viscosities measured at 185-230°C is 45kJ/mol close to the value of 42kJ/mol for PP.

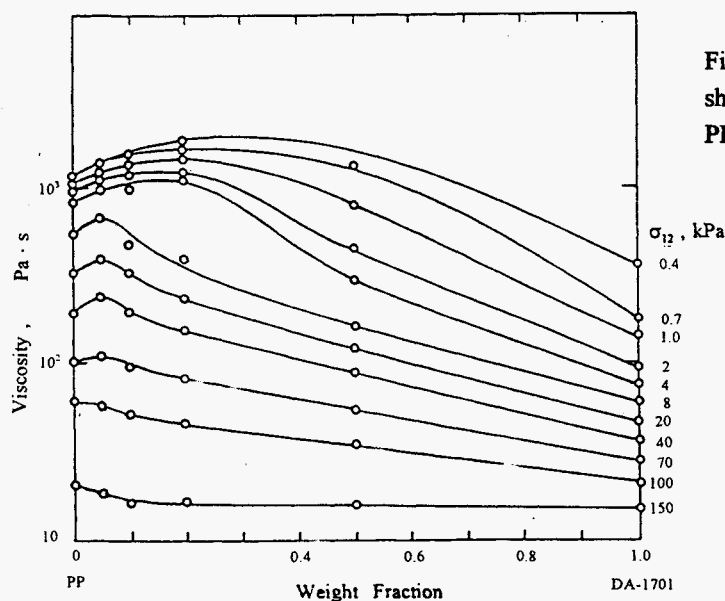


Fig. 6. Steady state viscosities at different shear stresses of the series C samples of PP/EDAM blends at 200°C

The first normal stress difference. The first normal stress difference, $\sigma_{11} - \sigma_{22}$, of the series A samples was measured by the cone and plate rheometer at 200°C. Experimental results are shown in the log-log plots of the normal stress as a function of the shear stress, σ_{12} , in Fig. 7. The data for EDAM and PP/EDAM 50/50 blend fall on the same straight line within experimental error with a slope of 1.4, while the data for PP and PP/EDAM 95/05 fall on another line with a slope of 1.7 and the normal stress values are much lower. The slope behavior for the PP/EDAM 80/20 blend shows a transitional behavior, resembling that of EDAM at low shear stresses and that of PP at high shear stresses. When $\sigma_{11} - \sigma_{22}$ is plotted vs σ_{12}^2 as shown in the insert of Fig. 7, the initial slope is a measure of steady shear compliance,

$$J_e = (\sigma_{11} - \sigma_{22}) / 2\sigma_{12}^2$$

The compliance of EDAM, $J_e = 7.6 \cdot 10^{-4} \text{ Pa}^{-1}$, is higher than that of PP, $J_e = 1.3 \cdot 10^{-4} \text{ Pa}^{-1}$. As a consequence the reversible shear strain at a given shear stress should differ by the same factor.

Characteristics of the entrance flow to an orifice. Elongational viscosity and elasticity of a polymer melt will show up in the entrance flow of a die of length-to-diameter ratio $L/D=0$. A thin metal plate with a hole of 0.76mm diameter at the centre was used in place of a capillary on the capillary extrusion rheometer. A dimensionless parameter e characterizing elongational flow effects has been defined^[9-11] as

$$e = \Delta P / 2\sigma_{12}$$

where ΔP is the pressure drop along the die and σ_{12} is the wall shear stress value for a die of $L/D=100$ at a shear rate $\dot{\gamma} = 4V/(\pi R^3)$, V being the volume efflux rate of the orifice flow and R the radius of the orifice. The values of e obtained from experimental data at 200°C under various shear rates for PP/EDAM blends of the series A samples are shown in Fig. 8. Again the curves fall into two groups. High values of e at low shear rates characterize the flow behavior of EDAM melt.

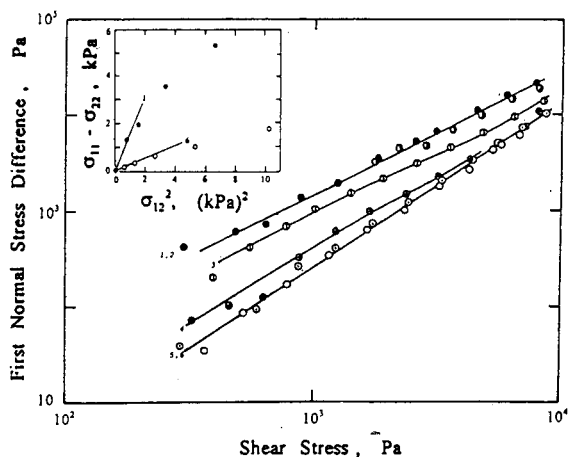


Fig. 7. Shear stress dependence of the first normal stress differences of the series A samples of PP/EDAM blends at 200°C: 1,2,3,4,5,6 - PP/EDAM 0/100, 50/50, 80/20, 90/10, 95/05, 100/0 blends respectively

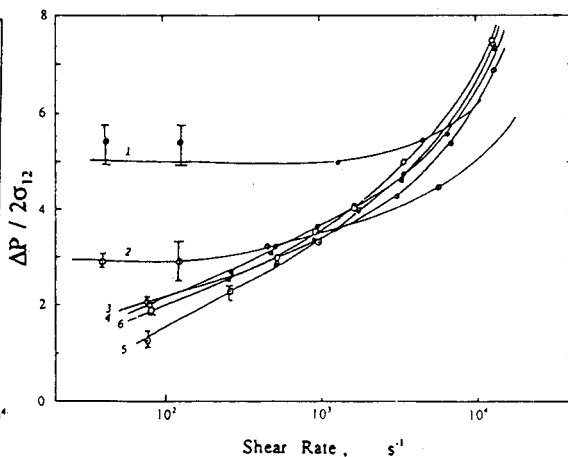


Fig. 8. Entrance flow characteristics of the series A samples of PP/EDAM blends at 200°C, the numbers 1-6 referring to Fig. 7

The rheological behavior presented above shows that PP/EDAM blends of up to 20% EDAM behave like PP while the PP/EDAM 50/50 blend behaves like EDAM in accordance with the phase reversal in the morphology of the blends. The blends of high EDAM content exhibit high elastic effects both in shear and in elongational flow at low strain rates. This elastic effect probably comes from strong interaction between the DAM moieties of EDAM copolymer chains, forming physical network in the melt which is disentangled at higher strain rates.

DYEING BEHAVIOR OF PP/EDAM BLENDS

EXPERIMENTAL

Noblen[®] HY-100 of Sumitomo Chemicals was used as the PP resin, which had a MFI of 13 (ASTM D1238, 230°C, 2.16kg load). Two kinds of EDAM copolymer, DA1701 of 28wt% DAM content and a MFI of 100 and DA3032 of 39wt% DAM content and a MFI of 300, were prepared in a high pressure radical polymerization plant and evaluated as the dyeable modifier for PP fibres. Two key chemicals for utilizing EDAM copolymer more beneficially as a dyeable modifier were confirmed in this work. One is an additive to accelerate penetration of dyestuffs into EDAM modified PP fibres, which is small pellet-shaped sodium stearate (SST) by Kao Atlas. The other is a dyebath auxiliary to render the dyed fibres a high color fastness and possessing an antistatic finishing effect, which is potassium salt of an alkylphosphate, Electrostripper[®] K

by Kao Atlas. The following compounding recipe was applied:

PP base resin	92-98 wt%
EDAM copolymer	8-2 wt%
SST	0-1 wt%
Additives: anti-oxidant Irganox ^R 1010	0.1 phr
Sumilizer ^R TPS	0.2 phr
UV-stabilizer Sumisorb ^R 300	0.5 phr

The components were melt-blended in a single-screw extruder (30mm diameter, L/D=28) at 240°C. The compounds were melt spun into multi-filaments (46d/f × 12f) on a conventional spinning machine made by Kawasaki Aircraft, which consisted of a single-screw extruder and a gear pump, a 12-hole spinnerette and a take-up systems. The fibre spinning conditions were:

Melt temperature	240°C
Take-up velocity	300m/min
Average residence time	10min

The multi-filaments were subsequently drawn into finer ones (15d/f × 12f) by an off-line stretching equipment with a hot plate heated to 110°C at a draw ratio of 3 and a winding speed of 120m/min.

Evaluation of dyeability were carried out by an exhaustion dyeing method according to the procedure schematically shown in Fig. 9. Two indices DR - percent dyestuff absorbed into the fibre before soaping and

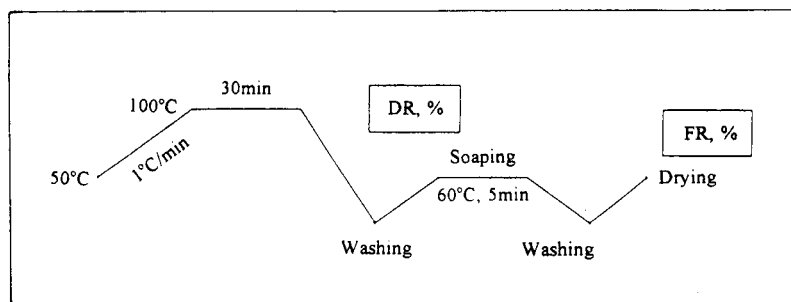


Fig. 9. Schematic showing the exhaustion dyeing procedure

FR - percent dyestuff fixed in the fibre after soaping, were calculated from the changes of the optical absorbance of the dyebath solutions. The recipe for dyeing was

Fibre sample	3 g
Dyestuff	0.8-2.0 wt% fibre
Formic acid or acetic acid	2.0 wt% fibre
Electrostripper ^R K	0-5.0 wt% fibre
Liquor ratio	1/60
Soaping - Na ⁺ laurylmonosulfate	2g/L, 60°C, 5min

RESULTS AND DISCUSSION

As is evident from Fig. 10 the percent dyestuff absorbed, DR, was remarkably improved by introducing 1 wt% SST in fibres, even though the amount of EDAM copolymer in the fibre was reduced from 8 wt% to 7 wt%. The extraction of Na⁺ in the acidic dyebath might produce some paths near the fibre surface, through which the dyestuff molecules can penetrate more easily. Furthermore the resulting stearic acid in the fibre might restrain the out flow of the dyestuff molecules once they had entered into the fibre.

Fig. 11 shows the relationship between the concentration of Electrostripper^R K and the percent dyestuff fixed in fibre, FR. The effect of improving FR by Electrostripper^R K is evident, however it seems practical to use 3 wt% of fibre because of the saturation trend in the higher concentrations. Formic acid is more preferable as a dyeing auxiliary than acetic acid because of its lower pH to result in higher FR.

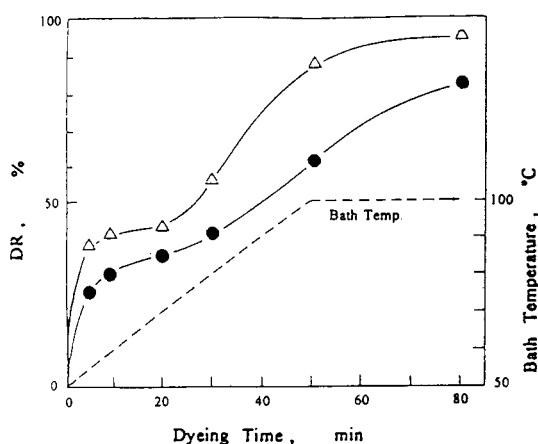


Fig. 10. Effect of sodium stearate in EDAM modified PP fibres on the percentage of dye-stuff absorbed in the fibres

	DA1701	SST	PP
△	7	1	92
●	8	0	92

Dyebath: Aminyl^R Blue E-PRL 1.1 wt% fibre
 Formic acid 2.0
 Electrostripper^R K 3.0

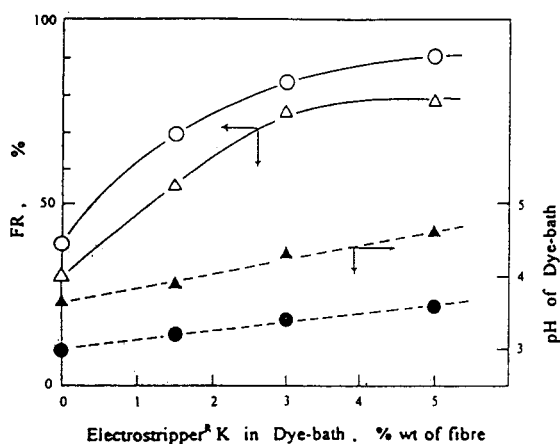


Fig. 11. Effect of Electrostripper^R K on the dyeability
 DA1701:SST:PP = 7:1:92 wt

Dyebath: Aminyl^R Blue E-PRL 1.1 wt% fibre
 ○, ● Formic acid 2.0
 △, ▲ Acetic acid 2.0

Table 1. Effect of Electrostripper^R K as a dyeing auxiliary

Dyestuff (C.I. No.)	Dyestuff Concentration wt% fibre	Formic acid (2 wt% fibre)				Formic acid (2 wt% fibre) + Electrostripper ^R K (3 wt% fibre)			
		FR %	LF Class	RF kv	EC kv	FR %	LF Class	RF kv	EC kv
Aminyl Yellow E-5GN (Yellow 110)	1.0	80	6	4-5	-3.5	92	6-7	5	-0.9
Aminyl Red E-2BL (Red 266)	1.8	85	4-5	5	-4.0	86	6	5	-1.4
Aminyl Blue E-PRL	1.1	85	4-5	5	-3.2	94	6	5	-1.4
Lanyl Yellow RR (Orange 87)	1.2	30	5-6	5	-5.5	68	6-7	5	-2.3
Lanyl Red GG (Red 211)	2.0	24	4-5	4-5	-4.7	92	5	5	-2.0
Lanyl Grey BG e/c (Black 58)	0.8	39	4-5	4-5	-3.0	83	6	5	-1.5

DA1701:SST:PP = 7:1:92

Aminyl^R - Acid dyestuffs manufactured by Sumitomo Chemical Co.

Lanyl^R - Premetallized dyestuffs manufactured by Sumitomo Chemical Co.

FR - Percent dyestuff fixed in the fibre after soaping

LF - Light fastness, JIS L-0842, carbon arc lamp, 80h, 63°C

RF - Rubbing fastness, JIS L-0849, rubbing tester type-2, wet cotton cloth, 200g load, 100 times

EC - Electrostatic charge, measured immediately after 10 times rubbing with cotton cloth, JIS L-0803, using clock meter at 33 times/min speed, 200g load, 50% R.H.

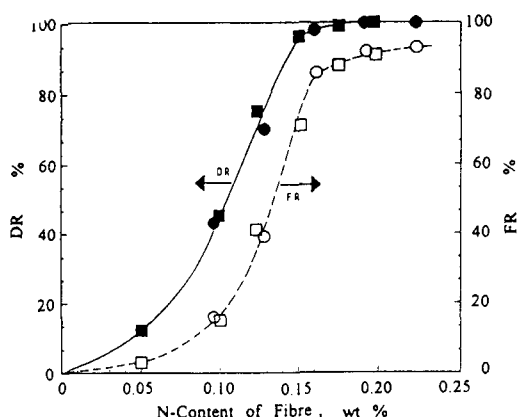


Fig. 12. Effect of N-content in the fibres on the dyeability DR and FR

DA1701	2-8 wt%	□, ■
or DA3032	3-7 wt%	○, ●
SST	1	
PP	balance	
Dyebath:	Aminyl [®] Blue E-PRL	1.1 wt% fibre
	Formic acid	2.0
	Electrostripper [®] K	3.0

significantly reduced even after soaping and washing, suggesting a notable antistatic finishing effect of Electrostripper[®] K used in the dyebath.

Fig. 12 shows the influence of N-content, namely the amount of EDAM copolymer in the fibres, on the dyeability in terms of DR and FR. It is interesting to note that the dyeability simply depends on the N-content in the fibres regardless of the DAM content of the EDAM copolymer used. From practical and economical view point it was decided to use 7 wt% of DA1701 in the fibres.

Some representative acid dyestuffs and premetallized dyestuffs were applied to reconfirm the above mentioned key points presented in Figs. 10-12 and the results are summarized in Table 1. When Electrostripper[®] K was added in the dyebath containing formic acid the results were all satisfactory in terms of dyeability FR and color fastness, the light fastness LF and the rubbing fastness RF. The electrostatic charge of dyed fibres was

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