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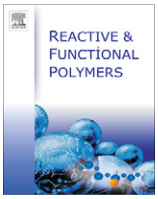

Lightly branched comb polyesters: Application in fast drying solvent-borne coating formulations

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ABSTRACT

Novel oxazoline-based comb-polymers possessing linoleyl or oleic side chains have been synthesized and used to produce low viscosity coatings. Inclusion of the polymers in model paint formulations results in coatings that exhibit faster drying times than commercially available alkyd resin formulations. The comb polymers were produced from diol substituted oxazoline monomers that were synthesized through a scalable, solvent free protocol and purified by simple recrystallisation. Co-polymerisation of the oxazolines with adipic acid at 160 °C in the bulk resulted in the targeted polyester comb type polymers. The polymers were soluble in a range of organic solvents and compatible with commercial alkyd resins. Model paint formulations containing up to 40 wt% of the linoleyl-based comb polymers exhibited a dramatic reduction in viscosity (from 35 to 13 Poise at 25 °C) with increasing quantities of polymer added. Dynamic mechanical analysis (DMA) studies revealed that the drying rate of the model paint formulations containing the comb polymers was enhanced when compared with that of commercial alkyd resins.

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1. Introduction

Reducing emissions of volatile organic compounds (VOCs) from paint formulation has received increasing attention in recent years, as a consequence of environmental concerns and the potential risks to human health assigned to prolonged exposure [1,2]. For example, recent legislation concerning VOC (in Europe 2010) requires a maximum level of 300 g/L [3], effectively eliminating many generations of solvent borne coatings from the market place. Therefore, there is a strong demand for new air drying resins to improve upon more conventional alkyd resin technologies which are now reaching, or have indeed reached the end of their product lifecycle.

Advances in polymer synthesis in the previous three decades have resulted in robust strategies to produce polymers with controlled molecular weights and branched structures on an industrial scale. Notable advances in coating applications include the synthesis of branched polymers (BPs) [4,5]. The compact nature of BPs results in high numbers of surface functional groups along with lower viscosity compared to conventional linear polymers [6,7]. These unique structural attributes make branched structures intriguing candidates as coating additives as they may serve to reduce the viscosity of the product formulation which, in turn, could lower the quantity of VOC thinner required whilst promoting efficient crosslinking during curing by reaction of their numerous of surface functional groups [7–15]. Within the family of branched polymers, numerous specific structures including combs [16], comb-on-comb [17] and arborescent polymers [18–23] also exhibit similar advantageous physical properties.

In this study, comb-type polymers were targeted that contain repeat units with reactive fatty acid side-groups. These polymers, which consist of a linear backbone with numerous lengthy side chains, exhibit rheological properties that are more comparable to hyperbranched polymers rather than conventional linear analogues [24–26]. As a consequence of this useful property, comb-shaped polymers have been employed in developing low viscosity and rapid drying organic coatings. Recent studies by Athawale et al. produced comb-type acrylic copolymers for surface coatings applications that exhibited lower viscosities and reduced drying times when compared to linear acrylic copolymers [27].

Another possible strategy based on comb polymer technology is blending commercial alkyds with comb polymers. Talroze et al. demonstrated that comb polymers can be used as flow modifiers for thermoplastic polymers [28]. It was shown that a dramatic decrease in blend viscosity could be achieved if the length of the side chains of comb polymers were less than the critical entanglement limit.

In this study, easily accessed lightly branched comb-structured polyesters containing oxazoline units as linker groups to reactive fatty acid side chains have been synthesized and fully character-

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ised. Blending studies of these materials with commercial alkyd resins has resulted in new formulations that exhibit more rapid drying than comparable commercial coating formulations.

2. Experimental

2.1. Materials and physico-chemical characterisation

Oleic acid, linoleic acid, dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), triethyl amine, tris(hydroxymethyl)aminomethane (THAM), adipic acid, and *N*,*N*′-dimethylformamide (DMF) were purchased from Aldrich. Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dichloromethane (CH_2Cl_2), methanol, acetone and 2-propanol were purchased from Fisher. Low odour white spirit (Exxsol D40 ex-Total), anti-skinning agent, methyl ethyl ketone oxime (MEKO ex-Elementis Pigments), and driers including Octa-soligen 10 (cobalt carboxylate 58%, naptha 40% and methoxy propoxy propanol 2%), Octa-soligen calcium 10 (calcium carboxylate 45% and naptha 55%) and Octa-soligen zirconium 18 (zirconium 2-ethyl hexanoate 56% and naptha 44%) were used as supplied by OMG Borchers. The alkyd used (a soy oil based alkyd with 70 wt% in low odour white spirit) was obtained from Cray Valley Ltd. Melting points were carried out with Stuart Melting Point Apparatus (SMP10) (UK). 250 MHz ^1H and 62.5 MHz ^{13}C NMR spectra were recorded on Bruker AC250 spectrometer. Infrared (IR) spectroscopic analyses were performed on a Perkin Elmer 1720-X Infrared Fourier Transform spectrometer on KBr discs using thin film. GPC was performed with Polymer Laboratories PL-GPC 120 with PL-AS-MT autosampler fitted with columns (PLgel guard plus 2 × mixed bed-D, 30 cm, 5 μm) in conjunction with refractive index (with differential pressure and light scattering) detector using THF as the eluent at 30 °C (flow rate 1 mL min^{-1}). Polymer molecular weight data is quoted with respect to polystyrene calibrants. For each GPC sample, a single solution was prepared by accurately adding 10 mL of solvent to an accurately known mass of *ca.* 20 mg of sample. The solutions were left for 2 h to dissolve/disperse and were then thoroughly mixed before being filtered through a 0.2 μm polyamide membrane. Modulated differential scanning calorimetry (MDSC) measurement was performed on a TA Instruments 2920 MDSC V2.6A. Thermo-gravimetric analysis was carried out on a TA Instruments AutoTGA 2950HR V5.4A and the samples (5–15 mg) were heated from room temperature up to 600 °C under dry nitrogen gas at a heating rate of 5 °C/min. MDSC and TGA data were collected and processed on Universal Thermal Analysis Software.

2.1.1. Viscosities studies

The comb polymers were diluted to 70 wt% solid by addition of white spirit at room temperature and stirred vigorously for 10 min in order to give an homogeneous pale yellow oil. These comb polymer solutions were mixed with commercial alkyd resins (a soy oil based alkyd with 70 wt% in low odour white spirit) at increasing comb polymer concentrations (from 5 to 50 wt% solid) and these mixtures were stirred vigorously for 10 min to give homogenous blends. This procedure ensured that the total solids content remained at 70 wt%. Viscosity data was collected using a cone and plate viscometer at both 25 °C and 50 °C.

2.1.2. Drying studies

Coating samples for drying studies were prepared by addition of these three drying agents (Octa-soligen 10, 0.5 wt%; Octa-soligen calcium 10, 2.0 wt%; Octa-soligen zirconium 18, 2.8 wt%) and MEKO into the blends and vigorously stirred for 10 min. Each sample (100 μl) was taken by capillary glass tube and coated on a rectangular glass braid substrate (size: 15.700 mm $(l) \times 10.000$ mm $(w) \times 0.310$ mm (h)). Dynamic mechanical analysis was conducted with DUPONT DMA 983 DMA (with fixed frequency: 1 Hz) operating in a shearing mode (isotherm 30 °C for 3 days). All the DMA data were collected and processed on Universal Thermal Analysis Software.

2.2. Small molecule synthesis and characterisation

2.2.1. Monomer **1**

Into a three-armed round bottomed flask was added oleic acid (86.00 g, 264 mmol) and tris(hydroxymethyl)aminomethane (THAM) (32.00 g, 264.00 mmol). The flask was degassed with nitrogen and heated slowly to 160 °C with vigorous stirring under a high flow rate of nitrogen to remove the water formed during the reaction. After being stirred for 48 h at 160 °C, the mixture was cooled down to 80 °C and slowly poured into acetone (1500 mL) with stirring. The solution was maintained at room temperature while a white solid formed which was collected by filtration and recrystallised from acetone to afford **1** as a white powder (61.13 g, 63%). M.p.: 72–74 °C; FTIR (KBr, cm^{-1}): 3350 (OH), 3051, 2924, 2851, 1658 (oxazoline ring), 1464 (symmetric COO-stretching), 1366, 1264, 1030, 989, 741. ^1H NMR (250 MHz, $CDCl_3$): δ 0.88 (t, J = 7.5 Hz, 3H), 1.30 (br, 20H), 1.61 (m, 2H), 2.02 (m, 4H), 2.29 (t, J = 7.5 Hz, 2H), 3.45 (brs, 2H), 3.63 (ABq, J = 12.5 Hz, 4H), 4.15 (s, 2H), 5.35 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.5, 23.1, 26.5, 27.6, 27.6, 28.7, 29.5–29.9 (6C), 30.12, 30.16, 32.3, 65.3, 72.2, 76.1, 130.1, 130.6, 171.2. CI-MS calcd. for $C_{22}H_{41}NO_3$ 367.3086, found 367.3090.

2.2.2. Monomer **2**

Into a three-armed round bottomed flask was charged with linoleic acid (25.00 g, 89.00 mmol) and tris(hydroxymethyl)aminomethane (THAM) (10.80 g, 89.00 mmol). The flask was purged with nitrogen and slowly heated to 160 °C with vigorous stirring under a high flow rate of nitrogen to remove the water formed during the reaction. After being stirred for 48 h at 160 °C, the mixture was cooled down to 80 °C and slowly poured into acetone (1500 mL) with stirring. The solution was maintained at room temperature and a white solid formed, which was collected by filtration and recrystallised from acetone to afford **2** as a white powder (26 g, 80%). M.p.: 60–62 °C; FTIR (KBr, cm^{-1}): 3353 (OH), 3084, 3010 (*cis*-$CH{=}CH{-}CH_2{=}CH$), 2927, 2852, 1656 (oxazoline ring), 1464 (symmetric COO-stretching), 1428, 1367, 1328, 1270, 1223, 1182, 1140, 1088, 1030, 993, 973, 949, 724, 670. ^1H NMR (250 MHz, $CDCl_3$): δ 0.89 (t, J = 7.5 Hz, 3H), 1.31 (br, 14H), 1.60 (m, 2H), 2.06 (m, 4H), 2.28 (t, J = 7.5 Hz, 2H), 2.77, (t, J = 7.5 Hz, 2H), 3.63 (ABq, J = 12.5 Hz, 4H), 4.15 (s, 2H), 5.35 (m, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.51, 23.00, 26.04, 26.53, 27.61, 27.62, 28.67, 29.53–29.58 (3C), 29.76, 30.03, 31.94, 65.49, 72.16, 76.07, 128.29, 128.49, 130.41, 130.66, 171.24. CI-MS calcd. for $C_{22}H_{39}NO_3$ 365.2930, found ($M+H^+$) 366.3001.

2.3. Comb polymer synthesis and characterisation

2.3.1. General procedure

Into a three-armed flask was added the calculated amount of adipic acid **3** and monomer **1** or **2**. The flask was purged with nitrogen and transferred into an oil bath maintained at 160 °C. After the mixture was molten it was vigorously stirred under a high flow rate of nitrogen to remove the water formed during the reaction for a period of 8 h. After this time ^{13}C NMR and IR spectroscopic analysis revealed that the resonance of the carboxylic acid group was not evident (see Supporting Information, Figs. S1 and S2), then the reaction mixture was submitted to a reduced pressure for 30 min to distil off residual water to yield a pale-yellow viscous oil.

2.3.2. Comb polymer **4**

This material was synthesized according to Section 2.3.1:- the molar ratio of adipic acid (2.49 g, 16.9 mmol) and monomer **1** (8.24 g, 22.6 mmol) was 3:4. Yield: 95% (9.60 g); FTIR (KBr, cm^{-1}): 3277 (O—H), 3002 (olefinic = C—H stretching), 2925, 2853 (CH_3/CH_2 stretching), 1741 (C=O ester group stretching vibrations), 1661 (oxazoline signal), 1463 (symmetric COO-stretching), 1378, 1242, 1166 (O—C stretching ester), 1061, 1002, 911; ^1H NMR (250 MHz, $CDCl_3$): δ 0.88 (t, $J = 7.5$ Hz), 1.30 (br), 1.66 (m), 2.02 (m), 2.29 (t, $J = 7.5$ Hz), 3.63 (m), 4.12 (m), 5.35 (m). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.1, 22.5–34.0, 62.6–66.1, 71.4–71.6, 72.1–74.2, 127.8–130.4, 169.6–173.5. $T_g = -34$ °C. GPC: $M_w = 5300$, PDI = 2.2.

2.3.3. Comb polymer **5**

This material was synthesized according to Section 2.3.1:- the molar ratio of adipic acid (1.65 g, 11.3 mmol) and monomer **2** (5.48 g, 15.0 mmol) was 3:4. Yield: 95% (6.40 g); FTIR (KBr, cm^{-1}): 3277 (O—H), 3006 (olefinic = C—H stretching), 2926, 2853 (CH_3/CH_2 stretching), 1740 (C=O ester group stretching vibrations), 1661 (oxazoline signal), 1462 (symmetric COO-stretching), 1378, 1244, 1164 (O—C stretching ester), 1059, 1000, 914. ^1H NMR (250 MHz, $CDCl_3$): δ 0.89 (t, $J = 7.5$ Hz), 1.31 (br), 1.66 (m), 2.06 (m), 2.32 (t, $J = 7.5$ Hz), 2.77, (t, $J = 7.5$ Hz), 3.63 (m), 4.15 (m), 5.35 (m). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.1, 22.6–34.1, 64.5–66.0, 71.4–71.9, 72.1–74.2, 127.9–130.2, 169.6–173.5. $T_g = -$ -24 °C. GPC: $M_w = 4400$, PDI = 2.0.

2.3.4. Comb polymer **6**

This material was synthesized according to Section 2.3.1:- the molar ratio of adipic acid (3.31 g, 22.6 mmol) and monomer **1** (8.24 g, 22.6 mmol) was 1:1. Yield: 88% (9.40 g); FTIR (KBr, cm^{-1}): 3373 (O—H), 3002 (olefinic = C—H stretching), 2925, 2853 (CH_3/CH_2 stretching), 1740 (C=O ester group stretching vibrations), 1663 (amide I and oxazoline signal), 1553 (amide II), 1463 (symmetric COO-stretching), 1380, 1244, 1165 (O—C stretching ester), 1060, 1006, 934. ^1H NMR (250 MHz, $CDCl_3$): δ 0.88 (t, $J = 7.5$ Hz), 1.30 (br), 1.64 (m), 2.02 (m), 2.32 (t, $J = 7.5$ Hz), 4.12 (m), 5.34 (m). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.1, 22.6–34.0, 62.8–66.0, 71.4–71.8, 72.0–72.3, 127.9–130.2, 169.7–173.4. $T_g = -37$ °C. GPC: $M_w = 50000$, PDI = 11.

3. Results and discussion

3.1. Synthesis and characterisation of oxazoline monomers and comb-type polyesters

The synthesis of oxazoline monomers **1** and **2** has been described previously [29,30], but extensive characterisation data was not reported. By modification of this method, these monomers were synthesized by the addition of three equivalents of linoleic or oleic acid with one equivalent of tris(hydroxymethyl)aminomethane (3:1 M ratio, respectively) in the bulk under nitrogen at 160 °C (Scheme 1). Recrystallisation from acetone produced monomers **1** or **2** as white powders in 63% and 80% yield, respectively. It was envisaged that the diol component of the monomers would be used to produce a polyester type polymer, whilst the alkene-containing side groups would undergo crosslinking during curing [31], producing the desired robust paint finish.

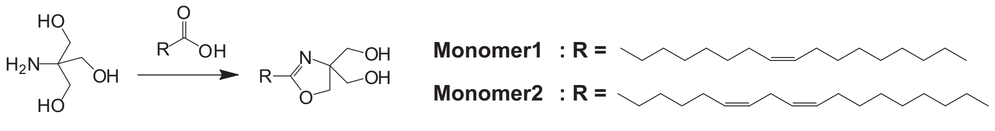
With monomers **1** and **2** in hand, attention turned to the synthesis of the targeted comb-like polymer structures. This was achieved by the addition of adipic acid (**3**) to either of the monomers at 160 °C in the bulk to deliver polymers **4**, **5** and **6** (Scheme 2). ^1H NMR spectroscopic analysis of the three polymers revealed an intense double doublet at *ca.* 4.1 ppm characteristic of the methylene protons between the newly-formed ester residues and the oxazoline ring, indicative of successful polyesterification. In addition there were two low intensity singlet resonances at 4.43 and 5.91 ppm which could not be removed despite repeated attempts to purify the polymers by precipitation. Oxazolines have previously been reported to undergo ring opening under acid conditions [32] as would be present at the beginning of the polymerisation procedure described here. The low intensity signals at 4.43 and 5.91 ppm were therefore attributed to the presence of an amide-triester residue within the polyester main chain – highlighted in Scheme 2. This assignment was confirmed by synthesising small molecule analogues of this structural subunit for spectroscopic comparison (see Supporting Information Fig. S3). As a consequence of the slow rate of the ring opening reaction the ratio between the oxazoline unit and ring opened triester branching unit is approximately 50:1 in the isolated polymers, as determined by ^1H NMR spectroscopy.

Comb polymers **4**, **5** and **6** were soluble in a range of organic solvents including acetone, $CHCl_3$, CH_2Cl_2, DMF, DMSO, THF and methanol. Only polymers **4** and **5** were completely soluble in white spirit, an important consideration for new paint formulation additives. GPC analysis of polymers **4** and **5** (Table 1) showed that these were primarily oligomeric in nature species ($M_n \approx 2$ kDa, DP ≈ 5) as would be expected from the molar inequivalence used in the monomer feed ratio. Polymer **6**, synthesized from a 1:1 stoichiometry of diol **1** and adipic acid **3** exhibited a higher M_n ($\approx$4500), but much higher PDI of 11 when compared to a PDI of approximately 2.1 for **4** and **5**. This broad polydispersity for what may have been considered a simple polycondensation reaction indicates the effect that even low levels of branching can have on molecular weight distributions.

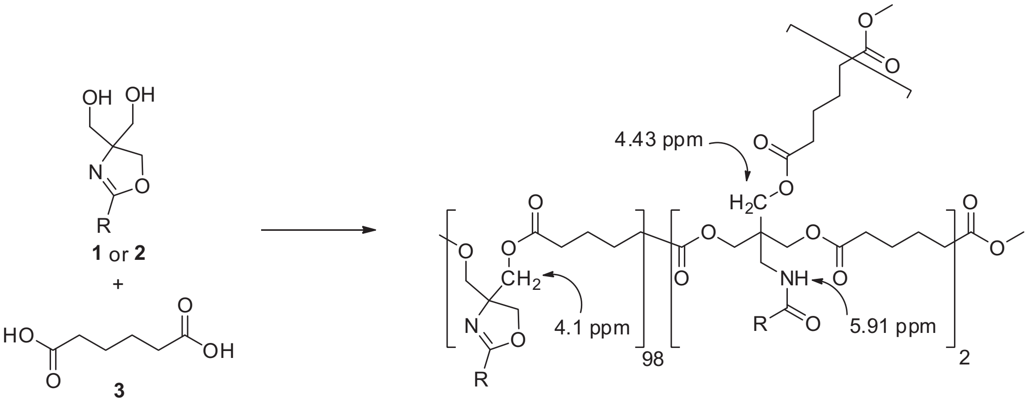
With respect to assessing the suitability of these polymers for coatings applications, all three polymers (**4**–**6**) exhibited glass transition temperature below −20 °C and high thermal stability with the onset of weight loss occurring at a minimum of 197 °C.

3.2. Drying behaviour of comb polymer and commercial alkyd resin blends

Blends of a commercially available alkyd resin with the diluted comb polymer **4** or **5** were obtained according to the procedures described in the experimental section. Based on the molecular weight characteristics of the comb polyesters in the blends, different concentrations were obtained ranging from 10% to 50% (weight percent, the weight of the comb polymers divided by the total weight of solid in the blends, gram/gram). A pronounced decrease of the viscosities of blends both at 25 °C and 50 °C was observed as shown in Fig. 1. This effect could be attributed to two factors: a disruption of the entanglement of polymer chains in the systems by



Scheme 1. Synthesis of oxazoline monomers **1** and **2**.



Polymer	Component monomers	Monomer ratio
4	**3**:**1**	3:4
5	**3**:**2**	3:4
6	**3**:**1**	1:1

Scheme 2. Synthesis of comb polymers **4**, **5** and **6**.

Table 1
Molecular weight, polydispersity and thermal properties of comb polymers (with onset, 50%, 90% decomposition temperature, weight residue at 500 °C and T_g data).

Comb polymer	M_w (Da)	M_n (Da)	PDI	T_g (°C)	T_{onset} (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	Weight residue at 500 °C (wt%)
4	5300	2400	2.2	−34	221	403	459	8.8
5	4400	2200	2.0	−37	197	400	457	5.9
6	50000	4500	11	−24	246	416	491	8.9

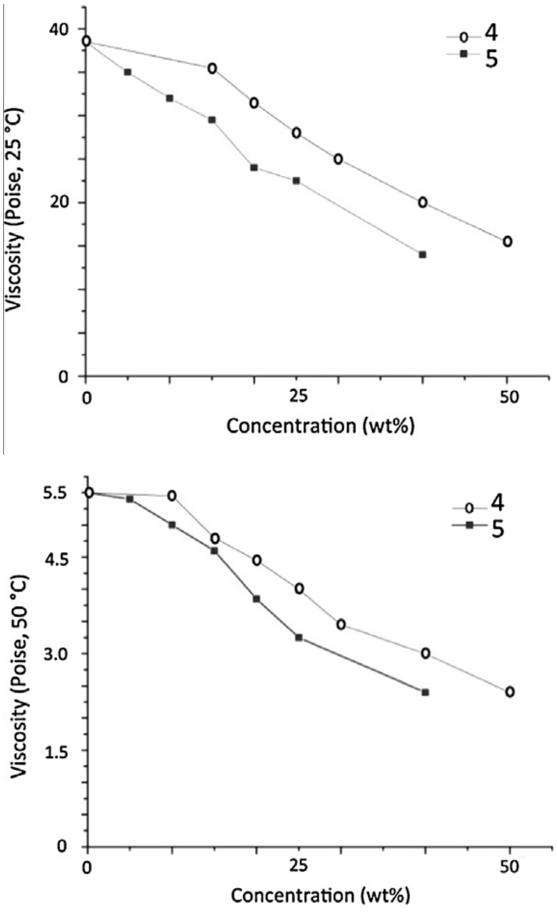


Fig. 1. Comb polymers **4** and **5** as viscosity-reducing agent in the blends at 25 °C (upper plot) and 50 °C (lower plot). The viscosity of blend decreased when different contents of comb polymers were mixed with commercial alkyd resin.

Table 2
Viscosities of comb polymers **4** and **5**.

Temperature (°C)	Viscosity of the polymers (poise, cone and plate)		
	Alkyd	**4** (70% solid)	**5** (70% solid)
25	38.5	4.0	2.8
50	5.5	1.0	0.8

comb polymers [33] and the large disparity of the viscosities between the comb-polyester and alkyd resin (Table 2).

The curing performance of the polymers was also investigated by dynamic mechanical analysis (DMA) over a drying time of 3 days. Conducting the DMA measurements in shearing mode provides information concerning progress of air drying and any increase in crosslink density [34,35]. Since 1,4-diene groups are the primary sites for crosslinking of drying oils such as linoleic acid [31], comb polymer **5** was used for studying of the drying behaviour of the blend rather than using **4**.

In a comparative study, two organic coating systems were formulated: coating-A (formulated with alkyd resin and driers in the presence of anti-skinning agent, methyl ethyl ketone oxime (MEKO)) and coating-B (formulated with blend of alkyd resin with comb polymer **5** with 5 wt% solid and driers in the presence of MEKO). These coating systems were submitted to DMA at 30 °C for a period of 3 days (Fig. 2).

The DMA data reveals that both systems exhibit two distinct drying stages: physical drying/solvent evaporation within the first 4 h with a slow increase of shear storage modulus (see the inset in Fig. 2) and after this induction period molecular crosslinking occurred. The physical drying rate of the blend was slightly higher when compared to commercial alkyd resin, presumably as a consequence of the viscosity-reducing effect of comb polymer **5** in the blend. Furthermore, after the induction period the blend possessed an accelerated crosslinking rate in the dry process. Thus, at equal

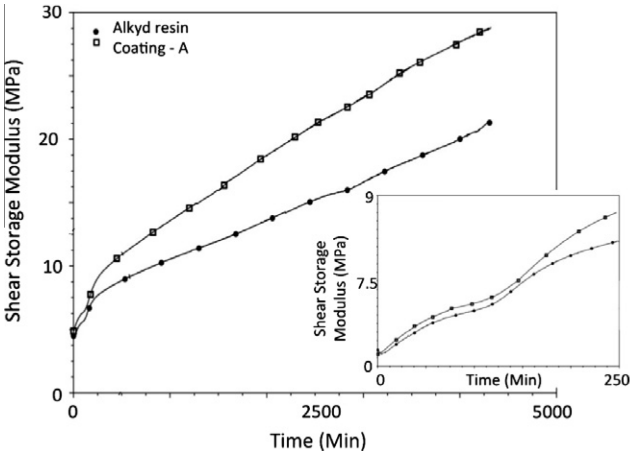


Fig. 2. DMA plots of alkyd resin (coating-A) and blend (coating-A): the shear storage modulus as a function of time measured on paint films coated on glass braid (with expanded plots in the first 4 h, left).

drying times the crosslinking density of oxazoline based blends are higher than that of commercial systems.

4. Conclusions

Comb polymers compatible with commercial alkyd resins have been synthesized by bulk co-polymerisation of adipic acid with monomers **1** or **2**. Extensive analysis of the resulting polymers revealed that they were not simple linear comb polymers, but contained low levels of branching as a consequence of ring opening of the oxazoline-based monomers. Blending the novel comb polymers with alkyd resins led to decreases in the viscosities of the blends. New coating formulations were prepared from blending commercial alkyd resins and comb polymer **5** which contained linoleyl side groups. Dynamic mechanical analysis revealed a typical drying process consisting of an initial physical drying/solvent evaporation period followed by chemical crosslinking. The drying rates of the two stages of the new system were more rapid than for the commercial alkyd resins.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2013.01.008.

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