LATEX AND POLY-DADMAC AS SOIL CONDITIONERS

by

SITI MASREAH BERNAS
Ir. (University of Sriwijaya, Indonesia),
MSc. (University of Wales, United Kingdom)

Department of Soil Science
University of Adelaide
Australia

Thesis submitted to The University of Adelaide
in fulfilment of the requirements for
the degree of Doctor of Philosophy

June 1995

TABLE OF CONTENTS

CHAPTER 6. The Effect Of Polymers On Growth Of Rye Grass

CHAPTER 7. Decomposition Of Latex In Soil As Determined By Monitoring Changes In $\partial^{13}C$

CHAPTER 8. General Discussion And Conclusion

LIST OF FIGURES

Figure **Page**

LIST OF TABLES

Table **Page**

SUMMARY

Two types of polymers, latex a (hydrophobic natural uncharged polymer) and poly-diallyl dimethyl ammonium chloride, or poly-DADMAC, (a hydrophilic synthetic positively charged polymer), were used as soil conditioners and their effects on the stability of soil structure, hydrophobicity, and on the growth of ryegrass were investigated. The rate of decomposition of latex in soil was also monitored.

The two polymers interacted with soils via significantly different mechanisms and so had different effects on water stable aggregation. Latex was capable of binding small aggregates into aggregates >2 mm at relatively low application rates (ie between 0.5 and 1.5 g kg^{-1}), depending upon the initial structural stability of the soils. Poly-DADMAC, by contrast, decreased the proportion of aggregates <0.125 mm and slightly increased the proportion of aggregates >0.25 mm.

The effects of poly-DADMAC and latex on soil tensile strength and friability appeared to depend primarily upon soil type, the type of polymer applied and its application rate. Latex (1 and 2 g kg^{-1} soil) did not affect the tensile strength and the friability of a Wiesenboden and a Red-brown earth. Poly-DADMAC (2 g kg^{-1} soil) slightly increased the tensile strength of the Wiesenboden and decreased its friability. It increased the tensile strength of the Red-brown earth but did not affect its friability.

Latex and poly-DADMAC decreased the amount of mechanically dispersible clay significantly, however there were no significant differences between the application rates of polymers of 1 and 2 g kg^{-1} soil. Poly-DADMAC at an application rate of 2 g kg^{-1} decreased the amount of mechanically dispersible clay to almost zero in the Red-brown earth, but not in

the Wiesenboden. This is probably a result of the higher clay content of the Wiesenboden.

Latex and poly-DADMAC did not affect water retention in the Wiesenboden and the Red-brown earth within the range of water available to plants.

Soils amended with 1.5 g kg^{-1} latex showed an increase in hydrophobicity as determined by M.E.D. values to about 1.4 for the Red brown earth and to about 1.8 for the Wiesenboden. M.E.D. is the molarity of ethanol drops which penetrate the soil surface in 10 seconds. These values indicate only moderate water repellence which would not adversely affect plant growth. The application of latex at a rate of 2 g kg^{-1} soil could be still tolerated on the Wiesenboden but would cause a problem with water repellence in the Red-brown earth.

The application of latex (1.5 g kg^{-1}) on the Red-brown earth and 0.5 g kg^{-1} on the Wiesenboden did not affect water run-off and infiltration on either soil. However, it decreased erosion significantly on both soils compared with the control.

Poly-DADMAC at the application rates of 1 g kg^{-1} on the Red-brown earth did not affect water run-off and infiltration but it decreased erosion significantly compared with the control. Poly-DADMAC at the application rate of 0.5 g kg^{-1} on the Wiesenboden increased water infiltration and decreased water run-off and erosion significantly compared with the control.

Latex iand polyDADMAC, when applied to soils in pots, did not affect the growth of ryegrass plants over a period of twelve weeks in the glasshouse.

Latex decomposed gradually in the soil, as measured by $\delta^{13}C$ values of the residual C and the CO_2 released during incubation of latex-amended soil. Latex is produced by a C_3 plant and has a low $\delta^{13}C$ value of -26.4‰. It was incubated in a soil which had grown sugar cane, a C_4 plant for decades. The

$\delta^{13}C$ value for the soil was -13.5‰. Changes in the $\delta^{13}C$ of soil plus latex and CO_2 released with time of incubation allowed calculation of the rate of decomposition of latex in the soil to be made. This means that both polymers can be used as soil conditioners, with latex as an aqueous emulsion being the most environmentally safe so far.

DECLARATION

I Hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To best of my knowledge and belief, no material described herein has been previously published or written by another person except when due reference is made in the text.

If accepted for the award of a Ph.D. degree, this thesis will be available for loan and photocopying.

Siti Masreah Bernas

ACKNOWLEDGEMENTS

I wish to thank my supervisors, Professor J.M. Oades and Dr. J. Churchman, for their guidance and encouragement throughout this project. I also would like to thank Mr. Iain Grierson for his guidance during the first stage of my reseach and to Dr. C.D. Grant for his help in measuring tensile strength. Thanks are due to other members of the staff of Department of Soil Science for their advice and assistance.

In particular I thank:
Dr. Z. Eusof (Rubber Research Institute of Malaysia) for providing latex; Mr. M.P. Snodgrass (Allied Colloids Australia Pty Ltd) for poly-DADMAC; Ms L. Giles for statistical analysis on Chapter 2; Mrs. R. Middleberg for statistical analysis in Chapter 3; Mr. A. McClure for doing S.E.M; Dr. J. Dighton for determination of $\delta^{13}C$; Dr. P.J. Clarke for ^{13}CNMR spectroscopy; Ms. J. Groom and colleagues for developing photographs and slides; and to all members of the organic matter group for contributing valuable knowledge during my study.

I also would like to thank AUSAID for financial support and University of Sriwijaya, Indonesia for allowing me to make this study.

Last but not least I appreciate very much my husband "Rachmad Mulyono" and my daughter "Zeolita Prabu Putri" for encouragement and understanding during my study.

Dedicated to

My Mother and my late Father

INTRODUCTION

The clearing of land for agricultural purposes initiates physical soil degradation such as soil erosion, slaking and hardsetting, sealing and crusting. These phenomena happen rapidly, mainly after tillage and where the crop canopy is not sufficient to protect soil surfaces.

Soil conditioners provide one of the answers to overcome these problems, which is why since the 1950's, scientists have been looking for a good soil conditioner. Several soil conditioners such as vinyl acetate-maleic acid copolymer (VAMA), hydrolysed polyacrylonitrile (HPAN), Krilium, poly-vinyl alcohol (PVA) and poly-acrylamide (PAM) were proposed from the 50's to the 70's . However all of these polymers are costly. PVA also shows only a slow dissolution in water, thus it was considered unsuitable (Theng, 1979). A soil conditioner is not only required to stabilise soil but also has to be cheap, environmentally safe, non toxic and often also biodegradable (De Boodt, 1993). It has to prevent erosion, at least over the first two months of application, be simple to apply, and have no negative effects on seedling emergence and plant growth (Ambrust and Lyles, 1975).

In order to provide a cheap and easily applied soil conditioner, Wallace and colleagues, for example, have used long chain (high molecular weight) poly-acrylamide polymers, which can be applied together with irrigation water at low application rates (Wallace *et al.*, 1986a; Wallace and Wallace 1986; and Wallace *et al.*, 1986b). This type of polymer has also been investigated by Mitchell (1986) and Ben-hur (1994). It was considered environmentally safe because it contains less than 0.05% monomer (Sojka and Lentz, 1994). As a synthetic polymer, however,it will have a long half life in soils.

Figure 1. Rubber trees (*Hevea brasiliensis*) (After R.R.I.M., 1970).

In tropical areas such as Malaysia, where the risk of erosion is relatively high due to an intense rainfall, researchers have applied modified latex (natural rubber) as a soil conditioner. Latex is favoured in Malaysia because that country produces the most rubber in the world today. Latex (rubber) as a natural product polymer from a tree called *Hevea brasilliensis* (Figure 1), has been applied as a soil conditioner by the Rubber Research Institute of Malaysia (R.R.I.M.) since the 1970's. However, R.R.I.M. workers have traditionally modified the rubber by mixing it with British Petroleum aromatic oils, stabilisers, or other materials, when it was applied as a soil conditioner. For example, Soong and Yeoh (1974) mixed rubber polymers with BP aromatic oil and this mixture stabilised sandy soils and gave better crop growth. Soong and Yeoh (1975) also applied that particular mixture and reported that it decreased erosion up to about 80% when compared with a control. Bachik *et al.*, (1985) mixed natural rubber with BP aromatic oil, an emulsifier, and a stabiliser. These authors also added sawdust, carbon black and peat to natural rubber; all of the mixtures have been found to decrease erosion successfully.

As calculated by Wah and Bachik (1985) the cost of application of a mixture of natural rubber and other materials is greater than the total cost of the other materials used (seed, seed binder and fertilisers). Natural rubber as an unmodified aqueous emulsion, however, has not yet been tried as a soil conditioner. If the unmodified rubber could be used this would introduce a cheap, easily applied and also environmentally safe alternative soil conditioner, since it is a natural product.

Poly-DADMAC was used for comparison, since this polymer has a positive charge, a high molecular weight and is hydrophilic. It has been used for water treatment to flocculate clays, colloids and metals (Letterman and Pero, 1990), however it has not been used as a soil conditioner.

Based on these considerations, this experiment was designed to investigate the effects of unmodified latex (natural rubber) as an aqueous emulsion, and also of poly-DADMAC, on the stability of soil structure, plant growth, and soil hydrophobicity. Since latex is a natural product, a knowledge of its decomposition rate in soils was considered important for determining suitable field application rates, and so a $\delta^{13}C$ labling technique was employed to monitor this decomposition.

CHAPTER 1

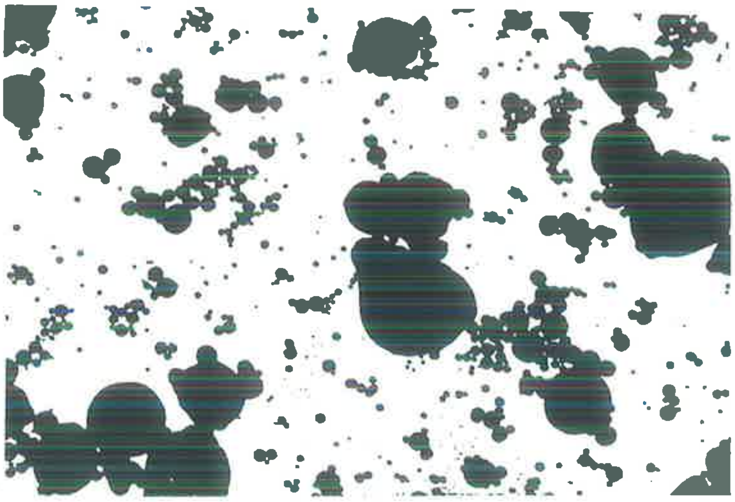
Review Of Literature

This literature review deals firstly with the chemical and physical properties of latex and poly-DADMAC before a discussion of the interactions of synthetic polymers with soil surfaces. Latex is a natural product and a neutral (un-charged) polymer, while poly-DADMAC is a synthetic, positively charged polymer. Hence we discuss the reaction or adsorption of neutral and positively charged polymers onto soil or clay surfaces. The effects of these polymers on soil physical properties, erosion, and plant growth will also be reviewed in this Chapter. The decomposition of organic polymers is included in the last part of this review.

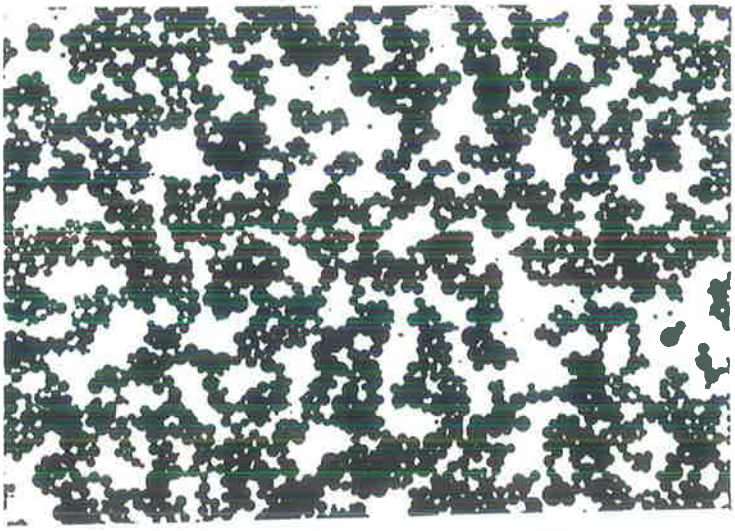
1.1. Properties of the polymers

1.1.1. Latex

In its raw state, latex, produced from the tree *Hevea brasiliensis*, is a white, milky, aqueous emulsion containing approximately 60% water, 35% rubber (poly-isoprene), less than 2% protein, and numerous other components (Davis, 1937). Its molecular weight is large and bimodal (1×10^5 and $>2 \times 10^6$) (R.R.I.M., 1970). However, Cornish *et al.* (1993) found that the molecular weight of natural rubber varies. The average is 1.5 million Dalton, and the maximum can be up to over 9 million Dalton. The emulsion consists of tiny almond-shaped particles with diameters from <0.25 μm and lengths from 4 μm (Figure 2) (Polhamus, 1962 and R.R.I.M., 1962). According to these authors, the mean diameter of rubber was 1.23 μm, however, diameters as low as 0.12 μm were detected by Cornish *et al.* (1993). The molecular structure of rubber



Big rubber particles: x 12.000



Small rubber particles: x12.000

Figure 2. Rubber particles (after R.R.I.M. 1962).

is poly-isoprene (R.R.I.M., 1970). It is uncharged and hydrophobic and has the following molecular formula:

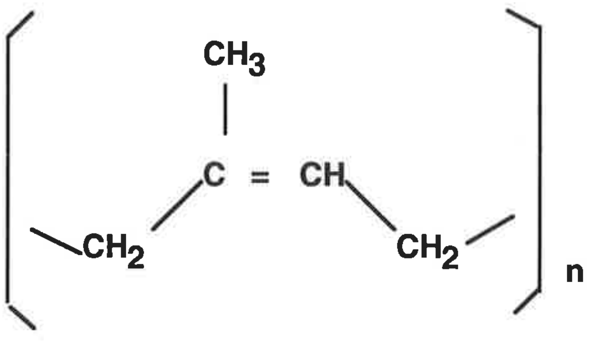


Figure 3. Poly-isoprene (after R.R.I.M., 1970).

1.1.2. Poly-Diallyl Dimethyl Ammonium Chloride (Poly-DADMAC).

Poly-DADMAC is one of the polyelectrolyte coagulants used in water treatments. It has a very high tendency to be adsorbed on the active surfaces of particles in aqueous suspension. Poly-DADMAC is a positively charged homopolymer, of molecular weight about 1 x 10^6 Dalton. Its chemical name is N,N-dimethyl-N-2-propenyl-2-2propen-1-1ammonium chloride, homopolymer $(C_8H_{16}N.Cl)_n$ (Lettermen and Pero, 1990). It is used in water treatment, to flocculate clays, metals, and colloids (Theng, 1979, Molyneux, 1984, and Letterman and Pero, 1990). The formation of poly-DADMAC according to Letterman and Pero (1990) is shown in Figure 3.

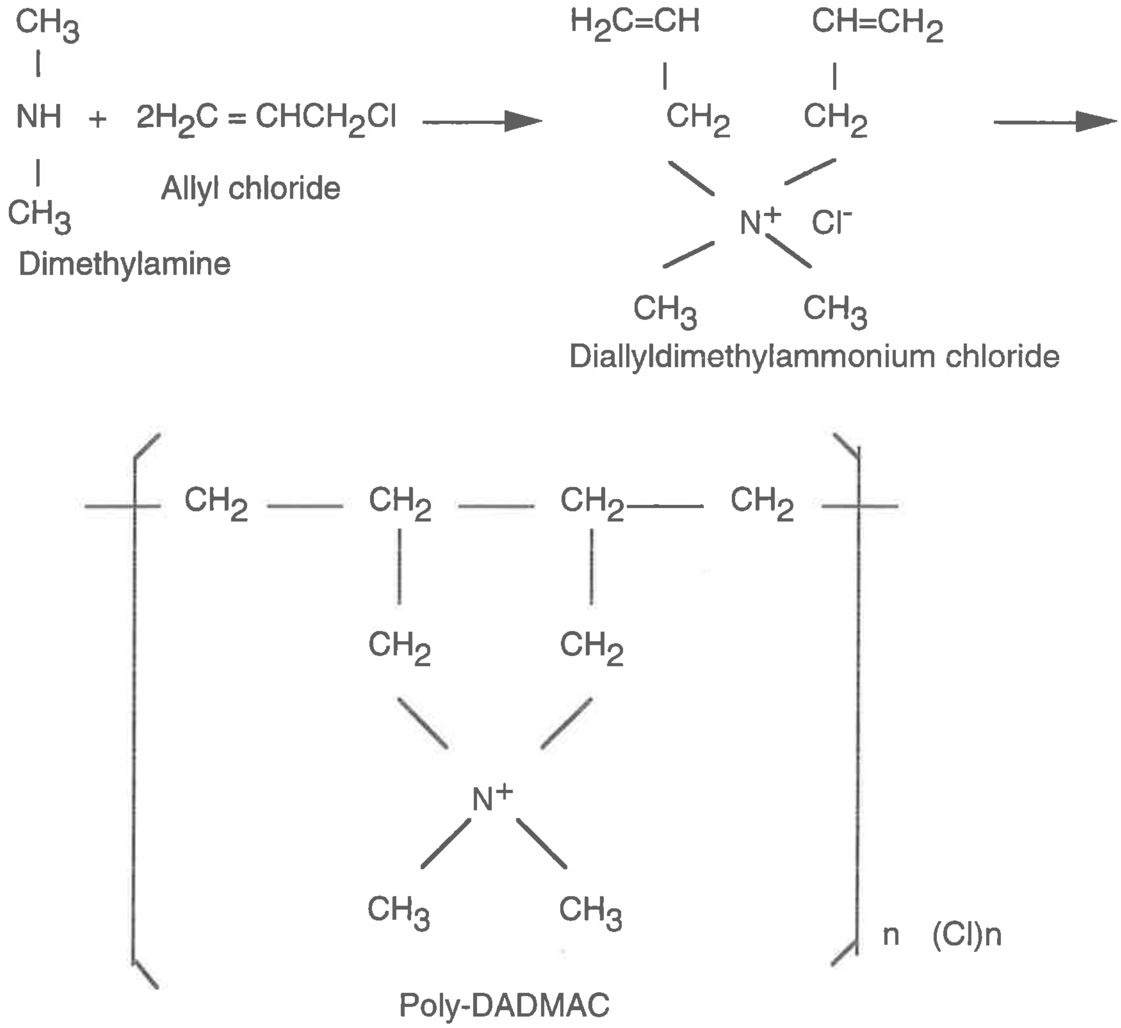


Figure 4. The formation of poly-DADMAC from the reaction of allyl chloride with dimethylamine (after Letterman and Pero, 1990).

1.2. Adsorption of polymers onto clay or soil surfaces

Most of the research on the adsorption of polymers on soil or clay surfaces, was done in the 1950's and 1960's (De Boodt *et al.* 1990), The high cost of the materials and lack of understanding of the reaction between polymers and soil materials or clays have contributed to a decline in the papers published since then. Hence most of the literature refers to that period. However some of the authors, as cited in this chapter, have provided significant information on the reaction between polymers and clay minerals or soil materials.

Before the discussion of adsorption onto soil surfaces or colloids, it is necessary to define adsorption. Hayes and Mingelgrin (1991) stated that "in the process of adsorption a chemical species does not transfer from one bulk phase to another, but it can accumulate at the surface". The authors further explained that when the molecules adsorbed on the surface of an adsorbent, they could be adsorbed in a monolayer or in several layers on the surfaces.

Adsorption of a polymer onto clay or soil surfaces will depend on the type, charge, and molecular weight of the polymer, clay properties, and electrolyte concentration in the solution (Greenland, 1965,1972; Theng, 1979; Ueda and Harada, 1968a;1968b). The review of the adsorption of polymers will therefore be considered in relation to their charges.

1.2.1. Uncharged or non-ionic polymers on clays

The most popular uncharged polymer is poly-vinyl alcohol (PVA); it has been discussed in detail by several authors (Greenland, 1963, 1965 and 1972 ; Williams, *et. al.*., 1967; Theng, 1979). Most experiments have been carried out on the reaction with clays of this polymer solution.

Greenland (1972) reported that in solution, linear, water soluble, neutral polymers would not be attached by all of their segments onto the clay surfaces. Only a few of the segments contacted to clay as "trains". Some of the segments projected out as "loops" with the end of segments which did not attach to surfaces appearing as "tails". Kavanagh et al. (1978) stated that when polyvinyl alcohol (PVA) was adsorbed on illite or montmorillonite, half of the PVA adsorbed was attached on the clay and another half existed as "loops" and "tails". However, in the case of gibbsite, only about 7% absorbed PVA was in contact with gibbsite, with the rest protruding out as "loops" and "tails" in the suspension. That explains why PVA is a good flocculant for gibbsite and a poor flocculant for clays.

This phenomenon was also noted by Greenland (1965a,b). He explained that uncharged polymers would not be good flocculants, unless they had very high molecular weights.

Greenland (1965a,b) further reported that polymers would form inter-particle bonding when added to a system of clays which were already close to each other. Greene *et al.* (1978) reacted PVA containing 12% acetyl groups with a Ca-illite suspension, and found that the polymer was strongly adsorbed by the clay but a very small amount of flocculation occurred.

The flocculation of the clay system by polymers also depends on electrolyte concentration (Greenland, 1965). Greene *et. al.* (1978) found that addition of Ca and PVA to a dispersed Ca-illite solution, caused flocculation to occur at a slower rate compared with adding $CaCl_2$ alone. Emerson and Raupach (1963) produced a model of the interaction between PVA, electrolyte and Na-montmorillonite which recognises that the amount of flocculation depends on whether the salt or polymer is added first. It is better to add polymer first and then salt in order to increase flocculation of montmorillonite.

Theng (1979) measured the amount of PVA adsorbed on montmorillonites saturated with different cations. He found that in a suspension of 0.5% w /v clay, the amount of PVA adsorbed was 0.8 % g g-1 clay on Na-montmorillonite, 0.3 % g g^{-1} clay on Ca-montmorillonite, and 0.15 g g^{-1} clay on Ce-montmorillonite. This is because the polymer could be adsorbed on both external and internal surfaces of Na-montmorillonite. Greenland (1963) states that the most important factor is the accessibility of the clay surfaces. It depends on the strength of interaction between exchangeable cation and alumino silicate layers.

Emerson and Raupach (1963) found that, when PVA was added to montmorillonite suspensions, there was no release of divalent cations. Therefore they suggested that PVA and clay are associated by H-bonding between OH groups on the polymer and O on the silicate surface of the clay. However, Greenland (1972) doubted this because PVA as for simpler alcohols could not form strong H-bonds to oxygens of the silicate surfaces, and he suggested that a direct or indirect reaction occurred with the exchangeable cation. Dowdy and Mortland (1967) showed evidence which supported this idea. Greenland (1972) also stated that silanol groups on clay surfaces were strongly hydrated and polymers could not be adsorbed on the silanol surfaces because they could not displace water from the surfaces. He proposed that polymer adsorption onto the siloxane surfaces was caused by multiple van der Waals forces deriving from the many surface-segment contacts.

Overall, the adsorption of non-ionic polymer on clays in suspensions depends on clay types, electrolyte concentration, the saturating cation, and also molecular weight of polymers. Interaction is likely through van der Waals forces.

1.2.2. Polycations (positively charged polymers) on clays

Polymers are adsorbed onto clays in suspension in the order cationic > nonionic > anionic respectively (Ben-Hur *et al.* 1992). The amount of positively charged polymer adsorbed is greater, because it can also penetrate between the interlayers of clay minerals. However coverage of the internal surfaces is very limited, because when the number of contact points is increased, mobility is reduced, which is why polycations accumulate around crystal edges (Lagaly, 1987). However, as observed by many researchers (see later), the amount of absorbed polymer does not control their behaviour as flocculants.

Black *et. al.* (1966) reported that cationic polymers could act as coagulants or as flocculants. As coagulants, they compressed the diffuse double layer around clay surfaces, while as flocculants, they formed inter-particle bonds, depending on the clay concentration in suspension. Cationic polymers were more effective than anionic and nonionic polymers with similar molecular weights in flocculating clay particles, even when they were of low molecular weight (Dixon *et al.* 1967).

The adsorption of the polymer also depends on the cation exchange capacity (C.E.C.) of the soil. Montmorillonite adsorbs more positively charged polymer than kaolinite clay (Black *et al.* 1966). Ueda and Harada (1968a) carried out research on the addition of poly-DADMAC-SO_2 onto a kaolinite suspension. They found that flocculation and sedimentation occurred immediately, when polymer was added. However, it was noted that further addition of polymer caused re-dispersion of the clay by a steric effect. It can be seen that the minimum amount needed for complete initial flocculation was inversely related to the molecular weight of the polymer (Figure 5). That is the polymer with DP=1430 required a lower concentration for maximum transparency than the polymer with DP=64.

Ueda and Harada (1968b) also experimented using poly-DADMAC-SO_2 with polymers having 2 different molecular weights. Both polymers decreased the cation exchange capacity and increased the anion exchange capacity of montmorillonite. However, the amounts of the two polymers adsorbed were different (Figure 6); the polymer with lower molecular weight (14,000 Da; DP = 67) was adsorbed more than the polymer with higher molecular weight (167,000 Da; DP = 791).

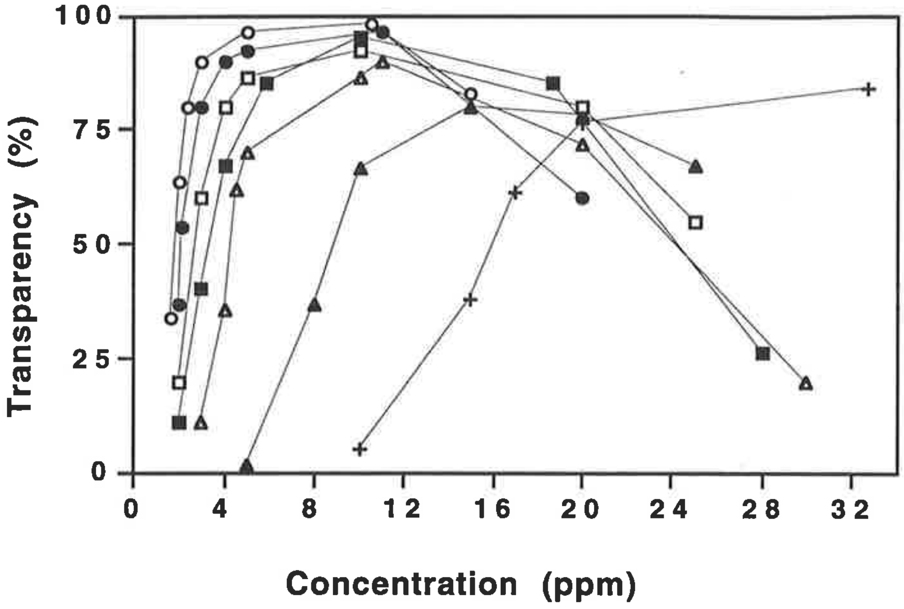


Figure 5. Effect of molecular weights [equated to degree of polymerization, DP] of Poly-DADMAmCl-SO$_2$ on flocculation of kaolinite. o DP = 1430; ● DP = 1090; □ DP = 702; ■ DP = 619; △ DP = 363; ▲ DP = 128; + DP = 64. After Ueda and Harada, 1968a.

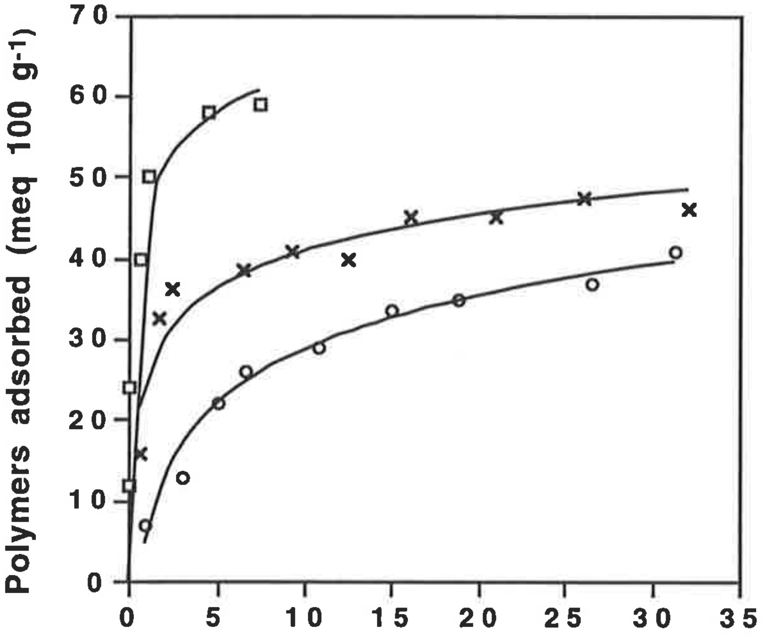


Figure 6. Adsorption of poly-DADMAC-SO$_2$ as copolymer I and II and ammonium acetate on bentonite at 30° C: x = copolymer I with molecular weight of 167,000Da and DP = 791;□ = copolymer II with molecular weight of 14,000 Da and DP = 67. o = NH_4COOH. (After Ueda and Harada, 1968b).

Cationic polymers can also flocculate silica particles, as shown by Iler (1971). Iler used cationic polymethacryloyloxythyl diethyl ammonium methyl sulfate to flocculate colloidal silica particles of different sizes. He reported that the amount of polymer needed depended on the diameter of silica particles. The larger the diameter of silica, the smaller was the amount of polymer needed to flocculate them (Table 1).

Table 1. The amount of polymers needed for flocculation of silica, based on particle sizes of silica (after Iler 1971)

Type of silica			Polymer (%) to :	
Name	Particle diameter (nm)	Specific surface area (m^2/g)	Flocculate all silica	Saturate silica surface
Experimental	4	650	10	36.25
Ludox SM	9	330	5.75	18.5
Ludox HS	14	200	4.55	12.25
Ludox TM	25	124	2.7	6.75
LudoxTM with 0.01 NaCl	25	124	2.7	7.25
Experimental	50	54	0.8	2.6
	70	40	-	1.55
	120	22	0.127	0.65
	124	22	0.125	0.55
	220	12	0.035	0.25

Roberts *et. al.* (1974) investigated the flocculation of a kaolin suspension with hydrolysed aluminium ions and cationic polymers. The addition of a low dosage of polymer (5 ppm) and low dosage of pre-added aluminium (5ppm) gave maximum sedimentation. This sedimentation was decreased as the amount of pre-added aluminium was increased to more than 20 ppm. This is because positively charged aluminium increases the positive charge of clay which suppressed the adsorption of cationic polyacrylamide and decreased the flocculation of kaolin suspension.

The effect of positively charged polymers on flocculation also depends on the pH of suspension. Ueda and Harada (1968a) used 4 types of polymers with different degres of basicity to flocculate kaolinite suspensions. At pH < 7 each polymer showed the same ability to flocculate kaolinite suspensions, but at higher pH, they showed different abilities to flocculate clay. This difference is derived from the basicity of these polymers.

It may be concluded that the adsorption of cationic polymers depends on the CEC, clay type, pH, and molecular weight of the polymers. The adsorption of these polymers occurs more rapidly than with nonionic and negatively charged polymers.

The reaction of polymers with the clay or colloids in suspension is easily monitored and well understood. However, when the polymers were applied to soils, the reactions were complicated. In addition, the characteristics of reactions in suspension may not represent reactions with soils, as will be discussed.

1.2.3. Polymers on soils

In recent years, Wood and Oster (1985), Mitchell (1986); Letey (1994) Ben-Hur (1994) among others, have investigated the mixing of polymers with irrigation water in order to stabilise soils. This gives a cheap and practicable way of reducing soil surface sealing, and also reduces dispersed clay in the irrigation water, which in turn minimises pore blockage in the soil profile.

The adsorption of soluble polymers on a clay and on a soil as a whole, may be not comparable. For example, polyanions are good flocculants in dispersed clay systems but do not necessarily import any stability to micro- and macroaggregates unless the system contains polyvalent cations, which can act as points of contact to the surface ie., hydrated oxides of iron and aluminium which coat clays or soil particles (Theng, 1979; Letey, 1994). According to Ben-Hur *et al.* (1992), the adsorption of polymers on soil surfaces also depends on the charges and molecular weights of the polymers and soil properties such as mineralogy and micro-morphology.

An investigation of the effects oin soil of applying three anionic polymers having different molecular weights and amounts of charge has been carried out by Nadler and Letey (1989). Two of the three polymers were polyacrylamides (PAMs) and had molecular weights (10 to 15 X 10^6 Dalton); each polymer had either low or high negative charge according to the amount of OH subsitution for NH_2 (2% substitution = low charge, virtually non-anionic; 21% substitution = high anionic charge). The third polymer was the natural polysaccharide, guar, which had a lower molecular weight than either of the two PAMs (2 x 10^5 to 2 x 10^6 Da) but had an anionic charge intermediate between them. The fine fraction of a soil was pre-treated in various ways to obtain i) a soil with high pH, ii) a soil with no organic carbon, iii) a calcium-saturated soil, and iv) a sodium-saturated soil. Results indicated that, for all for the sodium-saturated fraction, adsorption of the polymers onto the fractions depended primarily upon the extent of anionic charge on the polymer. The PAM with greatest negative charge was adsorbed linearly, the non-anionic PAM displayed a plateau at at the higher concentration, and the polysaccharide guar showed intermediate adsorption. For the sodium-saturated soil fraction there was little adsorption of any of the polymers.

Malik and Letey (1991) conducted an experiment using several polymers having different charges and applied them to several soils and three fine sand fractions. They reported that the adsorption of polymers on different soil types was not significantly different. They suggested that adsorption occurred mostly on external surfaces and not on the total surface, depending on clay typ e and clay content. To support this finding, they also measured the adsorption of polymers on the sand fractions, and reported that the adsorption was greater on the very fine sand than on the coarser sand. These results were the effect of very little charge on the soil being exposed to the polymers, so that the molecular sizes and conformation of the polymers affected their adsorption more than the electrostatic reaction. This also suggested that those polymers did not penetrate inside the aggregates. De Boodt (1993) stated that uncharged soil particles, like sand grains, had some affinities for polymers. The processes involved were van der Waals forces and negative entropy effects which increased with the molecular weight of the polymer. This adsorption might even increase if polyvalent metal ions were added.

Adsorption of anionic polyacrylamide and/or cationic polyacrylamide polymers by coarse and fine loams was irreversible, because these polymers had high molecular weights, were multisegmented, and flexible (Nadler *et al.* 1992). According to Greenland (1972) when a polymer is attached to the soil surfaces by many contact points, it is very difficult to detach all of them at the same time, just like a millipede attempting to lift all its legs from the ground simultaneously.

In conclusion, the adsorption of polymers on to the soils was also affected by factors affecting the adsorption of polymer onto the clay in suspensions, i.e. polymers and clay suspension properties. The type of adsorption depends mainly on polymer charges, and involves van der Waals , H-bonding, and electrostatic forces.

1.3. The effects of polymers on some soil physical properties

When polymers are applied to soils, the high molecular weight material is expected to affect important soil physical properties, e.g. water stability of aggregates and tensile strength. They may block or line soil pores, which will also affect soil water retention.

1.3. 1. Stabilisation of soil aggregates by polymers

An aggregate is a group of two or more soil particles which attach to each other more strongly than to adjacent particles (Kemper and Rosenau, 1986). The stability of an aggregate will depend on natural binding agents (transient, temporary, and persistent) Tisdall and Oades, (1982). Organic polymers may be included as one of the binding agents, and this will depend on the properties of the polymers.

Adhesive bonds are formed by interaction between polymers and clay or soil surfaces, as has been discussed previously. Generally, there are thousands to millions of polymer molecules occurring between two soil particles to create an adhesive bond, and the strength of this bond will depend on polymer-polymer and polymer-surface interactions. These bonds have to have mechanical strength and water stability in order to stabilise soil aggregates (Schamp *et al.* 1975). According to Ben-Hur (1994), polymers stabilised the soil through 2 main processes ie., adsorption of polymers on to the clay surfaces causes a physicochemical change at the clay surfaces, reducing repulsive forces between clay particles, and secondly, polymers act as a bridge between two particles inside an aggregate.

Charged and uncharged polymers stabilise the soil aggregates by rather different methods. Anionic polymers become attached to some particles, however only a few segments of the polymers are linked to each particle; uncharged polymers spread over the surface and form many bonds to each surface as they come into contact (Greenland, 1965b). The negatively charged polymers form "string of beads" while uncharged polymers spread like "coats of paint" around aggregates which are already close each other (Greenland, 1963). Greenland (1963) considered that larger polymers attach initially to more than one particle, and then a contraction reaction may draw them physically closer together. This process could be important in modifying the physical properties of soils by polymers (Greenland, 1972). PVA (a linear uncharged polymer) stabilises aggregates as a result of its adsorption on the inside pore surface of aggregates or its lining of the pore surface of aggregates (Emerson and Raupach, 1964; Kavanagh *et al.* 1978). Soil pore sizes can range from 1 µm to 50 µm, and polymers can have diameters from 1 to 10 nm when coiled, and have lengths from 100 to >1000 nm when stretched. So polymers can penetrate soil pores and can be adsorbed on internal surface of pores, on soil colloidal components inside pores, or on the quasi-crystal, domain, tactoids, or clay humus, or clay-humus-oxyhydroxide complexes (De Boodt, *et al.* 1990). According to Letey (1994) if polymers did not penetrate inside aggregates, the interaction between polymers and clay surfaces was not important in stabilising aggregates. In this case, polymers formed a network around the aggregates, and drying of these bonded polymers was irreversible and tightly adsorbed. Nadler and Letey (1989) found that the high adsorption of negatively charged polymers did not guarantee a higher stability of the soil aggregate. In the case of Na-soil, the addition of gypsum first, and then anionic poly-acrylamide increased the aggregate stability (Wallace *et al.* 1986b).

Not much information is available on the size of aggregates which have been stabilised by polymers. However, they are mainly macro aggregates as shown by several authors. Carr and Greenland (1975) amended soil with poly-vinyl alcohol (PVA) and found that it increased water stable >0.5 mm aggregates by up to 60%, while the PVA (100.000 MW) stabilised aggregates much better than PVA with (15.000 MW). Mukhopadhyay *et al.* (1994) reported that the application of 0.1% (w/w) polyacryllic acid type polymer increased the water stability of >2 mm aggregates by up to about 90%.

1.3. 2. The effect of polymers on tensile trsength

The stability of relatively dry soil will depend on the stability of its individual aggregates. Some researchers have measured the stability of soil structure or aggregates by subjecting individual aggregates or briquets of soil between two parallel plates to pressure, until the aggregate cracked; the critical pressure is recorded as soil tensile strength. This test is called the Brazilian test. Hence tensile strength is a measure of the strength of the failure zones (Braunack *et al.* 1979). Tensile strength or modulus of rupture is a standard method for measuring soil cohesion. There are several factors affecting tensile strength ie., clay content, water content, suction, wetting and drying, and cation content..

Mathers *et. al.* (1966) reported that increased clay content of soils led to a significant increase in unconfined compression strength over a range of water contents from about 10 % to about 0.1%. Similar phenomena were also observed by Kemper *et. al.* (1989). They measured tensile strength of the soil, which was called cohesion recovery from the remoulded state. These authors explained that clay produced more contact points between larger soil particles and formed bonds within the soil matrix, which is why the higher the clay content of the soil, the faster its cohesion recovery. Rogowsky *et. al.* (1968) investigated the strength of different soils, and showed that modulus of rupture increased in the order silty clay > loam > fine sand.

Water content affects tensile strength of soils as reported by Bohne and Lessing (1988); Mathers *et. al.* (1966); Dowdy and Larson (1971); and Kemper *et. al.* (1989). Kemper *et. al.* (1989) concluded that the first molecular layer of water adhered to soil surfaces through H-bonding to oxygen surfaces and by dipole ion bonding to the cation on exchange sites. When the soil contained a considerable amount of water, or was saturated, it would have a low tensile strength because the tension in the water phase was not strong enough to bring mineral surfaces close enough for ions or molecules to create bonds between them. Mathers *et. al.* (1966) found that maximum strength was gained when approximately one monolayer of water was on the total surface. The strength was a minimum at one half monolayer and increased again as complete dryness was reached. Bohne and Lessing (1988) stated that the stability of clay aggregates was a function of their water regime content and suction.

Dowdy and Larson (1971) measured the strength of montmorillonite saturated with different cations, and found that the strength of montmorillonite decreased in the following order Fe > K > Na > Al > Ca. Similar results were also reported by Mathers *et al.* (1966). They saturated a fine sandy loam soil with Na, Al and Ca, then the dry strength of soils were measured by unconfined compression strength. These authors explained that Na-saturation caused dispersion during the preparation of Na-soil, and this allowed reorientation of clay particles and produced greater contact between individual particles upon compaction. On the other hand Ca- or Al-saturated soils were not dispersed during preparation. Dowdy (1975) found that the strength of Fe-montmorillonite (366 kg cm^{-2}) was much higher than that of Na-montmorillonite (287 kg cm^{-2}). This might have been caused by saturated, hydrous iron oxide films being formed during preparation on the surface. These then acted as cementing agents between contact areas.

Organic matter tends to prevent direct contact or bonding between adjacent mineral surfaces since it decreases cohesion recovery (Kemper, *et al.* 1987) or modulus of rupture (Quirk and Panabokke, 1962). These authors stated that when organic polymers had been adsorbed and the aggregates were dried, the binding action of polymers was not restored if the samples were remoulded again even at the same bulk density.

Several authors (see later) found that sorption of polyvinyl alcohol with different molecular weights on clays and soils showed that tensile strength was directly related to the molecular weight of the PVA added. Williams *et al.* (1967) found that addition of increasing amounts of PVA of different molecular weights (25,000; 64,000; 70,000; and 100,000 Daltons) increased tensile strength of the B-horizon of Red brown earths, but the molecular weight of the PVA had no effect; that is, they were all equally as effective. Dowdy (1975) treated Na-montmorillonite with PVA (75,000 and 14,000 Daltons) and glucose and found that both PVAs increased the tensile strength of Na-clay significantly, but glucose did not affect the tensile strength. It may be that the polymers were adsorbed by external clay surfaces and this maximised the bridging action of each molecule. However, small molecules like glucose are too small to be able to form bridges between surfaces (Dowdy, 1975). Schamp *et. al.* (1975) applied poly-vinylacetate, synthetic rubbers (butadiene and isoprene) and natural rubber on pure sand at amounts of 0.25% and 0.5%. These authors reported that poly-vinylacetate significantly increased the dry strength of sand.

On the other hand synthetic rubbers and natural rubber did not affect its tensile strength at all.

Polymers also decrease the modulus of rupture of saline crusting soils. VAMA decreased the modulus of rupture of soils up to 3 times compared with untreated saline alkali soils (Allison, 1956). Similar results were also reported by Allison and Moore (1956), who applied two polymers (VAMA and HPAN) on crusting soils, and Oades (1976) found that PVA hindered crust formation.

It might be concluded that polymers increase the tensile strength of soil aggregates, however the strength decreases when soil is remoulded again. The greater the amount of polymer added the greater the increase in tensile strength. (The molecular weight of the polymer added, however, does not seem to affect the tensile strength of soils, at least those from the B-horizon of the Urrbrae Red-brown earth.) Polymers also decrease the tensile strength of saline crusting soils, and this is known to improve the emergence of seedlings.

1.3.3. The effects of polymers on water retention

The relationship between soil water content and soil water tension defines the soil moisture characteristic. The water retention of the soil basically depends on texture, structure, clay type, and organic matter (Klute, 1986). The water retained at low suction (between 0 and 1 bar) depends upon the pore size distribution, thus it is strongly affected by soil structure. The water content at higher suction is due to adsorption and hence is influenced by particle size distribution and the specific surface area of soils (Hillel, 1980).

De Boodt (1993) postulated that macroaggregates can contain macropores (from 30 to >50 µm) especially if macroaggregates consist of microaggregates. Thus polymers which have diameters from 0.1 to >1 µm can line the soil pores and adhere to the soil matrix on the pore wall, ie. a colloidal component within the pores, clay domains, or clay-humus. Beside lining the pores, polymers also cover soil aggregates (Greenland, 1963). Filling the pores or covering the soil aggregates by polymers could either decrease or increase soil water content at different water potentials, depending on polymer properties.

Kijne (1967) applied PVA and krilium to a Red brown earth (Urrbrae), and reported that PVA stabilised soil pores and thus water infiltrated more in PVA-treated soil than untreated and krilium treated soil. Mukhopadhyay *et. al.* (1994) stated that a soil conditioner from acrylic waste generally decreased soil water content at 0.3 bar and 15 bar suction on loamy sand and silty clay loam soils. Similar results were also reported by Pla (1975). Pla (1975) amended soils (Alfisol and Vertisol) with bitumen and PAM, and found that both polymers decreased the water content up to 11 % at 0.1 bar and 0.5 bar suction respectively. Bitumen decreased moisture content to a greater extend than PAM at similar water retention. However, both polymers decreased the bulk density and increased the hydraulic conductivity of the soils. This was caused by the creation of large aggregates which, in turn, formed air-filled macropores.

1.3.4 The effects of polymers on run-off, infiltration and erosion

Soil conditioning gives the needed physical properties to allow plant growth, decrease erosion, and conserve water (DeBoodt, 1975). In agriculture, polymers are applied mainly before plant growth, in order to decrease erosion for the first few months, where the vegetation can take over the erosion-controlling function. In this case, the applied polymer has to be readily effective. This will depend on the properties of the polymers, soil, climate and crops (Schamp, *et al.* 1975).

The properties of polymers, such as solubility, molecular weight, and charge, and also soil properties (especially texture) play an important role in reactions with the polymers, thereby determining runoff and erosion (Gabriels and DeBoodt, 1978). Several authors have shown that polymers have an affinity to stabilise all type of soils from clays to sands, and also all types of clay in the soil.

Results have shown that polyacrylamide (hydrophilic) on pure sand was readily washed out by a small amount of water. The addition of a cross-linker to PAM, linked the polymer chains together so that PAM acted as a coat of paint on the sand particles and stabilised them (Gabriels and DeBoodt, 1978).

PAM also can be applied to soils in arid or humid areas depending on the purpose as reported by De Boodt (1975). PAM was used on a calcareous infertile soil in France, where rainfall was very low, and the result was successful in a revegetation program. In Lembang, Indonesia, where rainfall is very high (between 3000-6000 mm), PAM was used to minimise erosion, because it created a hydrophilic soil; hence more water infiltrated into the soil and runoff was reduced .

A hydrophobic bitumen was also applied in tropical areas such as Malaysia and Indonesia (De Boodt, 1975). In the Puchong area (Malaysia), bitumen reduced run-off and erosion significantly, and In Djongol, Indonesia, successfully decreased erosion even though it increased runoff. However bitumen-treated soil led to a higher runoff than untreated soil.

Mousbach and Shrader (1975) applied PVA and PAM to a subsoil clay at a rate of 336 kg ha^{-1} each, and the results showed that these treatments minimised soil detachment and clod breakdown and therefore controlled sheet erosion.

Gabriels and DeBoodt (1975) reported that the application of polyvinyl acetate did not decrease splash erosion and runoff, but it did minimise soil loss.

These authors also found out that small quantities of bitumen emulsion (0.35 litres m^{-2}) highly diluted with water enabled the bitumen micelles to migrate and penetrate deeper into the sand, binding sand particles after drying. However, due to the hydrophobic nature of the treated sand, the treatment decreased infiltration and increased runoff.

PAM decreased runoff significantly up to 20% compared with a control on kaolinite or illitic soils (Stern *et al.* 1991). These authors observed visually that the PAM-treated surface soils were rough and aggregated in comparison with untreated surfaces, which were smooth and had no stable aggregates. PAM greatly minimised runoff, possibly due to the coating effect of the polymer, which hindered slaking and the dispersion of aggregates. Levin *et. al.* (1991) applied PAM (20 kg ha^{-1}) mixed with phosphogypsum (PG) at 5 Mg ha^{-1} and found that infiltration increased 3 times compared with a control on clay or sandy soils.

PAM maintained a high infiltration rate throughout rainfall intensities up to 80 mm on vertisol and loess soils. PAM with molecular weights of (10-15 x 10^6 Dalton) plus electrolyte (0.05N of NaCl-CaCl solution) gave the highest value of hydraulic conductivity (Shainberg *et al.* 1992).

Based on the above findings, it may be concluded that water soluble polymers minimised erosion by increasing water infiltration, and reducing run-off; on the other hand, hydrophobic polymers decreased erosion by stabilising soil aggregates physically against overland flow and rain drop energy. However, bitumen might increase or decrease run-off, depending on soil type. Thus the type of the polymer to be applied will depend on the purpose of the application.

1.4 The effects of polymers on plant growth

1.4.1 Positive effects

The purpose of using soil conditioners is to improve soil physical properties, to minimise erosion, and to store water. Soil conditioners are useful for erosion control in the stabilization of highways and stream banks. In agriculture, the aim of their use is to improve plant growth or to maintain high yield (De Boodt, 1975).

Addition of VAMA and HPAN on saline loam soils increased water stability of aggregates of > 0.1 mm, increased infiltration by up to 6 times, and decreased surface crusting at all levels of exchangeable sodium, and resulted in an increased sweet corn yield during 4 years of cropping (Allison, 1956). Wallace *et. al.* (1986b) applied anionic polyacrylamide on a sodic soil of pH 9.9 and showed improvements in seedling emergence and plant growth, even without the addition of gypsum, which was usually added to this soil. They explained these results by the creation of better aeration and increased water infiltration.

Rubio *et. al.* (1989) applied PAM in a seedbed preparation on a calcareous fine silty soil. These authors reported that PAM did not increase the total emergence of grasses. However oats emerged more rapidly in PAM-treated soil than in the control. Deep and large cracks were formed in the untreated pots and in those with the low applications of PAM, but not in soils with applications of PAM greater than 20 kg ha^{-1}.

In calcareous soil, Fe-deficiency is usually a problem, as a result of an excess of water and carbon dioxide (from microbial and root activities) forming bicarbonate with lime (Wallace and Abouzamzam, 1984). The application of

PAM decreased lime-induced chlorosis on soyabean plants (Glycine max, Menill) by improving aeration and available water (Wallace *et al.* 1986c).

De Boodt (1975) reported that in Belgium, France and Germany, the application of 0.2% of PAM on fertile silty loess soil had reduced erosion, and in turn promoted better sugar beet germination and increased sugar beet yield by from 8 up to about 10%.

Carr and Greenland (1975) found that the application of polyvinyl acetate had successfully increased emergence of rye grass by up to about 40%, and increased dry weight of shoots by up to 50%. These authors also reported significantly increased dry weight of tops and roots of tomatoes and barley compared with a control.

The effect of polymers on root growth was examined by Danneels *et. al.* (1992). These authors used a swollen hydrogel (potassium propenoate propenamide copolymer), and reported that Pisum roots grew more intensively in the hydrogel than in a bone glue (organic polymer); hydrogel has a good effect on root growth.

As reported by some authors (below), natural rubber as a soil conditioner generally shows a positive effect on seedling emergence and plant growth. Formation of natural rubber mixed with 2% aromatic oil, with emulsifier and stabilizer, had minimised erosion and increased cover crop growth over a period of 1 month with 210 mm rainfall in Malaysia. Soong and Yeoh (1975) also used this formulation, incorporating it into 15 cm depth of sandy soils. Their results showed that it increased maize yield by up to about 40% and soyabean yield by up to about 90%. However, Wah and Bachik (1985) found that natural rubber mixed with aromatic oil could result in poor grass germination possibly due to phytoxicity of the mineral oil. These authors added potassium hydroxide to the natural rubber emulsion, and increased the germination rate by up to about 35%.

It seems that a hydrophobic polymer, such as rubber, is useful for application in areas of intense rainfall. However, this type of polymer also had an advantage when applied in arid areas as discussed by De Boodt (below).

When hydrophobic soil conditioners were applied on the soil surface, they prevented evaporation and in turn hindered salinization and crusting on the soil top layer, which usually retard plant growth (De Boodt, 1993). Furthermore, De Boodt (1993) suggested supplying water for plant growth after the hydrophobic emulsion had been incorporated in to the soil surface.

On the other hand, hydrophilic soil conditioners, which can adsorb a lot of water, could prevent deep percolation or lateral flow movement, and also hold water against gravity when they were applied to soil. Nevertheless, the water held was still available for plant growth, as discussed by De Boodt (1993).

1.4.2 Negative effects

In the 1950's there were about 100 patented polymer soil conditioners (De Boodt, 1993). However, the phytotoxicity of these chemical materials were not investigated, as it was thought that soil conditioners were just like adhesive materials or glues. Since then the amount of soil conditioner used has declined. Nowadays, the polymers used have to be environmentally safe, nontoxic, and preferably even biodegradable. As chemicals, they can affect plant growth. However, little information is available about the negative effects of popular polymers used e.g. polyacrylamide and polyvinyl alcohol.

Sojka and Lentz, 1994 reported that polyacrylamide is toxic to plants. Its toxicity might be caused by the presence of some monomers in the polymer. In the USA, polyacrylamide is considered safe if it contains less than 0.05% monomer. Furthermore, Sojka and Lentz (1994) explained that the monomer can degrade rapidly in warm (30^{oC}) conditions in a few days. PAM also may not be decomposed and broken down into the monomer, because microorganisms feed on amide functional groups as nitrogen sources which in turn hinders the formation of acrylamide. The negative effects of using >1% PAM has been reported by Wallace *et. al.* (1986c). They found that the application of high concentrations (1-5% of dry weight of soil) had reduced phosphorus and silica contents in wheat and tomatoes, and the transport of manganese and boron in wheat.

The effect of polymers was also monitored by Danneels *et. al.* (1992). They used an organic soil conditioner which was called "bone glue", and found that the roots avoided growing in the layer or spot where bone glue was present. Unfortunately, they did not provide any explanation of why this occurred, or of the chemistry of bone glue.

It might be concluded that applicationof 0.2% polymer (PAM) reduced erosion and increased plant growth. On the other hand, polymers will not have any negative effect on plant growth,, if they contain <0.005% of their monomer.

1.5 The decomposition of organic polymers

When organic materials are added to soils, they will be utilised by organisms as energy sources if the situation is favourable. There are many factors affecting the decomposition of organic matter in the soil, ie the environment, the soil, and the composition of organic matter itself. Environment and soil factors affecting the decay of organic matter are temperature, moisture and/or aeration, soil texture, and soil pH (Jenkinson, 1977). The composition of plants also determines the process of decomposition (Collins *et al.* 1990; Oades , 1989).

Jenkinson (1977) had monitored the decomposition of organic matter at the Rothamsted Station for a long period of time, and he also collaborated with Ayanaba in 1990 in examining the decomposition of rye grass in tropical Africa (Nigeria). They found that the same type of organic matter decomposed 2 times faster in the tropical area than in the temperate area due to differences in temperature (Figure 7).

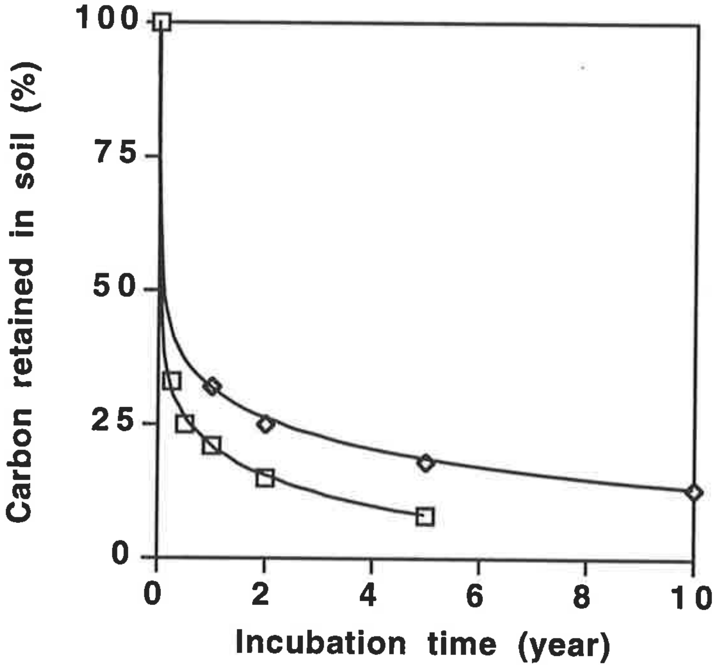


Figure 7. Decomposition of rye grass under temperate and tropical conditions: ◊ = temperate and □ = tropical (After Jenkinson, 1977, and Ayanaba and Jenkinson, 1990).

Drying organic matter at different temperatures before incubation also affected decomposition of humus (Joger and Bruins, 1975). These authors treated organic matter by drying at different temperatures , then moistening and incubating it at 29°C for 4 weeks. After about 60 cycles, the loss of organic matter as CO_2 was 31.2; 18.0; and 17.0% when the drying temperature was 85°C or 35°or not dried, respectively.

In the short term there was no difference in decomposition of organic matter between pH 4.9 and 8.1, but the extent of decomposition was different with a strongly acid soil (pH 3.7) (Jenkinson, 1977). Over the long term (5 years), however the effects of pH on the decomposition of organic matter were not significantly different even in the strongly acid soil.

Martin and Haider (1986) reported that under the same climate, soil texture determined C in the humus form and found that up to two to four times as much C was stabilised in the fine textured soil as in the sandy soil. A similar result was also reported by Jenkinson (1977); he found that a soil containing higher clay (17.5%) retained more labelled C than the soil with a lower clay content (7.6%) after a period of over 10 years.

Since plant materials are composed of different compounds (Oades, 1989), the decomposition of organic matter also depends on its composition. In general, lignin decomposes more slowly than carbohydrate (Herman *et al.* 1977), and Parr and Papendick (1978) also reported that the rates of decomposition are in the order: cold water soluble plant material > structural carbohydates > lignin. Because different parts of plants contain different organic subtrates ie soluble C, nonstructural carbohydrates, cellulose and hemicellulose, their decomposition depends on their content of the various materials (Collins *et.al.* 1990). These authors found that decomposition as well as the contents of soluble C plus nonstructural carbohydrate in plant parts decreased in the order: leaf > leaf sheath > chaff. However, if decomposition was based on the contents of cellulose and hemicellulose, the reverse order would be followed. Amato *et al.* (1983) also measured the decomposition of different parts of the Medic plant, and found that the rate of decomposition after 20 weeks was in the order: leaves > stems > roots > pods. However, ground pods were decomposed as easily as stems.

Martin and Haider (1986) specified in detail how the composition of organic matter affected the rate of decay. These authors explained that easily decomposed materials are small-molecular-weight substrates such as sugars, amino acids, and aliphatic acids. These materials decay in a few hours or days. Proteins and polysaccharides also rapidly decompose but at a slower rate. The next most easily decomposable components were phenols (including benzene rings), followed by phenolic polymers and then by microbial melanin. It seems that the larger or higher the molecular weight of an organic molecule, the longer it takes to be decomposed by organisms.

Since long chain synthetic organic polymers have high to very high molecular weights, decomposition of this type of material will take as much time as that of long chain polymers of organic material from plants. In the 1950's, hydrolyzed polyacrylonitrile was one of the popular polymers, however it is not used any longer due to its high cost. Decomposition of this polymer was monitored by Martin (1953), who mixed labelled HPAN with silty clay loam soil and incubated it at 27°C at field capacity water content. It was reported that, after 39 days of incubation, the carbon dioxide released was about 0.97% of the total amount of added soil conditioner; 13% of that amount was produced during the first 24 h. Among other popular polymers used quite recently are PVA and PVAc; these polymers could persist in the soil for some years (Carr and Greenland, 1975). A very high molecular weight poly-acrylamide is used nowadays in water irrigation. It seems that this polymer does not breakdown into monomers, because, with microorganisms using amide functional groups as nitrogen sources, this evidently hindered the formation of acrylamide (Sojka and Lentz, 1994). These authors also reported that some of the monomer in poly-acrylamide could decay rapidly in a few days in warm (30°C) temperature. Barvenik (1994) found that the decomposition rate of the monomer was even faster than this. This author reported that the half life of acrylamide (AMD) was from 18 to 45 h under aerobic conditions at 22°C.

It has been recognized that natural rubber (poly-isoprene) is oxidised by microbes. It is for this reason that many experiments have been carried out to produce long term antioxidants for rubber eg phenols, amines, organo sulfur and organo phophorus compounds (Khorasani, *et al.* 1993).

1.6 Objectives

Since latex water emulsion and poly-DADMAC have not yet been used for soil conditioners, as discussed in the literature review, this research aimed to investigate the use of these two polymers in bringing about improvements in soil physical properties and plant growth. There were 4 objectives of the experiments which were designed to determine whether these polymers could be used as a soil conditioner ie:

1. to assess the degree and mode of the stabilization produced by latex and poly-DADMAC; this included measurement of water stable aggregates under wet sieving, mechanically dispersible clay, tensile strength and friability, water retention, and soil hydrophobicity,
2. to examine the effect of these polymers on infiltration, run-off and erosion,
3. to identify their effects on plant growth, and
4. to monitor the decomposition of latex.

CHAPTER 2

The Comparison Of The Effects Of Latex And Poly-Dadmac On Water-Stable Aggregates

2.1. Introduction

Soil erosion is a serious problem in many tropical countries today. The Rubber Research Institute of Malaysia (R.R.I.M.) has been investigating the use of latex mixed with aromatic oil (petroleum products) and stabilisers as a soil conditioner to minimise erosion in field trials since the early 1970's. Soong (1979) reported that when a latex-aromatic oil mixture of <0.2% dry rubber content (D.R.C.) was applied to sand, it increased yields of maize by up to 90%, soya beans by up to 30%, and ground nuts by up to 42%, and also improved soil physical properties, i.e. it aggregated sand particles. This research involved field experiments only, however, and no basic scientific principles have yet been established. Neither has the application of latex without aromatic oil and stabiliser been investigated. The possibility of diluting natural, aqueous emulsions of latex and spraying it directly onto the soil would simplify procedures, reduce costs and promote its wider use as a soil conditioner.

The use of latex in the stabilisation of soil aggregates was compared with that of poly-diallyl dimethyl ammonium chloride (poly-DADMAC) another high molecular weight polymer having contrasting properties; poly-DADMAC has never been used as a soil conditioner to our knowledge.

Poly-DADMAC, as a long chain polymer, might be considered an effective soil conditioner, because the water stability of aggregates depends largely upon the molecular weight of water soluble polymer applied (Schamp, *et. al.* 1975).

This experiment was to investigate and assess the stabilisation produced by latex and poly-DADMAC polymers on a range of different soils, with particular reference to the basic mechanisms by which these two materials might stabilise soil.

2.2. Materials

2.2.1. Polymers

An emulsion of latex and dilute ammonia, containing approximately 60% dry rubber content (D.R.C), was donated by The Rubber Research Institute of Malaysia in Kuala Lumpur in 1992, and stored at 3^{o} C. Before application to the soil, the emulsion was diluted to about 1% D.R.C. (w/v) with de-ionised water, since at this concentration the emulsion did not block the nozzle of the sprayer. In order to minimize any effects on soil structure that might be caused by adding different amounts of water to the soils, the 1% stock solution was further diluted to appropriate concentrations so that equal volumes of water were utilised at all application rates to all soils.

A stock solution of poly-DADMAC containing about 40% active material (w/v) was obtained from the Allied Colloids Company in Melbourne, and this solution was also diluted to 1% (w/v) before spraying on the soils. The 1% stock solution was further diluted in a similar manner to the rubber emulsion.

2.2.2. Soils

These experiments were carried out using four soils from the 0 - 100 mm surface layer, including three Alfisols or Red brown earths, which are referred to as "Urrbrae", "Evans", and "Quiggley", and one Mollisol, referred to as "Wiesenboden". The Urrbrae soil is a structurally degraded red brown earth sampled from a wheat/fallow rotation plot from the Waite Long-term Rotation Trial, Waite Campus, University of Adelaide. The Evans and Quiggley soils were from locations on the Martindale Farm, University of Adelaide in the mid-North region of South Australia. The Mollisol is a self mulching, hydromorphic black earth sampled from a permanent pasture in the Waite Campus. Physical and chemical properties of the soils are shown in Table 2. All soils were dried at 40^{o} C for 3 days, then passed through a 9.5 mm sieve, before use in the experiments.

2.3. Methods

2.3.1. Measurement of water stable aggregates

Wet Aggregate Stability was measured for each soil based on the method of Kemper and Rosenau (1986). Soil samples (25 g each, 3 replicates) were sprayed with latex or poly-DADMAC at application rates of 0, 0.25. 0.50, 0.75, 1.0, 1.5, 2.0, 3.0, and 5.0 g polymer per kg soil. After drying for 3 days at 40^{o} C, the soil samples were placed on a nest of sieves (2.0, 0.5, 0.25, and 0.125 mm diameter apertures), and these sieves immersed in water inside a cylinder, then raised and lowered through an amplitude of 2 cm at a rate of 38 times per minute for 5 minutes. The material on each sieve was then collected, dried at 105^{o} C for 24 hr, and

Table 2. Selected physical and chemical properties of soils used, D = dominant clay mineral and p = clay mineral present (After Chittleborough and Oades, 1980 and Stace *et al.*, 1972).

Properties	Soils			
	Red-brown earths			Claremont
	Urrbrae	Quiggley	Evans	Wiesenboden
Particle size distribution (%)				
Clay	17	25	31	55
Silt	30	33	34	26
Sand	53	42	31	18
pH (H_2O)	6.1	6.2	6.3	6.8
EC (dSm^{-1})	0.115	0.104	0.125	0.168
C.E.C. (mmol kg^{-1})	79	190	220	570
Carbon (%)	1.06	1.72	1.61	3.3
Clay minerals:				
Illite	D	D	D	p
Kaolinite	p	p	p	p
Randomly interstratified minerals	p	p	p	D
Quartz	p	p	p	p

weighed. The amount of soil on each sieve was expressed as a proportion of the total sample weight. These data were then analysed in order to calculate any significant differences between treatments. The experimental design used was based on a factorial randomized complete block design.

2.3.2. Scanning electron microscopy of aggregates

Scanning electron microscopy (S.E.M.) was used for a qualitative assessment of the extent to which latex penetrates aggregates and how aggregate binding occurs. Samples were prepared as follows.

The soils described in Section 2.3.1 that remained on the 2 mm sieve were recovered after drying and weighing. Individual aggregates were then crushed between parallel rigid plates such that they cracked through their centres. All the crushed aggregates were then placed back on the 2 mm sieve, re-immersed in water, and agitated for an additional 30 minutes to separate material strongly stabilised by latex (>2 mm) from that not as strongly stabilised (<2 mm). The >2 mm fraction was collected, re-dried and samples prepared for examination (gold-coated) under a Cambridge Stereoscan X250 electron microscope. Control samples (not treated with latex) were included in this procedure for comparison.

2.4. Results and discussion

Both latex and poly-DADMAC polymers were found to increase the water stability of aggregates of all soils (Figures 8a and 8b), however the degree and mode of stabilization by the two polymers were different. The results will be discussed separately for each polymer.

2.4.1. Water stable aggregates of latex treated soils

Latex increased the proportion of water stable aggregates >2 mm of all soils (Figures 8a and 8b). The percentage of water stable aggregates >2 mm were increased in proportion to the amount of latex added up to about 2 g kg^{-1} soil, then the addition of >2 g kg^{-1} soil resulted in a plateau in the plot of water stable aggregates against amount of latex added. Based on the HSD Tuckey test ($P=0.05$), the optimum value (above which no significant increase occurred) was achieved at an application rate of 1.5 g kg^{-1} for Urrbrae and Evans soils, while 0.75 g kg^{-1} was required for the Quiggley soil and 0.5 g kg^{-1} for the Wiesenboden soil.

The ability of latex to create and stabilise aggregates >2 mm of all soils, may be caused by rubber as an uncharged polymer coating around aggregates already in close proximity to each other. It may attach to several particles or smaller aggregates binding them together. These effects are likely to be similar to those of another uncharged polymer (polyvinyl alcohol), as explained by Greenland (1963). Uncharged rubber adsorbed onto soil surfaces only through physical attraction ie H-bonding and van der Waals forces, and may attach to any material in the soils. The hydrophobic nature of rubber was also an important factor in explaining the increased water stability of aggregates, because rubber-rubber and rubber-soil surface interactions would not be broken by the action of water.

The differences in the optimum application rates for each soil may be caused by the initial stability of each soil, and the stability of a soil may depend on its organic matter content. The Wiesenboden had the highest content of organic matter (Table 2). In the case of the Wiesenboden, the water stable aggregation was almost 100% (see Figure 8b). This may be because the Wiesenboden was well aggregated when latex was sprayed on it which led to a good coating on the surfaces of aggregates.

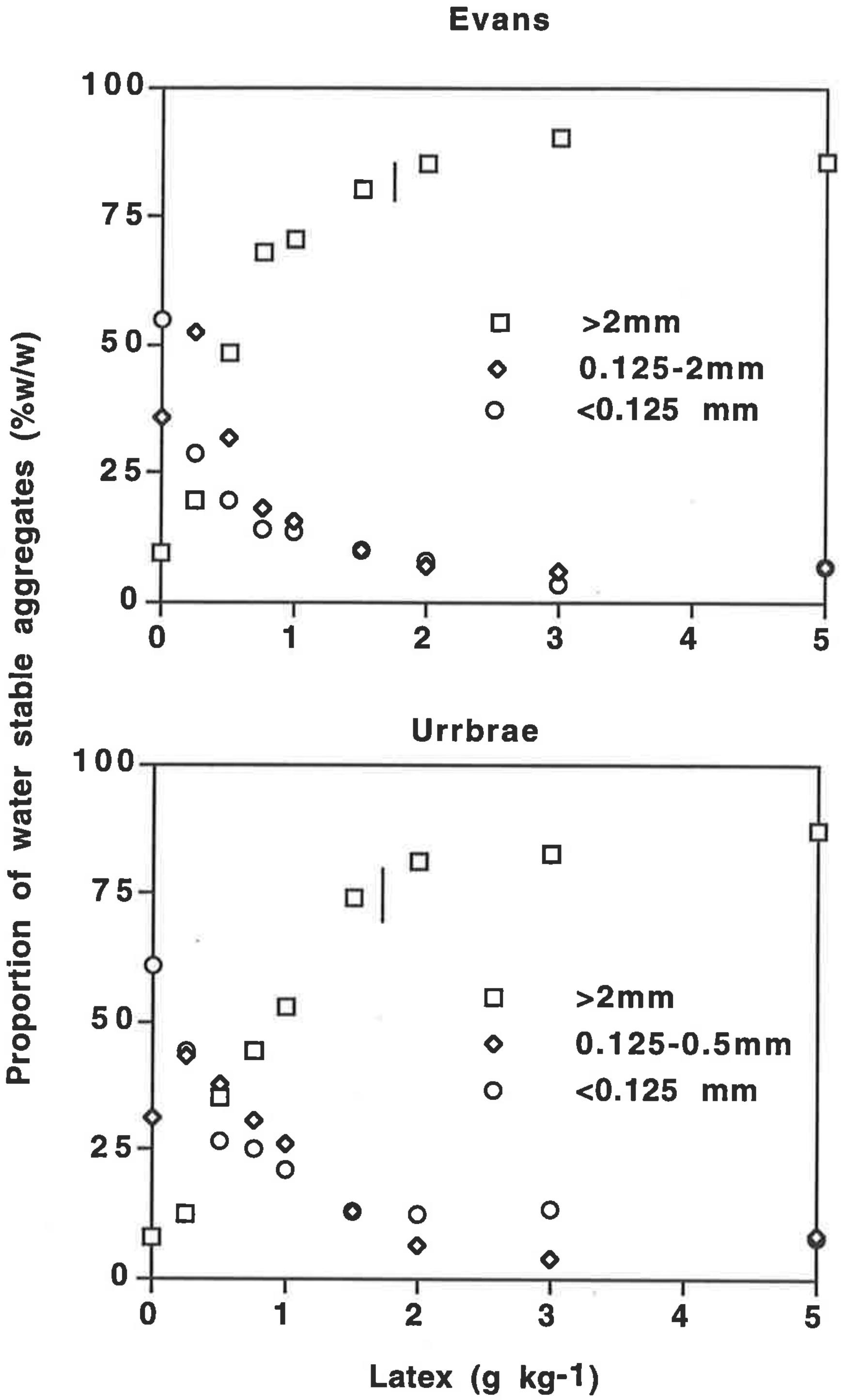


Figure 8a. The effects of latex on water stable aggregates of Urrbrae and Evans soils; Vertical bars represent levels of significant difference $(SD)_{0.05}$ = 11.36 for Urrbrae and 8.06 for Evans.

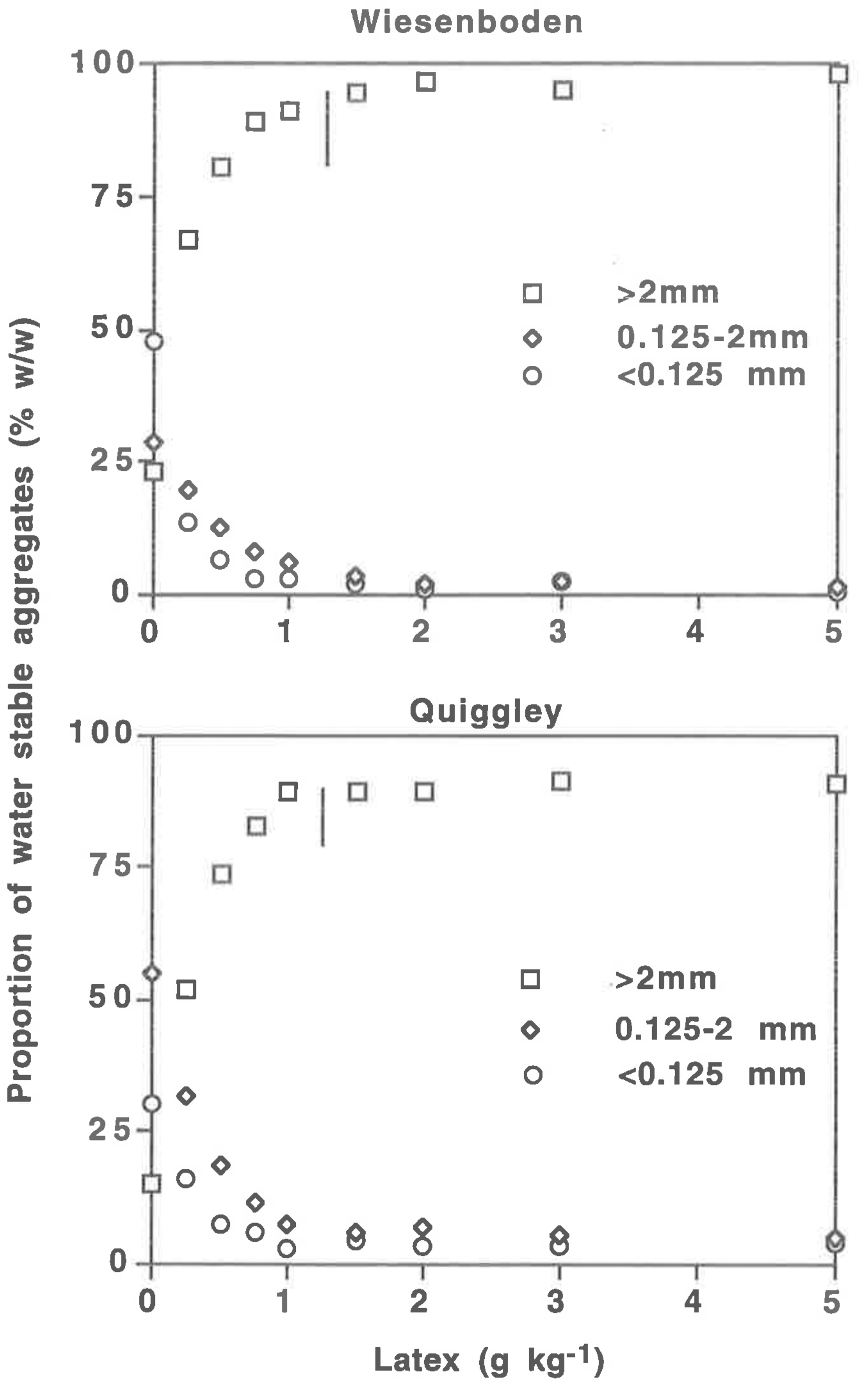


Figure 8b. The effects of latex on water stable aggregates of Quiggley and Wiesenboden soils; Vertical bars represent levels of significant difference $(SD)_{0.05}$ = 10.56 for Quiggley and 13.19 for Wiesenboden.

2.4.2. Water stable aggregates of poly-DADMAC treated soils

The application of poly-DADMAC generally increased the overall size of water stable aggregates, although the magnitude of this effect was small in comparison to that of the latex polymer, particularly with respect to larger aggregates (>2 mm). The main effect of poly-DADMAC was to moderately reduce the proportion of aggregates <0.125 mm in all four soils. Generally this reduction of fine aggregates has important implications for the prevention of crust formation and increased infiltration rates (Loch and Foley, 1994). The application of poly-DADMAC (1 g kg^{-1} of soil) decreased the proportion of aggregates <0.125 mm by about 30% in Urrbrae and Evans soils. A similar decrease (of 30%) in aggregates <0.125 mm required about twice this rate (2 g kg-1) in the Quiggley soil.

The magnitude of the effect on the fraction <0.125 mm would appear to relate to the properties of the poly-DADMAC polymer i.e. its positive charge, high molecular weight and hydrophilic nature. As a positively charged polymer, it may interact electrically with clay or soil surfaces, and this reaction is irreversible. Due to its high molecular weight, initial attachment leads to "loops and tails". Thus it flocculates and binds colloidal materials and creates aggregates >0.125 mm; this mechanism is typical of other positively charged polymers (Greenland, 1963). On the other hand, the hydrophilic nature of poly-DADMAC gives it a relatively low cohesive strength, which reduces its ability to surround and bind aggregates into larger units (e.g. >2 mm) to the same extent as is possible with latex.

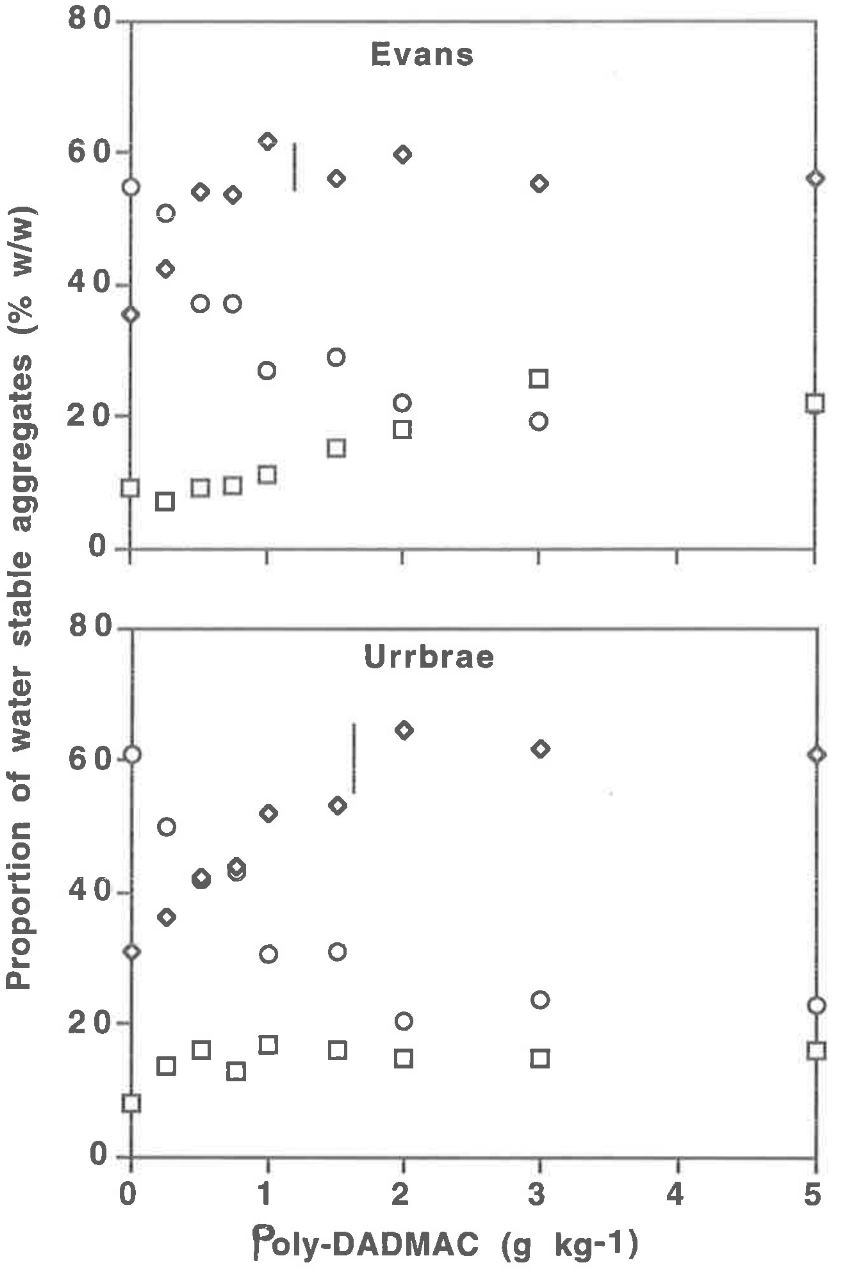


Figure 9a. The effects of poly-DADMAC on water stable aggregates of Urrbrae and Evans soils; Vertical bars represent levels of significant difference, $SD_{0.05}$ = 11.36 for Urrbrae and 8.06 for Evans). Aggregate sizes (□ = >2; ◊ = >0.125-2; o = <0.125) mm

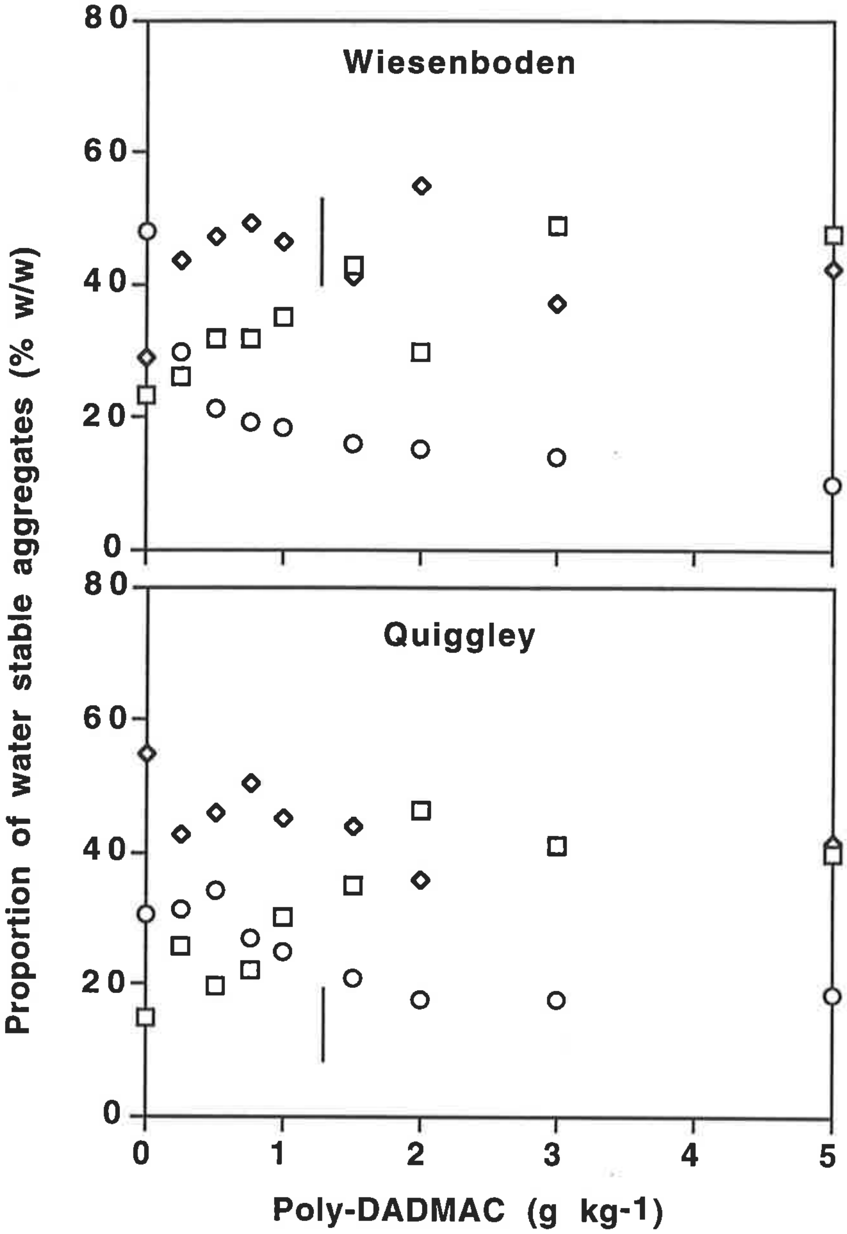


Figure 9b. The effects of poly-DADMAC on water stable aggregates of Quiggley and Wiesenboden soils; Vertical bars represent levels of significant difference, $SD_{0.05}$ = 10.56 for Quiggley and 13.19 for Wiesenboden). Aggregate sizes (☐ = >2; ◊ = >0.125-2; o = <0.125) mm

Nonetheless, as with the latex polymer, the effect of poly-DADMAC on water stable aggregation, however small, varied in accordance with the initial stability of the soils. The reduction in aggregates <0.125 mm for Urrbrae and Evans was accompanied by increases primarily in the intermediate aggregate size ranges (0.25 to 2 mm), while this size range was relatively unaffected in the Quiggley and Wiesenboden soils.

2.4.3. Scanning electron microscopy of water stable aggregates

Scanning electron micrographs (S.E.M.) of Urrbrae and Wiesenboden soils are presented in Figures 10a,10b and 10c. These showed that rubber acts as a binding or stabilising agent, it could be seen under SEM as shown by arrow on Figure 10c; and the evidence of its effects upon both soils also can be identified.

After 30 minutes repeated wet sieving, crushed latex treated soils showed more porous aggregates than natural aggregates (without latex treatment) for both soils. This could be caused by latex binding between particles of the soil matrices where this binding was not destroyed by water action during the wet sieving. Hence latex may have bound some of the soil materials inside aggregates; soil material which was not bound by latex was washed out, which left cavities between the latex-stabilised soil matrix. It seems that latex occurred between small soil particles or matrices, though the depth which latex penetrated inside the aggregate could not be identified from the figure. Latex could have stabilised aggregates as a "coat of paint" or else had penetrated inside aggregates and formed bonds between soil materials.

2.5. Conclusions

The experiments led to the following main conclusions:

Latex was able to increase aggregate stability without the use of the traditional aromatic oil and stabilisers, at application rates comparable to previously published values (ie. < 2 g polymer kg^{-1} soil).

Either latex penetrated inside the aggregates or else it acted primarily as an external "coat of paint" which was capable of binding small aggregates into larger aggregates >2 mm at relatively low application rates (ie. between 0.5 and 1.5 g kg-1), depending upon the initial structural stability of soils. Latex could be seen clearly under S.E.M. as a binding agent between soil particles.

Poly-DADMAC can decrease the amount of aggregates <0.125 mm and slightly increase the proportion of aggregates >0.125 mm.

Latex and poly-DADMAC might be used as soil conditioners, however further investigations ie their effects on tensile strength, water retention, dispersible clay, hydrophobicity, and soil erosion are needed, before they are recommended for this purpose.

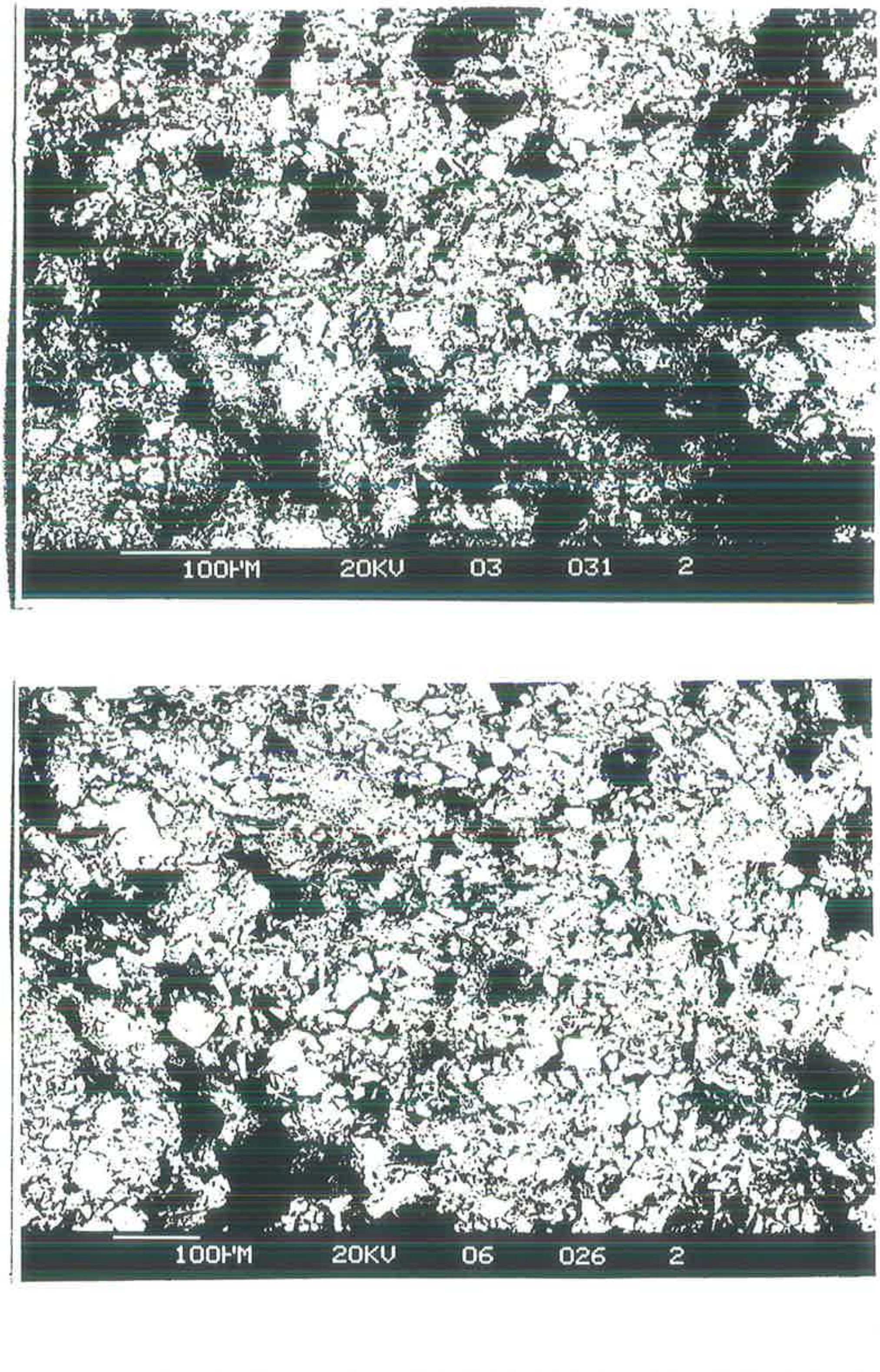


Figure 10a. Crushed-latex treated soil (above) and untreated (below) of Urrbrae soil under S.E.M.

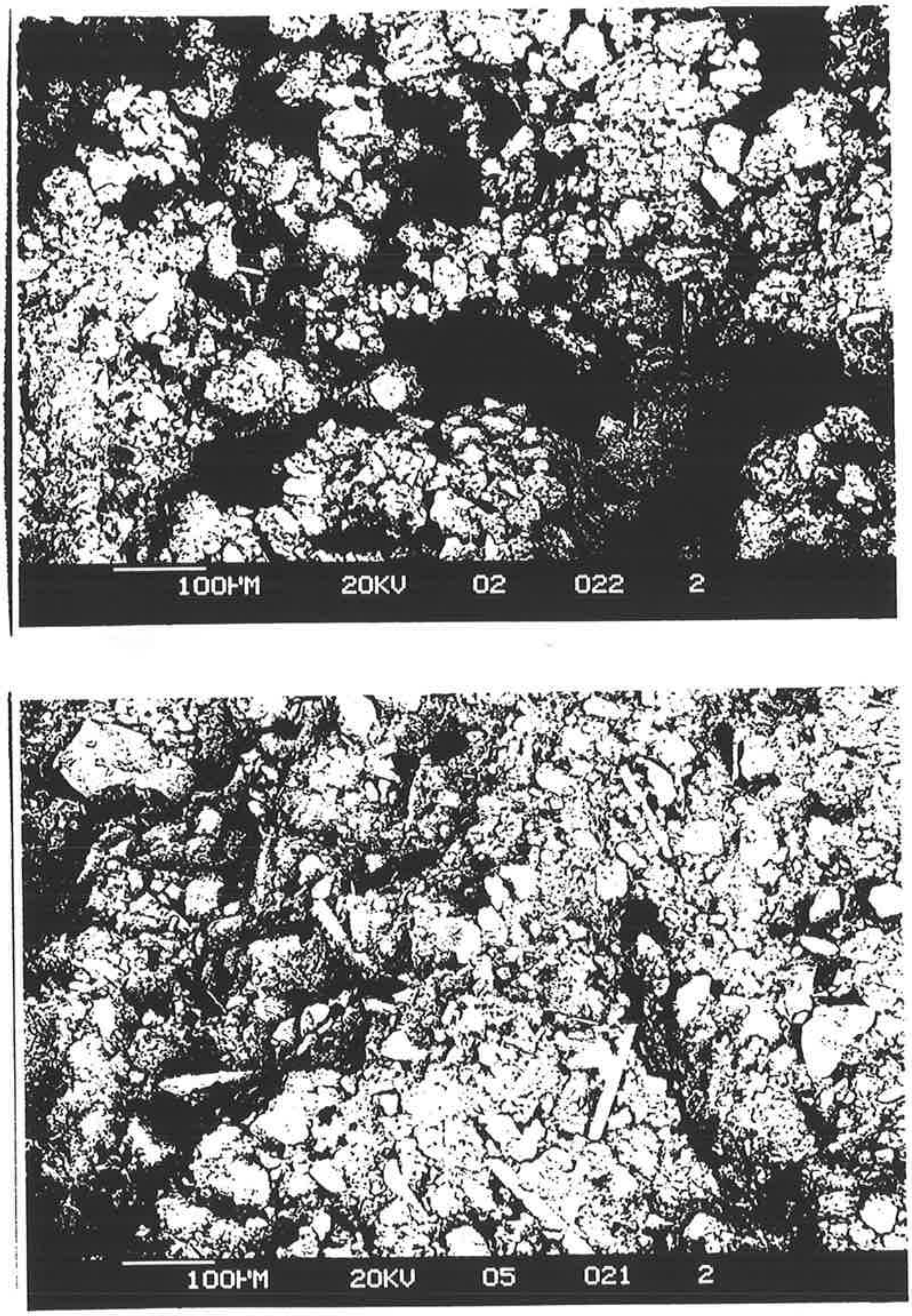


Figure 10b. Crushed-latex treated (above) and untreated (below) of Wiesenboden under S.E.M.

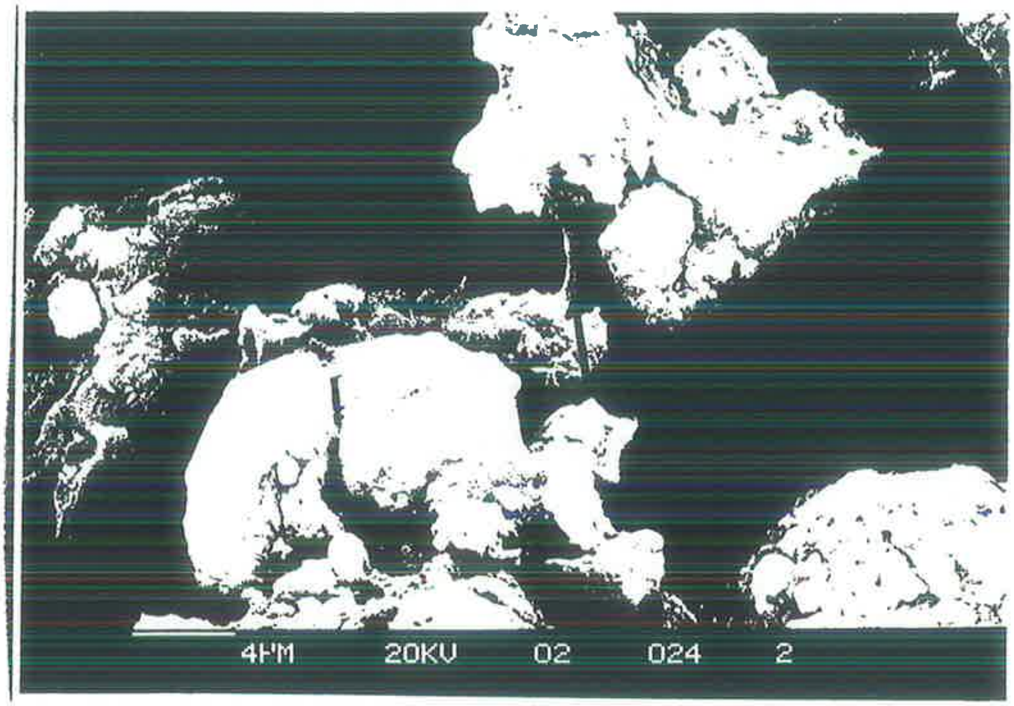


Figure 10c. Close-up of latex as a binding agent between soil particles under S.E.M.

CHAPTER 3

The Effect Of Latex And Poly-Dadmac On Tensile Strength And Friability

3.1. Introduction

Latex and poly-DADMAC as water emulsions have been shown to increase the proportion of water stable aggregates (in Chapter 2). Latex stabilised aggregates >2 mm and poly-DADMAC increased the proportion of water stable aggregates >0.125 mm in the Urrbrae and Wiesenboden soils.

When polymers are applied to the soils, they may also affect soil adhesion, because polymers can act as bonding agents between mineral surfaces, especially when the polymer-treated soil is dried (Kemper, 1987 and Quirk and Panabokke, 1962).

High application rates of polymers such as polyvinyl alcohol have been shown to increase the tensile strength of soils and clays (Williams *et. al.*, 1967 and Dowdy, 1975). However low application rates of butadiene and isoprene did not affect the tensile strength of sand (Schamp *et. al.*, 1975).

Latex (uncharged) and poly-DADMAC (positively charged) may affect soil adhesion or tensile strength differently, and soil type may also play an important role in tensile strength.

This experiment was designed to find out how latex and poly-DADMAC,when applied at typical application rates of not more than 2 g kg^{-1} (Soong 1979; Carr and Greenland 1975) affected soil tensile strength and friability·

3.2. Materials and methods

3.2.1. Soils This experiment was conducted using two soils: an Alfisol (Urrbrae) and a Mollisol (Wiesenboden). Soil samples were taken from the 0 - 100 mm surface layer. The properties of the soils were presented in Chapter 2.

3.2.2. Preparation of latex and poly-DADMAC

Each polymer was diluted into 1%w/v bulk solutions before spraying onto the soils. The properties of the polymer have been discussed in Chapters 1 and 2.

3.2.3. Soil tensile strength and friability

Soil samples (about 20 kg) for each treatment were dried in the oven at 40^{o} C for 3 days. Then latex and/or poly-DADMAC was sprayed at application rates of 1 and 2 g per kg soil, and dried again as above. Every treated soil was sieved for 1 min on an Endicott shaker in order to isolate nine different aggregates size classes: (>19, 19 to 12.7, 12.7 to 9.5, 9.5 to 6.7, 6.7 to 5.6, 5.6 to 5.0, 5.0 to 4.0, 4.0 to 3.4, and 3.4 to 2.0) mm.

Tensile strength was determined on each size class by an indirect tension (crushing) (Brazilian) test described by Dexter and Kroesbergen (1985). Each aggregate was crushed by a vertical force applied between two flat horizontal plates on a loading frame (Figure 11).

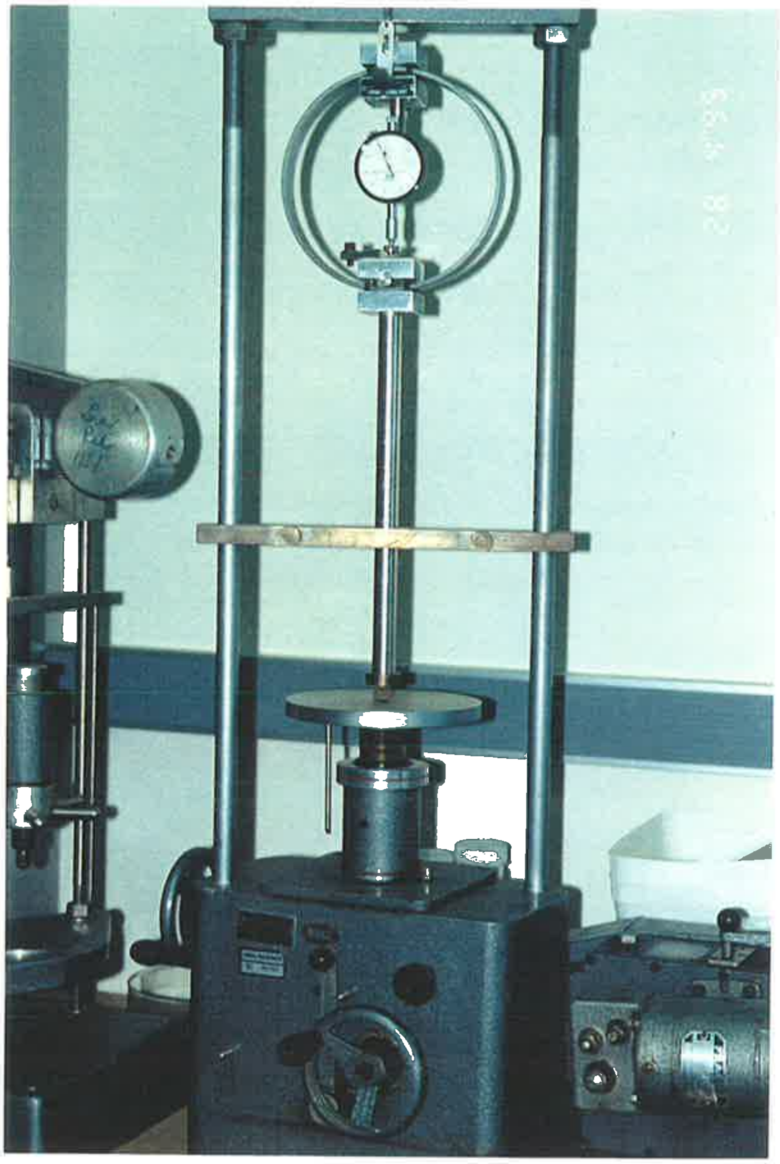


Figure 11. Loading frame for measuring tensile strength of aggregates.

Tensile strength (Y, kPa), was calculated for each aggregate using the equation

$$Y = 0.576\ F/d^2$$

where F is the force (N) required to fracture the aggregate and d is the effective spherical diameter (m) of each aggregate, calculated as

$$d = \underline{d}\ (M_o/M_a)^{0.33}$$

where $\underline{d}$ is the mean diameter of aggregates (average of its shortest, intermediate and longest diameters, m); M_o is the mass (kg) of individual aggregate; and M_a is the mean mass (kg) of the twenty five aggregates used as replicates.

The soil friability constant, k, was calculated according to the analysis presented by Utomo and Dexter (1981), and represents the slope of the linear regression of the log-transformed values of aggregate tensile strength, s (kPa), against aggregate volume, V (m^3):

$$\log_{10} s = A + k \log_{10} V.$$

The regression intercept, A, represents the extrapolated tensile strength of 1 m^3 samples of the bulk soil (Utomo and Dexter, 1981).

3.3 Results and discussion

Effects of soil friability appeared to depend primarily upon soil type and to a lesser extent upon the type of polymer applied and its application rate. Firstly, the tensile strength of all aggregates of the Wiesenboden was greater than that of the Urrbrae soil, and this was largely due to its higher clay content and more reactive clay fraction. For the Wiesenboden, latex had no effect on the tensile strength of the soil aggregates across the entire range of sizes from 2 mm up to 50 mm diameter, and therefore had no significant effect on the friability constant, k, regardless of application rate (bottom, Figure 11a, Table 3).

As shown by the relatively large k values and small A values for the Wiesenboden in Table 3, this soil was already 'very friable' to 'mechanically unstable' according to the classification proposed by Utomo and Dexter (1981). Poly-DADMAC, on the other hand, appeared to reduce the friability constant slightly in this soil, particularly at the higher application of 2 g kg^{-1}) (Table 3). The fact that the overall elevations (average tensile strengths) shown for the Wiesenboden in Table 3 did not change substantially due to poly-DADMAC (ranging from 2.26 to 2.31, which corresponds to tensile strengths of between 182 and 204 kPa) indicates that the polymer acted by reducing the strengths of the smaller aggregates and increasing the strengths of the larger ones (Figure 11b). Nonetheless, the Wiesenboden remained in the 'friable' to 'very friable range, and so the physical significance of this result is not entirely clear at this stage.

The Urrbrae soil by contrast, had a 'non friable' control (k = 0.0493±0.0395 in Table 3) and a slightly greater extrapolated tensile strength (i.e. for 1 m^3 aggregates) than all the other soils shown in Table 3 (A = 1.27, representing 18.6 kPa), despite the lower clay content of this soil. The overall low tensile strength measured for the Urrbrae soil (smaller elevations in Table 3) compared with that of the Wiesenboden, rendered this soil sensitive to the effects of the polymers, particularly to those of poly-DADMAC, even at the low application rates used here.

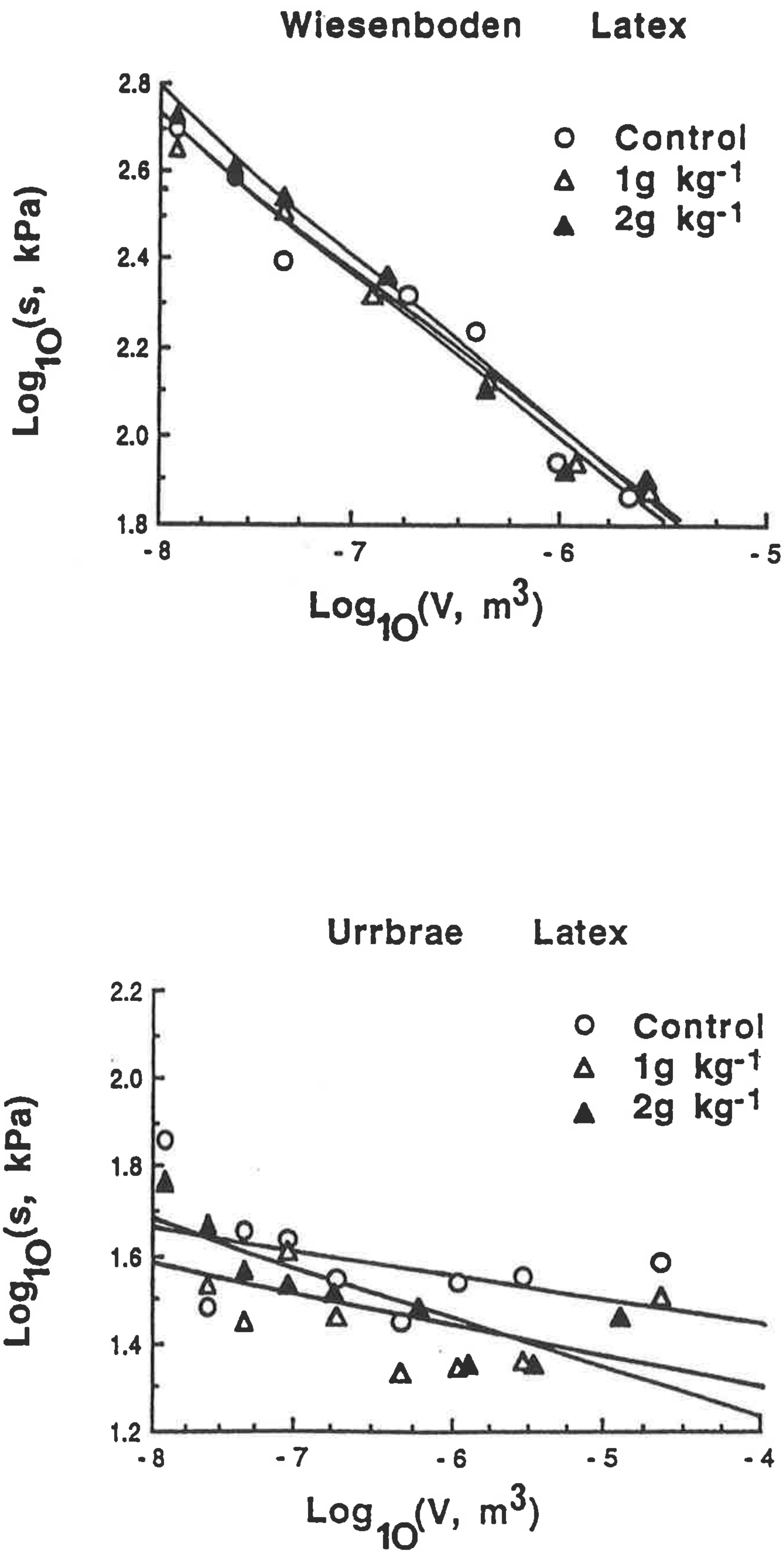


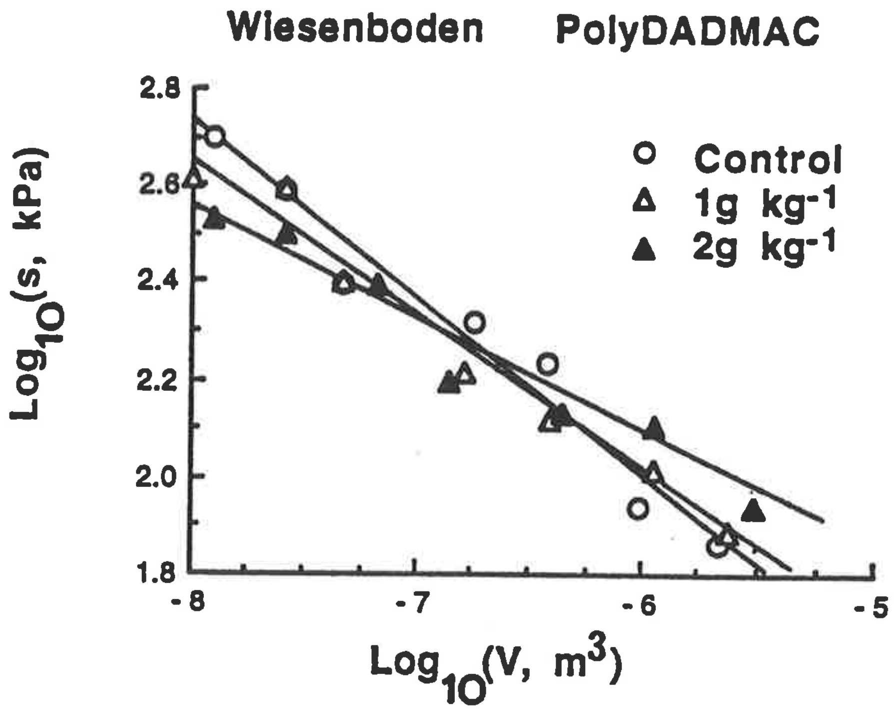
Figure 11a. Tensile strength of aggregates (s, kPa) as a function of aggregate volume (V, m^3) for Wiesenboden and Urrbrae soils treated with Latex at 1 and 2 g kg^{-1} (○ control; △ 1 g kg^{-1}; ▲ 2 g kg^{-1}).

Table 3. Friability constants, k (slope) and A (intercept), plus Elevations and Percentages of Variation, for the Wiesenboden and Urrbrae soils treated with two polymers and applications rates

Polymer	k±s.e.	95% conf. int. for k^{A}	A±s.e.	Elevations ±s.e.	%Var.^{B}
		Wiesenboden soil			
Control	0·365±0·032	(−0·427, −0·303)	−0·1921±0·22	2·291±0·020	95·6
Latex					
1 g kg^{-1}	0·3611±0·016	(−0·392, −0·330)	−0·1581±0·11	2·291±0·011	98·9
2 g kg^{-1}	0·3891±0·024	(−0·437, −0·341)	−0·3261±0·17	2·311±0·0022	97·7
Poly(DADMAC)					
1 g kg^{-1}	0·3181±0·022	(−0·362, −0·279)	0·1031±0·15	2·271±0·021	97·1
2 g kg^{-1}	0·2481±0·023	(−0·294, −0·202)	0·5821±0·16	2·261±0·022	94·9
		Urrbrae soil			
Control	0·04931±0·040	(−0·127, 0·0281)	1·271±0·26	1·591±0·039	6·6
Latex					
1 g kg^{-1}	0·07471±0·042	(−0·156, 0·00703)	0·9971±0·28	1·491±0·041	21·6
2 g kg^{-1}	0·1121±0·027	(−0·164, −0·0600)	0·7871±0·18	1·521±0·031	67·5
Poly(DADMAC)					
1 g kg^{-1}	0·09641±0·016	(−0·127, −0·0654)	1·201±0·10	1·801±0·020	81·9
2 g kg^{-1}	0·1281±0·052	(−0·231, −0·0253)	0·8541±0·34	1·681±0·049	38·1

[A] 95% confidence interval for slope (= k±1·96 s.e.).

[B] Percentage of variation accounted for by the linear regression model.



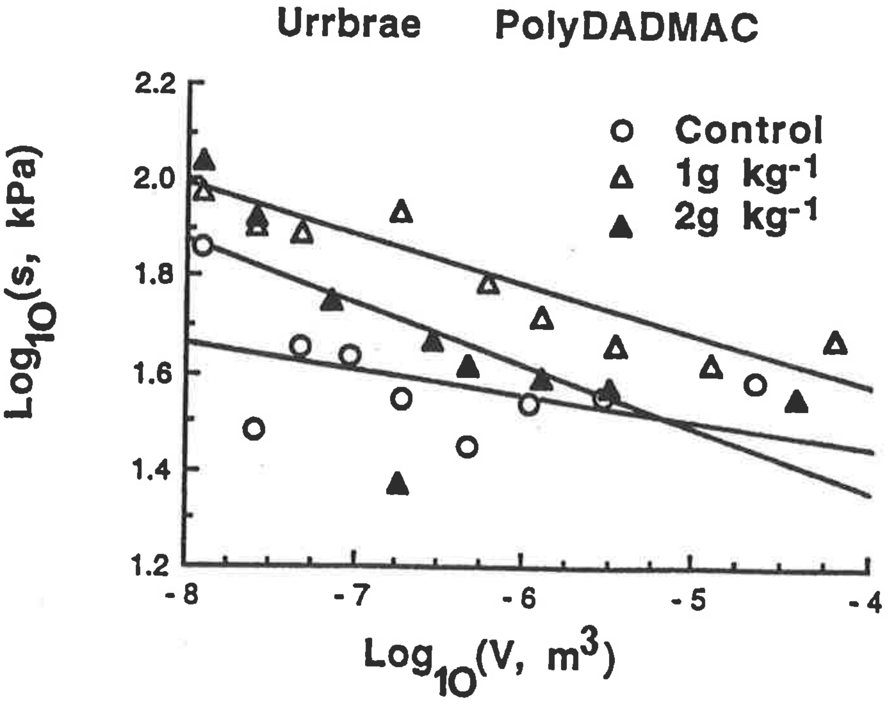


Figure 11b. Tensile strength of aggregates (s, kPa) as a function of aggregate volume (V, m^3) for Wiesenboden and Urrbrae soils treated with PolyDADMAC at 1 and 2 g kg^{-1} (○ control; △ 1 g kg^{-1}; ▲ 2 g kg^{-1}).

3.4 Conclusions

With increasing application rate, poly-DADMAC increased the friability of the Urrbrae soil to a greater extent than did latex, and this was probably because it could penetrate inside aggregates and thus create greater adhesion between soil particles upon drying. As the greater elevations in Table 3 show for poly-DADMAC, it also increased the tensile strength of virtually all aggregate sizes cmpared with latex (Figure 11b). While both polymers increased k into the 'slightly friable' and 'friable' ranges, with moderate reductions in A, the effects due to poly-DADMAC appeared to be greater than those for latex.

It is doubtful whether higher application rates of latex than those for the experiments on either of the two soils used here would cause any signficiant increase in their friabilities. Furthermore, the associated problems of adding too much latex (e.g. surface sealing and reduced infiltration) would diminish the practical utility of applying this natural polymer.

CHAPTER 4

The Effects Of Latex And Poly-Dadmac On The Dispersion Of Clay Or Soils, Water Retention And Hydrophobicity

4.1. Introduction

Latex (natural polymer) significantly increased the proportion of water stable aggregates >2 mm and poly-DADMAC (synthetic polymer) increased the proportion of those >0.125 mm as shown in Chapter 2.

Latex as a neutral and hydrophobic polymer bound smaller aggregates into larger aggregates through Van der Waals forces, and this bonding was not destroyed by the action of water during wet sieving.

The flocculation of clays by polymers depends on clay type, C.E.C., pH, electrolyte concentration, saturating cation, and the molecular weight and type of polymer, as discussed in Chapter 1.

The aims of this experiment were:

a) to investigate the effects of latex and poly-DADMAC on the mechanically dispersible clay of two soils, i.e. a Red-brown earth (Urrbrae) and a Wiesenboden (Claremont),

b) to investigate how these two polymers affect soil water contents at different water suctions, and

c) to examine the development of hydrophobicity of the Red-brown earth and Wiesenboden soils after additionof these two polymers.

4.2. Materials

4.2.1. Soils

Samples were taken from the 0-100 mm surface layer of the Red-brown earth and Wiesenboden. The preparation of soil and soil properties are presented in Chapter 2 and Table 2 respectively.

4.2.2. Polymers

Preparation of polymers before application to the soil is discussed in Chapter 2.

4.3. Methods

4.3.1. Mechanically dispersible clay

Air dry soil samples were sprayed with either latex or poly-DADMAC at application rates of 1 and 2 g kg^{-1}, then dried again at 40^{o} C for 3 days and sieved using an Endicott Shaker in order to isolate different aggregate size classes : (12.7 - 19.05; 9.5 - 12.7; 6.7 - 9.5; 5.0 - 6.7; 4.0 - 5.0; 3.0 - 4.0; and 2.0 - 3.0) mm.

Mechanically dispersible clay was determined following a method of Rengasamy *et. al.* (1984). Sub-samples (10g, 3 replicates) from each aggregate size group were placed in 150 cm^3 bottles containing 50 cm^3 deionised water, and then mixed on an end-over-end shaker for one hour. The suspension was transferred to 150 cm^3 beakers. After an appropriate sedimentation time, an aliquot was taken for measurement of clay content using a Hach Ratio Turbidimeter which had been calibrated for each soil .

4.3.2. Soil water retention

Air dried soil samples of <2 mm were sprayed with 1.5 g kg-1 latex or poly-DADMAC and then dried in the oven at 35° C for 3 days. The treated samples were put into a cylndrical column about 30 mm high and 30 mm diameter, saturated and equilibrated at the following soil water potentials (-0.003; -0.002; -0.01; -0.03; -0.1; -0.3; -1;-10; and -15 bar). The measurements of water potentials >-0.1 bar were made using sintered funnels and for <-0.3 bar were made using pressure plates. The soils were equilibrated for 1 week for the higher potentialsand 2 weeks for lower potentials in order to approach equilibrium (Klute, 1986).

4.3.3. M.E.D. test

Because latex is a hydrophobic organic material it was necessary to check its effect on the wettability of soils. This test following King (1981) measures the wettability of the soil in terms of the molarity of ethanol droplets which just penetrate the soil surface in 10 seconds (M.E.D.). It gives a measure of hydrophobicity. Air dried soils were sieved through a 1 mm aperture, then latex was added at application rates of 0; 0.5; 1.0; 1.5; and 2.0 g kg-1 soil; treated soils were dried again in the oven at 40° C for 24 hr. The M.E.D. values of the soils were then determined at a constant temperature (20° C).

4.4. Results and discussion

4.4.1. Mechanically dispersible clay

Latex and poly-DADMAC both significantly reduced the amount of mechanically dispersible clay in the Red brown earth and Wiesenboden (Figure 12b) compared with the untreated controls (Figure 12a). However there was no significant difference between the application of 1 and 2 g of polymer per kg soil (Figure 12b).

There were no significant differences between the amounts of mechanically dispersible clay from aggregates of different sizes treated with latex or poly-DADMAC (Figure 12a). These results contradict those of Kay and Dexter (1990). The reason may be that these authors measured mechanically dispersible clay for only 3 minutes, while in this experiment measurements were made after one hour end-over-end shaking (Rengasamy *et al.*, 1984). One hour end-over-end shaking may be enough to break the aggregates completely, hence all of soil materials are exposed to water. It may be that the mechanically dispersible clay will correlate with aggregate surface area in only stable aggregates, where only the clay on the outer surface of aggregates will disperse.

An increase in the amount of latex applied from 1 to 2 g kg^{-1} soil had no significant effect on mechanically dispersed clay. It appears that latex saturated clay surfaces at the lower application rate and further application may have led to coalescence of rubber micelles on the outside surface of aggregates.

Dispersed clay contents of poly-DADMAC treated soils were much lower in the Red-brown earth than in the Wiesenboden. This is probably because the Red-brown earth soil had a lower clay content, and thus lower cation exchange capacity than the Wiesenboden. Therefore, while the addition of 2 g kg^{-1} soil of poly-DADMAC was sufficient to cause almost complete flocculation in the Red-brown earth, this was not the case in the Wiesenboden.

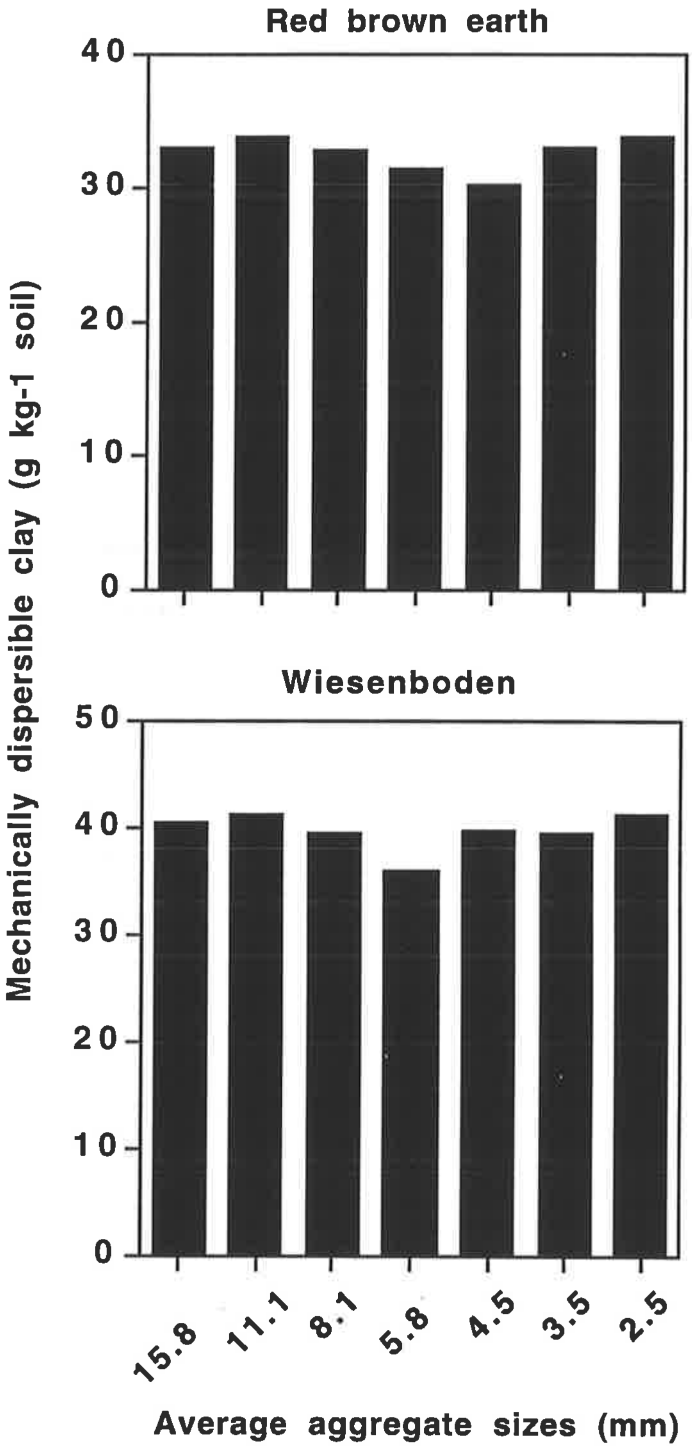


Figure 12a. Average mechanically dispersible clay from different aggregate sizes of the untreated Red-brown earth and Wiesenboden.

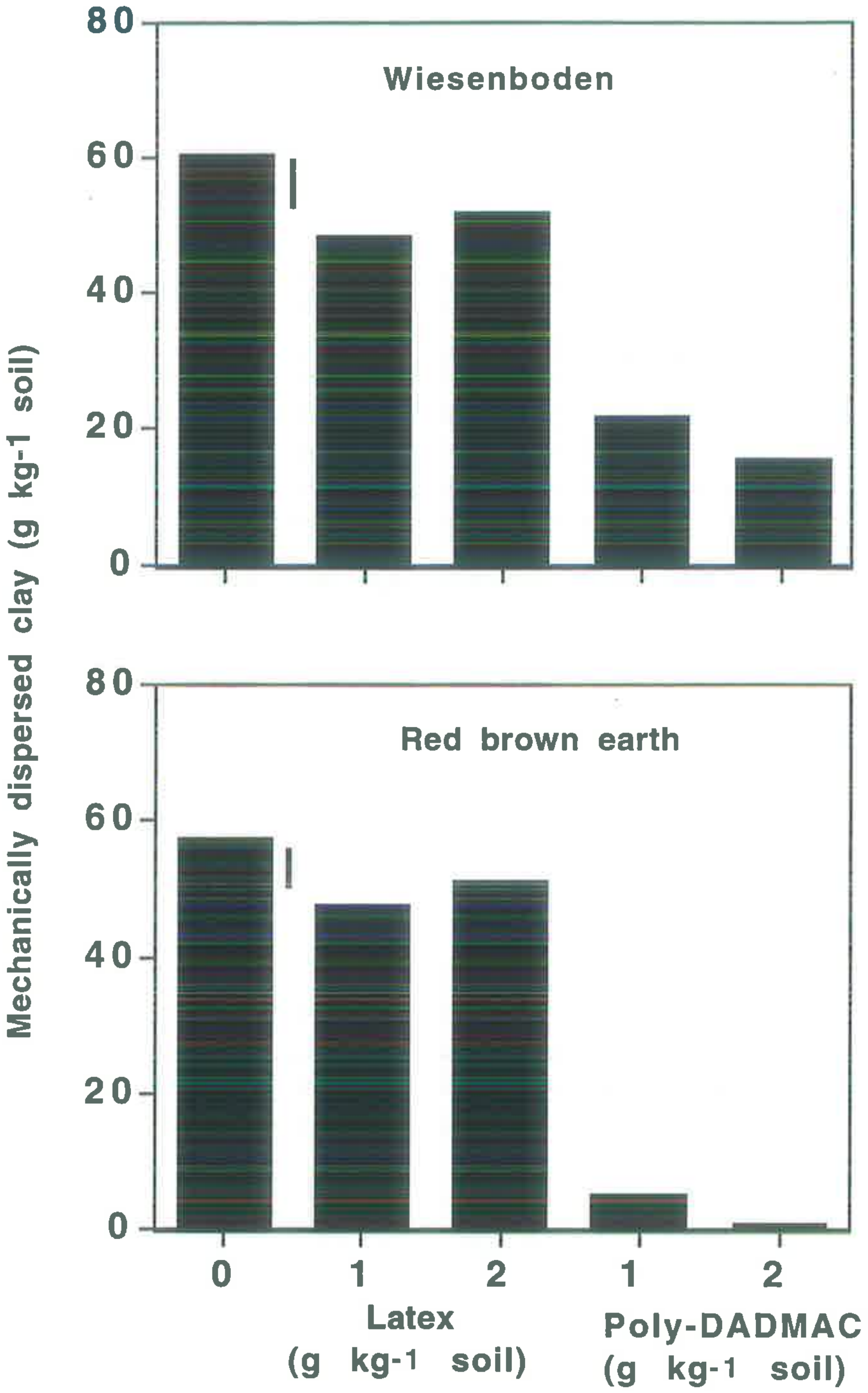


Figure 12b. The effects of latex and poly-DADMAC on mechanically dispersible clay of the Red-brown earth and Wiesenboden.

4.4.2. Soil water retention

Figure 13 indicates that the Wiesenboden (with higher content of reactive clay) has the capacity to adsorb more water than the Red-brown earth. Latex and poly-DADMAC did not affect the water retention of the Red-brown earth, but both polymers reduced the water content of the Wiesenboden at small potentials. At potentialss of about -0.003 and -0.005 bar, the water content of the untreated Wiesenboden was about 42% and 50% respectively, and the application of 1.5 g kg^{-1} latex or poly-DADMAC decreased the water content to about 38% and 40% respectively (Figure 13), indicating an influence primarily on macro-porosity.

4.4.3. M.E.D. values of latex treated soils

Latex affected the M.E.D. values of the Red-brown earth and the Wiesenboden significantly. The more latex that was applied, the higher was the M.E.D. value of the soils.

For the Red-brown earth, amendment with latex at 1.5 g kg^{-1} led to an increase in the M.E.D. value to about 1.4 M which indicates moderate water repellence (King, 1981). According to this author, this dose will not affect plant growth. However, 2 g kg^{-1} doubled the value to 2.7 M (Table 4), a much more severe water repellence, which may have implications for germination and growth of crops and pastures (King, 1981). This effect could be caused by the weak structure of the Red-brown earth, which disperses or slakes in water and forms a seal on the soil suface (Figure 14). Hence, when aqueous latex emulsion was applied at low concentrations in order to spread it evenly onto the <1 mm air dried soil, soil aggregates slaked into smaller sizes, the surfaces of

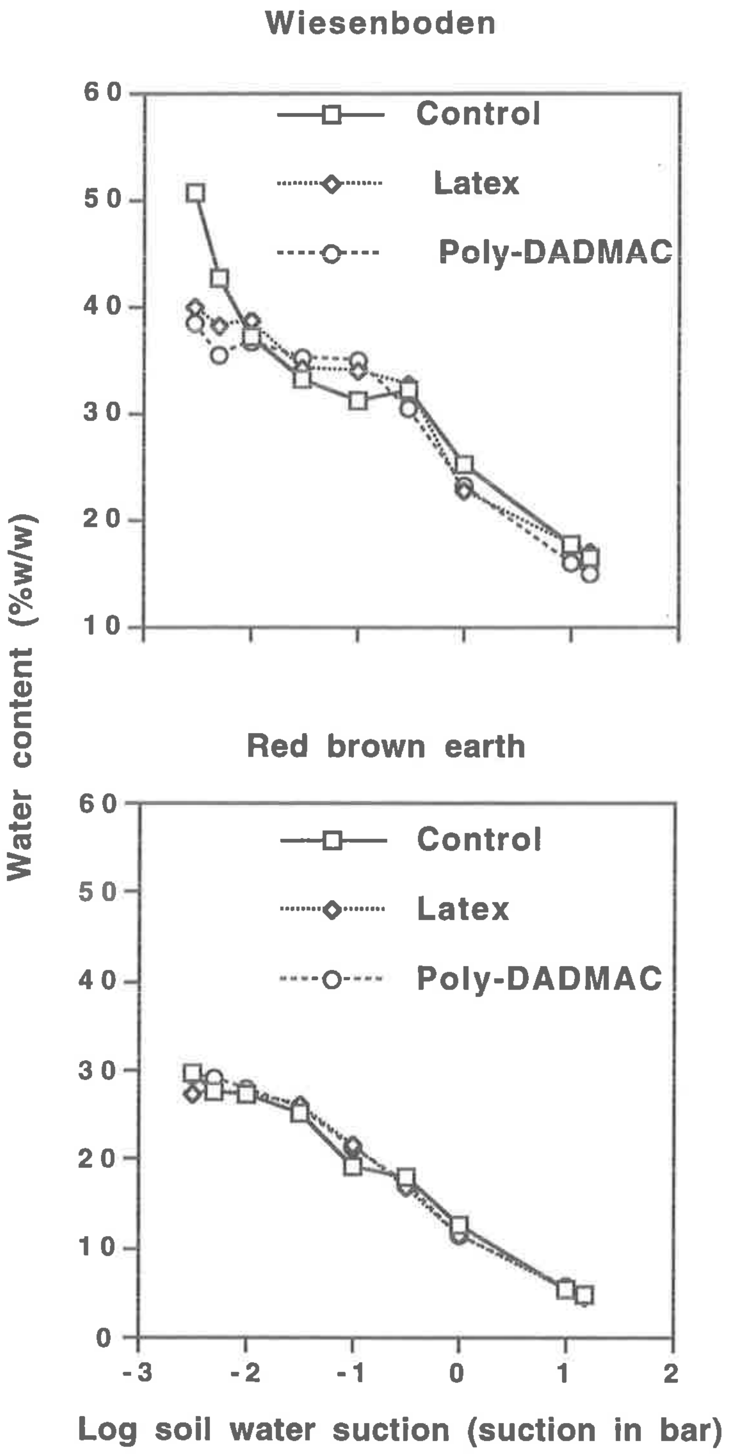


Figure 13. The effects of latex and poly-DADMAC on the water retention of the Red brown earth and Wiesenboden.

Table 4 . The effects of latex on M.E.D. value of the Red-brown earth and Wiesenboden.

Latex	M.E.D. value(Classification)*	
($g\ kg^{-1}$)	Wiesenboden	Red brown earth
0	0	0
0.5	0.5 (low)	0.5 (low)
1.0	1.5 (moderate)	1.2 (moderate)
1.5	1.8 (moderate)	1.4 (moderate)
2.0	2.1 (moderate)	2.7 (severe)

*According to King (1981).

which were coated by latex (Figure 14). Therefore 1.5 g kg^{-1} of latex is tentatively suggested as the optimum dose, this supports the results for the optimum dose from wet sieving as discussed in Chapter 2.

In the case of the Wiesenboden, applications of up to 2 g kg^{-1} latex to the soil increased the M.E.D. to only 2.1 M, which indicates moderate water repellence (King, 1981). This result could arise because the soil is a self mulching clay, and remained self mulching at this dose of application of latex; as seen in the Figure 14, the soil still produced many cracks. M.E.D. values were only measured on the surface where there were no cracks.

4.5. Conclusions

Latex and poly-DADMAC decreased mechanically dispersible clay significantly, however there were no statistically significant differences between the two application rates of polymers of 1 and 2 g kg^{-1} soil.

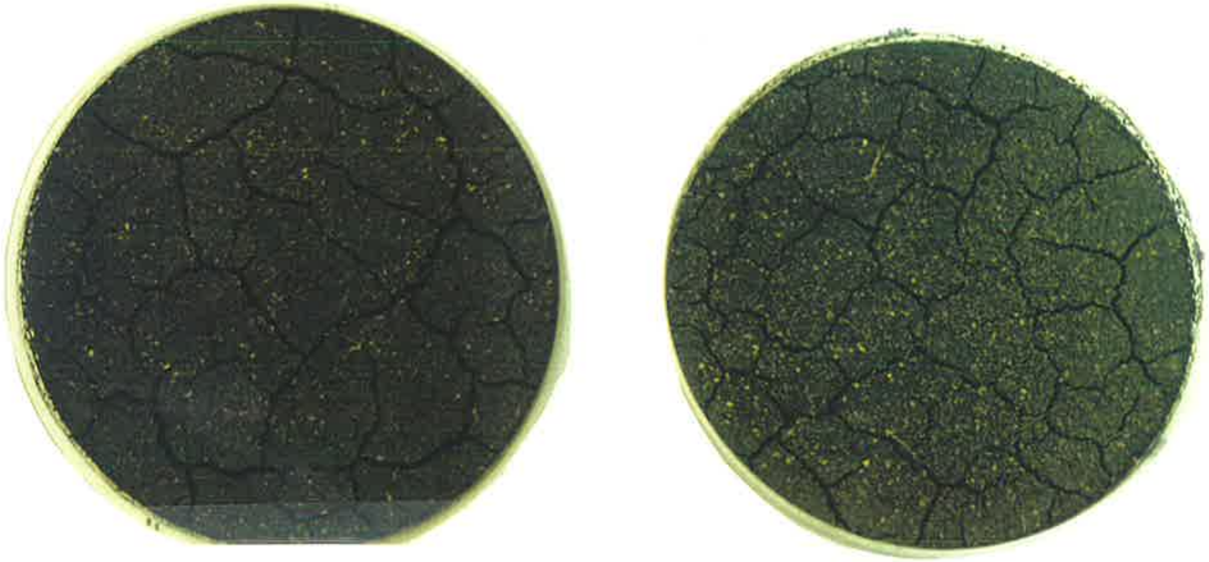
Application of the polymers at rates of 1.5 g kg^{-1} primarily affected macropores (drainage) in the Wiesenboden and had no effect on water retention of the Red-brown earth.

Red-brown earth (Alfisol)

Control

Latex (2g kg^{-1})

Wiesenboden (Mollisol)



Control

Latex (2g kg^{-1})

Figure 14. The surface of latex amended soils during measurement of M.E.D.

Soils amended with 1.5 g kg^{-1} latex showed increased M.E.D. values to about 1.4 for the Red-brown earth and to about 1.8 for the Wiesenboden. These values are 'moderate' so would not be expected to adversely affect plant growth. The application of latex at a rate of 2 g kg^{-1} soil could still be tolerated on the Wiesenboden but might be expected to cause problems of water penetration in the Red-brown earth. Further investigations are needed into their effects on erosion and plant growth.

CHAPTER 5

The Effects Of Latex And Poly-Dadmac On Water Infiltration, Run-Off And Erosion

5.1. Introduction

Erodibility of soil depends on texture, aggregate stability, shear strength, infiltration capacity, organic matter content and chemical composition (Morgan, 1986). All of these factors work together and determine the stability of soil against rapid wetting, raindrop impact, and overland flow. Of these factors, organic matter content correlates most strongly with the stability of the soil (Hartmann and De Boodt, 1974, Bruce-Okene and Lal, 1975, Tisdall and Oades, 1982, De Ploey and Poesen, 1985 and Ekwue, 1991), and different kinds of organic matter stabilise aggregates of different sizes (Tisdall and Oades, 1982). One of the reasons is that natural organic materials provide a hydrophobic coating to soil pores as well as providing inter-particle bonding, therefore preventing the slaking of aggregates.

Lax and Garcia-Orenes (1993) reported that carbohydrates (from a municipal waste composting plant), were effective as aggregating agents in soils. Some natural or synthetic soil conditioners such as carbohydrates, have a similar effect on soils. Latex (natural polymer) and poly-DADMAC (synthetic polymer) increased the proportion of water stable aggregates >2 and >0.125 mm, and simultaneously decreased mechanically dispersed clay significantly (Chapter 2). These two materials, which are hydrophobic and hydrophilic respectively, may affect infiltration and run-off, and thus soil erosion, differently. Latex is a hydrophobic material and may decrease infiltration rates. However, because it stabilises aggregates >2 mm and coats aggregates, it might prevent erosion. Aggregates >400 µm were detached by rainfall but not transported by shallow overland flow (Bradford and Huang, 1993), and the erobility of aggregates >2 mm was lower than of aggregates <2 mm (Quessar *et. al.*, 1993) . On the other hand, hydrophilic poly-DADMAC reacts electrostatically with clay minerals and stabilises aggregates >0.125mm (Chapter 2). Soil amended with poly-DADMAC might also be stable against erosion because these aggregates can not be dispersed by water. Increases in proportions of aggregates <0.125 mm decreased infiltration rates acting as a seal (Glanville and Smith,1988; Loch and Foley, 1994).

Since their influence on these important properties of soils is unknown, the effects of latex and poly-DADMAC on infiltration, run-off and the stability of soils to simulated rainfall were investigated.

5.2. Materials

5.2.1. Soils

Two soils, Urrbrae, a Red-brown earth (Alfisol) and Claremont, a Wiesenboden (Mollisol) were used. The characteristic properties of these two soils are taken from Stace *et al.* (1972) and Chittleborough and Oades (1980) (see Table 2). All soils were taken from 0-100 mm depth, and were sieved to <9.5 mm after drying. Ten kg of soil was then placed in a deep layer of 35 mm depth in a tray 300 mm wide and 750 mm long and with drainage holes in its base which was tilted at an angle of 5^o and subjected to simulated rainfall, as described below.

5.2.2. Organic polymers

The methods of treatment of soils with latex and poly-DADMAC are presented in Chapter 2. The application rates of latex were based on the optimum dose for aggregate stability as indicated by wet sieving results, in this case 1.5 g kg^{-1} for the Red-brown earth and 0.5 g kg^{-1} for the Wiesenboden. Poly-DADMAC were applied at rates of 1 g kg^{-1} for Red-brown earth and 0.5 g kg^{-1} for Wiesenboden (Chapter 2). Untreated soils were also subjected to simulated rainfall for comparison.

5.3. Methods

5.3.1. Simulated rainfall

A rotating disc rainfall simulator (Morin *et. al.*, 1967) and associated equipment described by Malinda *et. al.* (1992) was used to generate simulated rainfall with an intensity of 100 mm h^{-1}, and a kinetic energy of 29 J m^{-2} mm^{-1} rain· The soils were subjected to simulated rainfall for 20 minutes and the run-off was collected every 3 min after initiation of run-off. The total run-off and sediment were then measured. The total infiltration was calculated from total rainfall subtracted from total run-off. Photographs were taken after the soils had been subjected to simulated rainfall. One of these (Fig 18) is included as an example of the 3 replicates of each treatment.

These data were then analysed in order to calculate any significant differences between treatments. The experimental design used was based on a randomised complete block design. The Tukey's test which is called the Honestly significant difference (*hsd*) was used to see if there was any difference at the 0.05 level (Steel and Torrie, 1960).

5.3.2. Measurement of water stability of aggregates

After the soils were subjected to rainfall, samples were taken from the 0 - 5 mm depth, put in plastic Petri dishes with lids on and sealed. The proportion of water stable aggregates (wet soil samples) was measured (Chapter 2). Data were analysed statistically as above.

5.4. Results and discussion

5.4.1. Run-off and infiltration

Latex

The effects of latex on water run-off and infiltration of the Red-brown earth and Wiesenboden are presented in Figs 15 and 16. The results shows that there were no significant differences between latex treated soils and controls from both soils.

As a hydrophobic polymer, latex was expected to increase run-off and decrease infiltration, because it hindered water penetration into soil. This proved not to be the case, however, and while the differences were not statistically significant at P = 0.05, application of latex at the rates used here invariably caused a small decrease in runoff for both Wiesenboden and Urrbrar soils (Figure 15). Corresponding increases in infiltration were observed for both soils (Figure 16), but these, too, were not statistically significant at P = 0.05.

Poly-DADMAC

Poly-DADMAC did not increase water run-off and did not decrease infiltration significantly compared with controls on the Red-brown earth.

Wiesenboden

Red brown earth

Figure 15. The effects of latex and poly-DADMAC on the total run-off of the soils. Bars with the same letter do not differ significantly at the 0.05 level.

However, it decreased water run-off and increased infiltration significantly on the Wiesenboden (Fig 15 and 16).

Poly-DADMAC may have been more effective in reducing run-off and increasing infiltration in the Wiesenboden than in the Red-brown earth, because as a positively charged polymer, its adsorption onto soil surfaces or clay surfaces would be strongly influenced by the high cation exchange capacity due to a high 2:1 type clay content of the Wiesenboden (Table 2). The application of 0.5 g kg^{-1} poly-DADMAC might form inter linkages between clay particles and create larger aggregates >0.125 mm compared with the Red-brown earth. These aggregates would not block soil pores. Also, as a hydrophilic material it enabled more water to infiltrate into the soil. The effect was increased infiltration and decreased run-off. The untreated Wiesenboden may have slaked and produced aggregates <0.125 mm and in turn these aggregates blocked the pores thus increasing run-off and decreasing infiltration.

Positively charged poly-DADMAC applied to the Red-brown earth at 1 g kg^{-1} did not affect water run-off and infiltration. This is because the Red-brown earth has a low clay content, and its clay fraction is dominated by illite, giving the soil a very low C.E.C. (Table 2). The formation of >0.125 mm aggregates did not affect the water infiltration of this soil, which contains a high sand fraction 53% (Table 2). It may be suggested that when a hydrophilic polymer is applied to sandy soils or soils with a very low C.E.C., the addition of a cross linker to the polymer is necessary, as proposed by Gabriels and De Boodt, (1978).

Hence the rate of application has to be considered in relation to the clay content and type, which determines the cation exchange capacity of a soil.

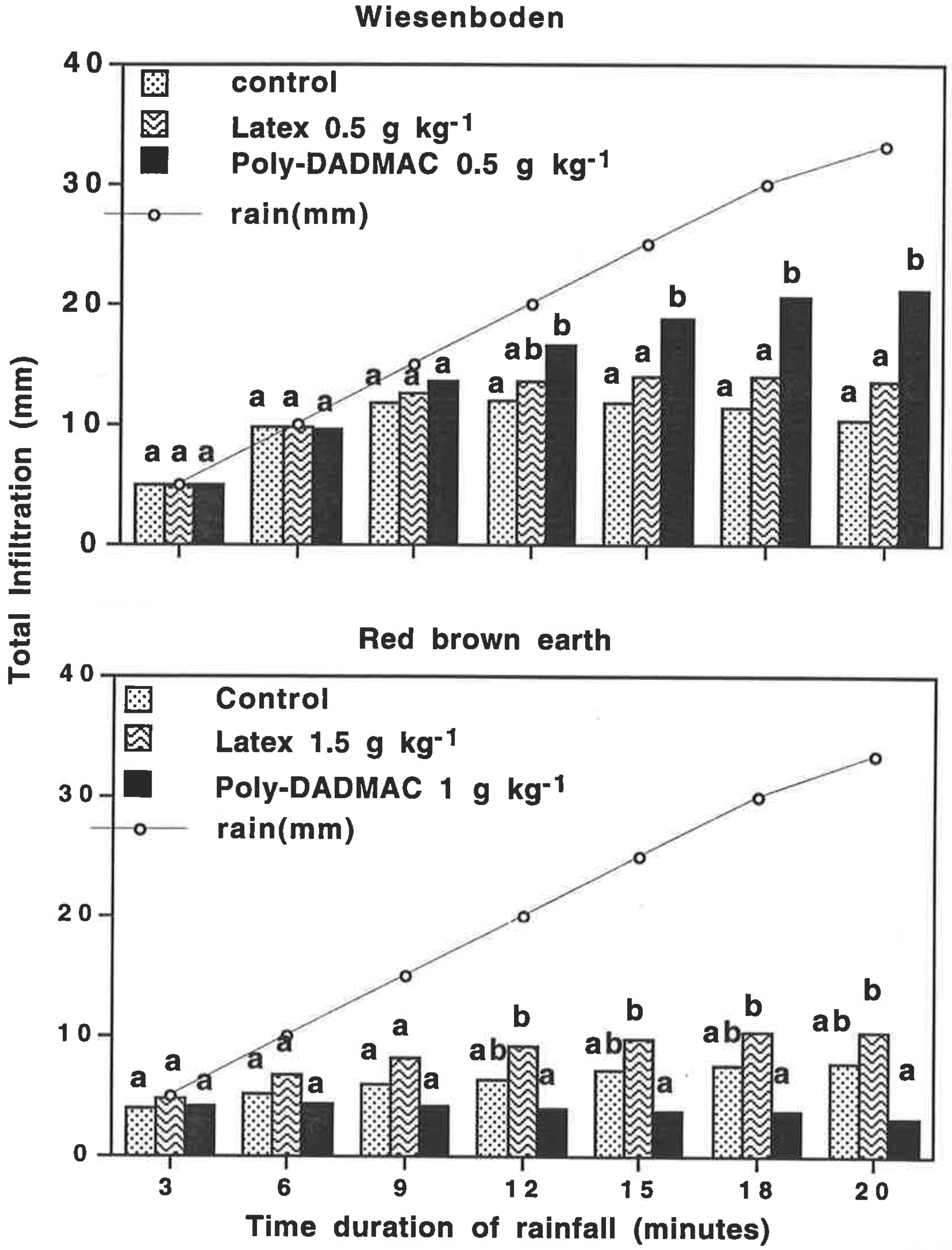


Figure 16. The effects of latex and poly-DADMAC on total infiltration of rainfall into the soils with time. Bars with the same letter do not differ significantly at the 0.05 level.

5.4.2. Erosion

Latex

The application of latex at rates of 1.5 g kg^{-1} on the Red-brown earth and 0.5 g kg^{-1} on the Wiesenboden decreased erosion significantly compared with controls. Latex decreased erosion by about 77% on the Red-brown earth and by about 74% on the Wiesenboden (Figure 17). As stated previously, latex did not decrease water run-off significantly on both soils so latex behaves just like a hydrophobic bitumen (De Boodt, 1975). This means that latex-stabilised aggregates must be strong and are not broken or splashed by raindrop impact and also are not detached by overland flow, thus decreasing erosion. Latex seems to be effective on both the Red-brown earth and Wiesenboden.

Poly-DADMAC

Treatment with poly-DADMAC limited erosion significantly on the Red-brown earth, even though at this application rate, it did not affect run-off and infiltration significantly as discussed previously. This was caused by the poly-DADMAC polymer's high molecular weight, which enabled soil aggregates to be stabilised against raindrop impact and overland flow.

Poly-DADMAC decreased erosion of the Wiesenboden significantly compared with the control. Decrease in erosion by the application of poly-DADMAC on the Wiesenboden was possibly due to hydrophilic material absorbing more water (though this was not confirmed) and hence decreasing run-off of water and increasing water infiltration. Hence there was not enough overland flow to erode the soil. Even though this soil has a high organic matter content and is self mulching, erosion was still high without latex and poly-DADMAC treatments, especially under a high energy and a high intensity

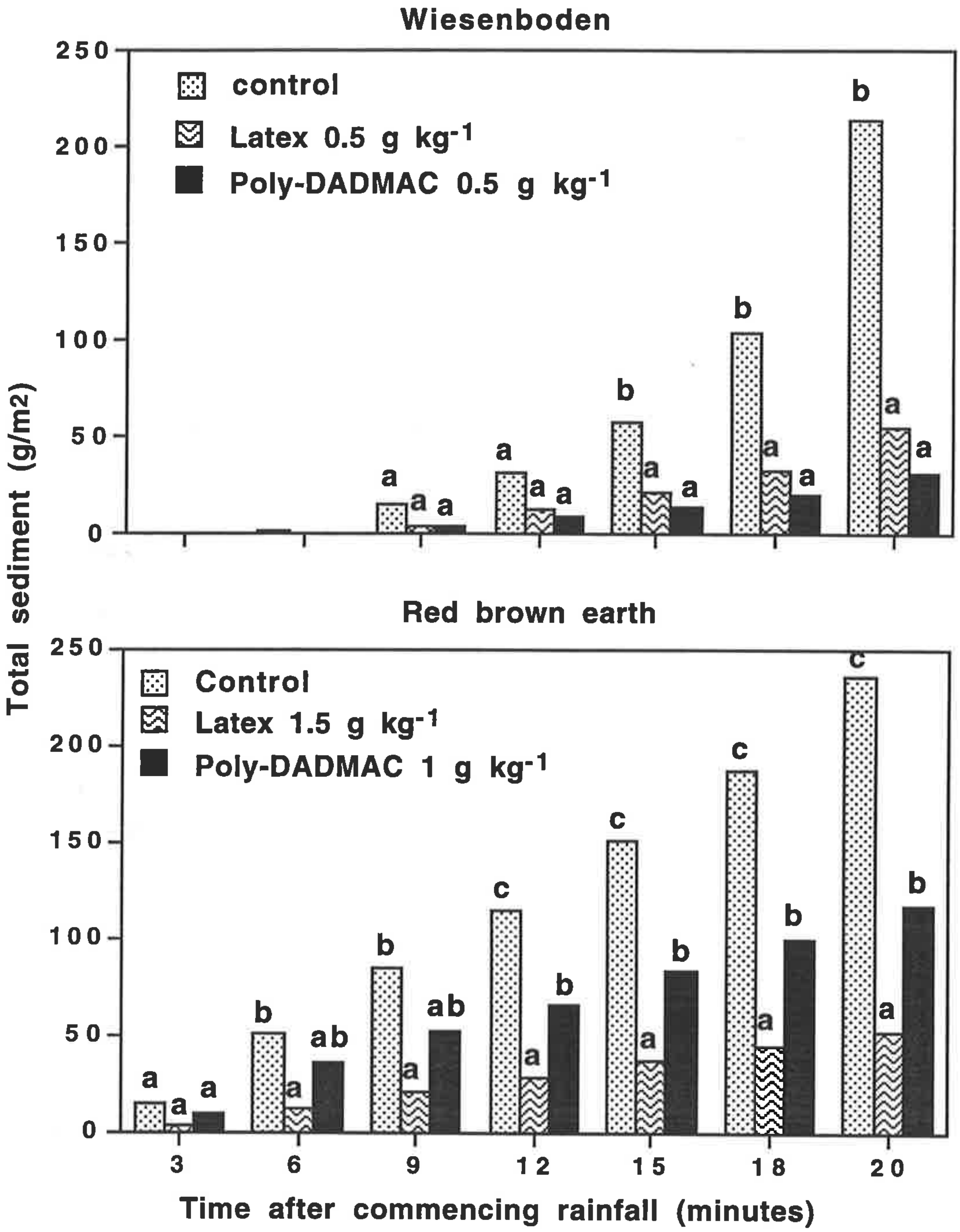


Figure 17 . The effects of latex and poly-DADMAC on soil erosion. Bars with the same letter do not differ significantly at the 0.05 level.

of rainfall (Fig 17). This is particularly the case after tillage, when bonds between soil particles are broken and the plant canopy has not yet covered soil surfaces. This is the most fragile situation and a material like a polymer is needed which can minimise erosion.

5.4.3. Water Stable Aggregation after Simulated Rainfall

The results of water stable aggregation for the Red brown earth showed that latex increased water stability of aggregates >2 mm significantly to about 90% and decreased the proportion of unstable aggregates <0.125 mm significantly to about 5% compared with the control after the soils had been subjected to simulated rainfall (Fig 19).

The application of latex (1.5 g kg^{-1}) on the Red-brown earth maintained the stability of aggregates > 2 mm against rainfall. This means that these aggregates were not broken into smaller sizes even by high energy (29 J m^{-2} mm^{-1}) and high intensity (100 mm hr^{-1}) after 20 min rainfall. This result is similar to those from the previous study in which latex created aggregates >2 mm after wet sieving without the soil being subjected to simulated rainfall (Chapter 2). It showed that latex treated soil aggregates were very stable against the action of water.

The application of poly-DADMAC (1 g kg^{-1}) on the Red-brown earth also stabilised aggregates >0.5 mm significantly and decreased aggregates <0.125 mm significantly compared with the control. This also means that aggregates stabilised by poly-DADMAC were not broken into smaller sizes (<0.125 mm) under a high energy of rainfall.

Figure 18. Untreated (right) and latex (1.5 g kg^{-1}) treated Red-brown earth (left) after 20 min subjected to rainfall.

On the other hand, the application of latex and poly-DADMAC (0.5 g kg^{-1}) to the Wiesenboden produced less effect than the application of 1.5 g kg^{-1} latex and 1 g kg^{-1} poly-DADMAC to the Red-brown earth, and there was no significant difference between treatments on the Wiesenboden; (Fig 19).

On the other hand, the application of latex and poly-DADMAC (0.5 g kg^{-1}) to the Wiesenboden produced less effect than the application of 1.5 g kg^{-1} latex and 1 g kg^{-1} poly-DADMAC to the Red-brown earth, and there was no significant difference between treatments on the Wiesenboden; (Fig 19).
It seems that, at these doses of application on the Wiesenboden, the aggregates >2 mm were broken into smaller sizes by high energy rain. The results also indicate that water stable aggregates (from wet sieving) were not always stable against raindrops. This finding is similar to that of Reichert and Norton (1994). However, soil aggregates, although broken down into smaller sizes under rainfall, were still strong enough to resist erosion.

5.5. Conclusions

The application of 1.5 g kg^{-1} of latex did not affect water run-off and infiltration on the Red-brown earth, but it decreased water erosion significantly compared with the control.

The application of 0.5 g kg^{-1} of latex also did not affect water run-off and infiltration on the Wiesenboden, however it minimised erosion significantly compared with the control.

Poly-DADMAC at the application rate of 1 g kg^{-1} on the Red-brown earth did not decrease water run-off or increase water infiltration significantly compared with the control, however it decreased erosion significantly compared with the control.

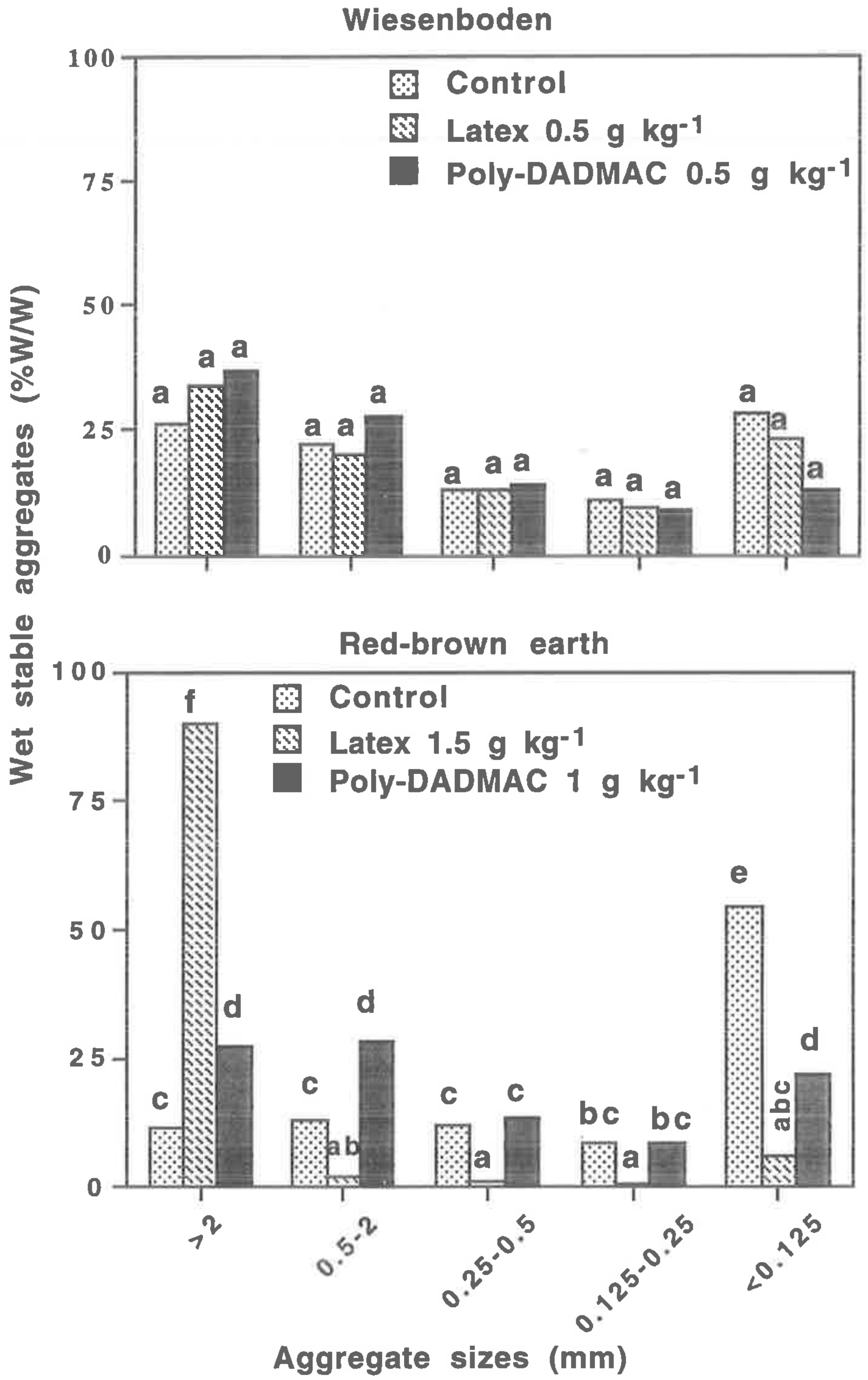


Figure 19. The effects of latex and poly-DADMAC on water stable aggregates after 20 min simulated rainfall. Bars with the same letter do not differ significantly at the 0.05 level.

Poly-DADMAC at the application rate of 0.5 g kg^{-1} on the Wiesenboden decreased water run-off and erosion, and increased water infiltration significantly compared with the control.

Aggregates of the Red-brown earth which were stabilised by latex and poly-DADMAC against wet sieving were not broken into smaller sizes (<0.125 mm) after high energy rainfall for 20 min. However, aggregates of the Wiesenboden, which were stabilised by latex and poly-DADMAC were not stable to rainfall.

Both polymers can be used as soil conditioners. These polymers are sufficiently effective to warrant testing under field conditions, including investigations of their effects on plant growth.

CHAPTER 6

The Effects Of Polymers On The Growth Of Rye Grass

6.1. Introduction

The purpose of using soil conditioners is to improve soil physical properties, minimise erosion, improve water storage, improve plant growth or maintain a high yield (De Boodt, 1975; Gabriels, 1990; and Wallace and Wallace, 1986).

Latex without aromatic oils and stabilisers and poly-DADMAC have been shown to increase the proportion of water stable aggregates, decrease mechanically dispersible clay, and significantly decrease erosion, as discussed in the previous Chapters. This means that the two polymers can be used as soil conditioners.

However, the application of latex at the rate of 1.5 g kg^{-1} soil increased soil hydrophobicity to give only moderate water penetration (Chapter 4), but moderate water repellance generally does not induce significant problems with germination and plant growth (King, 1981). Hydrophilic poly-DADMAC as a positively charged material may also affect plant growth i.e. as a large poly-cation it may hinder the adsorption of cationic nutrients for plant growth or may bind anionic nutrients, thus making them unavailable to plants.

Since these polymers may create the above problems, this experiment aimed to investigate the effects of the two polymers on the growth of grass. Poly-vinyl alcohol was also applied for comparison; this polymer has not been found to have any negative effects on plant growth (Carr and Greenland, 1975; Stefanson, 1974).

6.2. Materials and methods

6.2.1. Soil

The Urrbrae Red-brown earth (see Table 2) was sampled from 0 - 100 mm, wetted to a water content at its plastic limit and then passed through a 5 mm sieve, collecting everything held on a 2 mm sieve. This 2-5 mm fraction was dried at 40° for 3 days.

6.2.2. Polymers

Besides latex and poly-DADMAC, poly-vinyl alcohol (PVA) was also applied to the soil for comparison. All the polymers were applied at 1.5 g kg^{-1} soil. The polymers were sprayed evenly on to the aggregates of 2 to 5 mm diameter, then the treated aggregates were dried as above. Soil (1.5 kg) was placed in a plastic pot for the growth of grass.

6.2.3. Ryegrass

Four seeds of rye grass were planted in each pot in the glass house; 2 plants were left after 2 weeks. The plants were watered once a week to field capacity (determined at -10 kPa) when they were 1-4 weeks old, and then twice a week when they were older. The rye grass was harvested when it was 12 weeks old. Grass roots were separated from soil by washing with reverse osmosis water. Shoot length and dried root weight were measured after drying the roots in an oven at 70^{o} C for 24 hr.

6.2.4. Measurement of root length

The measurement of estimated root length followed the method of Tennant (1975). The preparation of the root subsamples was as follows: each root was cut into 0.5 cm lengths and dispersed in water, then spread evenly on black filter paper and sprayed with a diluted PVA glue (10%) in order to adhere the roots on the filter paper. The paper plus roots was dried at 70° C for about 1 hr, stored between 2 filter papers, and held under a heavy load. Using a 0.5 x 0.5 cm grid square on transparencies as shown in the Figure 20, the measurement of root length was carried out by calculating the number of intercepts between the grid line and the root under microscope with 10 times magnification. The root length was calculated as following:

Root length (R) = Number of intercepts (N) x Length conversion factor.

Length conversion factor = 0.3928 for 0.5 cm grid squares.

Figure 20. Roots on the black filter paper and under the transparency gridline (0.5 cm).

6.4. Results and discussion

The effects of latex, poly-DADMAC and PVA on dried shoot weight, root weight and root length plus visual effects are shown in Figs 21-24. The addition of PVA And latex resulted in a significant increase in root length (figure 22) whereas the addition of poly-DADMAC did not. None of the polymers had significant effects on shoot or root weight (Figure 21), despite the fact that they all minimised crack development, and presumably improved the structure for plant growth (Figure 23) All pots were fertilised identically, and so it is possible that polymer treatment effects were masked.

PVA and latex significantly increased root length of rye grass to about 1300 m and 1214 m, respectively, compared with 652 m for the control (see also Figure 24).

6.5 Conclusions

The polymer treatment effects were minimal with respect to plant growth, and there were no negative effects (e.g. toxicities) for any of the polymers relative to the control.

Application of the polymers to the Urrbrae soil at the rates used here will produce no difficulties with plant growth that might be associated with hydrophobicity.

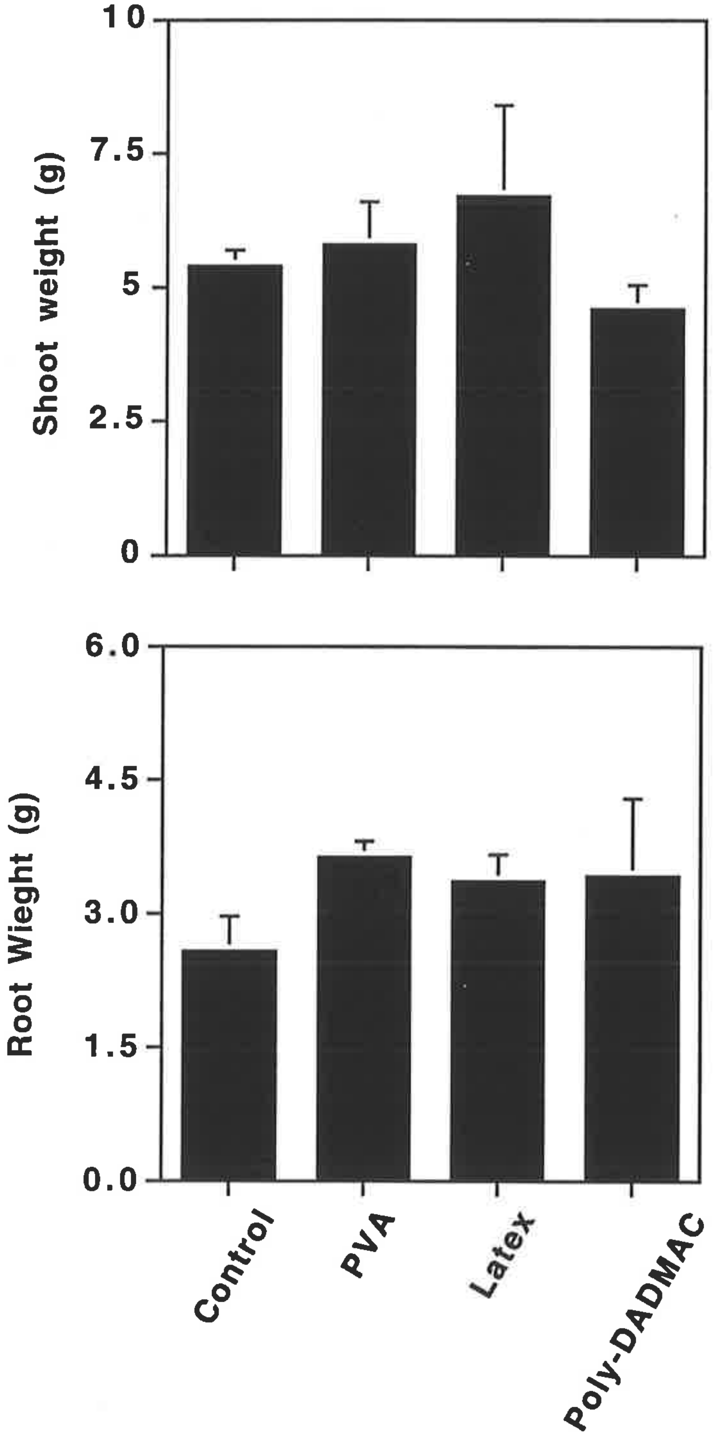


Figure 21. The effects of polymers on dry shoot and root weight of ryegrass.

The length of the bar is the standard deviation of each treatment.

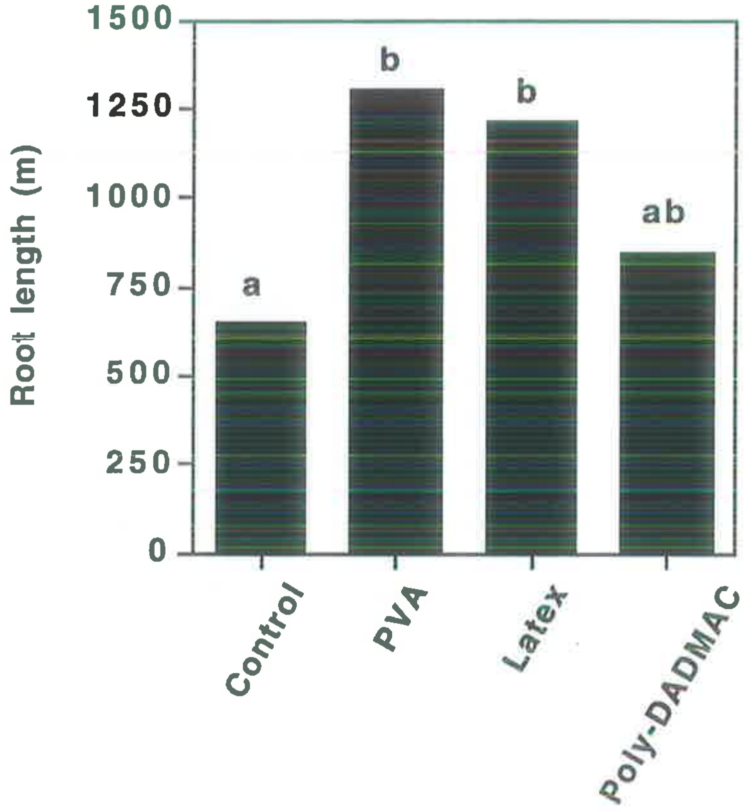


Figure 22. The effects of polymers on root length of rye grass. Columns with the same letter do not differ significantly at the 0.05 level.

Figure 23. Rye grass growth at 3 weeks old, Control = untreated soil, Latex = latex treated, behind latex treatment is polyvinyl alcohol treated soil, and behind control is poly-DADMAC treated soil.

Figure 24. Comparison of polymer treated soils with untreated soil on removal from the pots after harvesting rye grass at 12 weeks.

CHAPTER 7

Decomposition Of Latex In Soil As Determined By Monitoring Changes In $\delta^{13}C$

7.1 Introduction

Several methods can be used to monitor the decomposition of organic materials in soils. Labelling with ^{14}C and determining both $^{14}CO_2$ released with time and the residual ^{14}C has been used many times with labelled chemicals and plant materials.

More recently with the availability of mass spectrometers for the measurement of isotopes, particularly ^{13}C, it has been possible to monitor $\delta^{13}C$. This has enabled the decomposition of organic materials to be studied in soils when the added organic materials have possessed a different natural abundance of ^{13}C compared with the natural abundance of ^{13}C in the indigenous organic materials. The natural abundance of ^{13}C in natural organic materials is about 1.1%. However, it is different for C3 plants (Calvin cycle) and C4 plants (Hatch Slack cycle) which have different photosynthetic pathways. C3 plants generally have lower $\delta^{13}C$ values (-24 to -34$^{o}/_{oo}$) compared to C4 plants (-6 to -19$^{o}/_{oo}$) (Smith and Epstein 1971). The $\delta^{13}C$ values are measured in parts per thousand and are compared to a standard the Pee Dee Belemnite from South Carolina (Smith and Epstein 1971). The $\delta^{13}C$ values are thus differences in parts per thousand from this standard.

Growing C3 plants in a soil which has previously been under C4 vegetation can be viewed as an *in situ* labelling of the newly incorporated organic matter because it has a $\delta^{13}C$ value which is measurably different from the original soil organic matter. With time after a change of vegetation from C4 to C3, or vice versa, it is possible to measure the change in $\delta^{13}C$ of the soil organic matter and thus deduce rates of addition and turnover of organic matter. This method has been used successfully by a range of workers (e.g. Balesdent and Mariotti, 1987; Skjemstad *et. al.,* 1990; Golchin *et. al.,* 1995).

The aim of this experiment was to investigate the rate of decomposition of latex and its by-products when latex (from a C3 plant) was incorporated in soil which had previously been under sugar cane (a C4 plant) for decades. The fate of latex added to soil is unknown and it is necessary to establish that latex is decomposed in soil before it is applied on a field scale. Simultaneously we need to establish that latex has sufficient longevity in soil to function as an effective stabiliser for a significant period. The work of earlier chapters established that latex has promise as a soil stabiliser by stabilising aggregates, decreasing erosion and not inhibiting the growth of grass.

7.2 Materials and methods

7.2.1 Soil

A soil sample was obtained from 0-100 mm depth at a site near Ingham in Queensland where sugarcane had been growing for approximately 30 years. This soil was kindly sent by Dr Ross Nable (CSIRO Townsville). The soil is of the Trevonne series and is classified as a Mottled Eutrophic Yellow Kandozol in the New Australian system and a Haplustalf in Soil Taxonomy. It is a fine sandy loam with pH (H_2O) of about 5.5. This soil was used because it has A high $\delta^{13}C$ ($-13.5^{o}/_{oo}$). The soil sample was dried at $30^{o}C$ for 3 days and sieved using a 2 mm aperture.

7.2.2 Polymer (latex)

A latex emulsion containing 1% dry rubber content (DRC) was diluted to 0.2% with deionised water and sprayed evenly onto the dry soil to give an amount of latex-C equal to that of the C content of the soil (0.66%). Untreated soils (water only) and latex-amended soils were wetted further to a water potential of -10 kPa and were incubated at 25°C for up to 20 weeks as described below.

7.2.3 Incubation and sampling regime

Soil (25g < 2 mm) was placed in a plastic container (150 ml capacity) and 20 ml of 0.1 M NaOH was placed in a plastic container of 50 ml capacity. Both containers were placed inside a jar with a sealable lid (Fig. 25). Untreated and latex-amended samples were replicated three times. The NaOH solutions were removed after 1, 2, 4 and 7 days and thereafter at weekly intervals for up to 20 weeks.

7.2.4 The measurement of trapped CO_2

Two ml of NaOH solution from jars incubated with untreated soil, latex-amended soil and no soil (empty container) were titrated with 0.1 M HCl using an ABU80 Autoburette and Titrigraph. The amount of HCl that was used to decrease the pH from >10 to 8.3 and then to pH 4.3 was automatically recorded and the values of C from CO_2 evolved was calculated following Franson (1980).

Figure 25 Soil (E) and NaOH (26E) were incubated inside the jar during trapping CO_2.

7.2.5 $\delta^{13}C$ analyses

The untreated soil and latex-amended soils were sampled each week for four weeks and then at intervals of 4 weeks up to 20 weeks. The carbon isotopic ratio ($\delta^{13}C$) of these samples and latex (as dry rubber), the untreated soil and the latex-amended soil were kindly determined on a VG Isogas SIRA 10 spectrometer by John Dighton (CSIRO, Adelaide). All data were calculated with reference to the PDB standard.

7.3 Results and Discussion

The $\delta^{13}C$ of the untreated sugarcane soil was $-14.0^{o}/_{oo}$ and the latex $-26.4^{o}/_{oo}$. Thus when latex was added to the soil so that the latex C matched that of the soil organic C, the $d^{13}C$ value would be expected to be $-19.95^{o}/_{oo}$. This, in fact, was the $\delta^{13}C$ value measured for the soil amended with latex before incubation (Fig. 26). The data in Fig. 26 show a scatter of $\delta^{13}C$ values close to $-14^{o}/_{oo}$ for the untreated soil over the 20 week period of the incubation as expected. For the latex-amended soil the $d^{13}C$ values increased with time indicating that C from latex was being released as CO_2. This shows that the soil microbial biomass population was utilising latex as a substrate and mineralising some of the latex C to produce CO_2. Some of the latex C must have been incorporated into the soil microbial biomass and its metabolic products.

If we make the assumption that no indigenous C was lost during the incubation period, we can calculate the relative proportions of indigenous C (from sugarcane), plus the C from latex. If δ_t = $\delta^{13}C$ at time t for the latex-amended soil, δ_e = $\delta^{13}C$ for latex, and δ_o = $\delta^{13}C$ for the C in the soil which

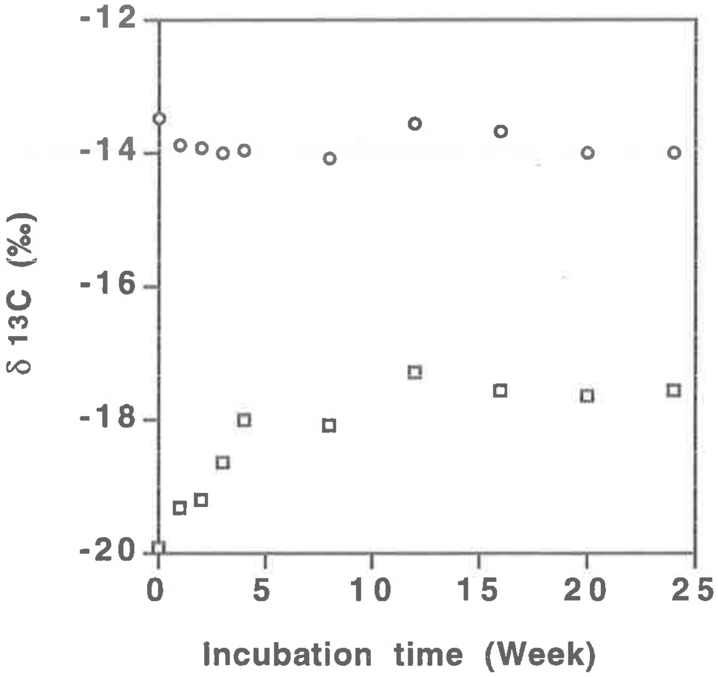


Figure 26. The $\delta^{13}C$ of the untreated-soil (m) and latex amended-soil (□) during laboratory incubation for 20 weeks.

has grown sugarcane, and f is the fraction of C in the soil from the sugarcane, then their relationship can be expressed:

$$\delta_t = (\delta_o - \delta_e)f + d_e$$

The results of these calculations are shown in Table 5. The changes in $\delta^{13}C$ during the incubation (Fig. 26) were relatively rapid over the first four weeks, and the calculations (Table 5) show that only one third of the C in the latex-amended soil came from latex. Based on the assumption that no indigenous C was lost from the soil, the indications are that after 4 weeks incubation one half of the C from latex had been released as CO_2. This indicates that latex must be decomposed by the microbial population relatively quickly and would certainly not persist in soils for any appreciable time.

The assumption that no indigenous soil C was lost during the incubation, however, is clearly not tenable. Two attempts were therefore made to determine the mineralisation of indigenous C during the incubation period to enable corrections to be made to the data in Table 5. The first approach was to measure the CO_2 released from both the untreated soil and the latex-amended soil during the incubation. Assuming that the addition of latex did not influence the decomposition of the indigenous soil C, the amount of C mineralised to CO_2 that was derived from latex in the amended soil could be calculated. Results for the first 4 weeks of the incubation are shown in Table 6. The data show that after 4 weeks 10.4% of the indigenous C was lost, and 39% of the latex C was lost. For the first two weeks there was not much difference in the rates of decomposition of the two sources of C but from 2-4 weeks mineralisation of C from latex was much faster than that from the indigenous C. From the data for 4 weeks in Table 6 it can be calculated that the untreated and latex-amended soils contained 5.9 g kg^{-1} indigenous C, and 4.0 g kg^{-1} latex C, respectively. Using the formula:

Table 5. Total C (%) from sugar cane plant and from latex in the latex-treated soils for a 20-weeks laboratory incubation based on^{13}C analyses

Time of incubation (weeks)	The proportion of carbon (%) from sugar cane plant	latex or rubber plant
0	50	50
1	55	45
2	55	45
3	60	40
4	65	35
8	64	35
12	71	30
16	68	32
20	68	32

Table 6. Total carbon loss from untreated and latex-amended soil during 4 weeks incubation

Time of incubation (days)	C loss untreated soil		C loss latex-amended soil		C loss from latex	
	g kg^{-1}	%	g kg^{-1}	%	g kg^{-1}	%
1	0.10	1.5	0.15	1.14	0.05	0.7
2	0.18	2.7	0.33	2.5	0.15	2.3
4	0.25	3.8	0.52	3.9	0.27	4.1
7	0.37	5.6	0.87	6.5	0.50	5.3
14	0.37	5.6	0.87	6.5	0.50	5.3
21	0.61	9.2	2.30	17.4	1.69	25.6
28	0.69	10.4	3.26	24.7	2.57	39.0

$$\delta_t = (\delta_o - \delta_e)f + \delta_e$$

the value of δ_t that should have occurred after 4 weeks incubation can be calculated. The value obtained for $\delta^{13}C$ of the latex-amended soil after 4 weeks incubation should have been -18.7$^o/_{oo}$. This agrees well with the value measured for the soil (-18.1$^o/_{oo}$) and is well within the experimental errors for the direct measurement of $\delta^{13}C$. The corrections that would need to be made in Table 5 after 4 weeks incubation would be to change the proportions of C in indigenous C and latex C from 65% and 35% to 60% and 40% respectively. Because CO_2 measurements were not made beyond 4 weeks it was not possible to compare $\delta^{13}C$ values calculated in this manner with the measured values.

It is clear from the data in Fig. 26, however, that most of the change in $\delta^{13}C$ values during 20 weeks of incubation occurred by the 4th week; from 4 to 20 weeks, $\delta^{13}C$ values remained between -18 and -17$^o/_{oo}$. After 4 weeks incubation of the latex-amended soil the residual C content was 9.99 g kg^{-1} according to the data for 4 weeks incubation in Table 6. The C content measured in the latex-amended soil after 20 weeks incubation was 10.5 g kg^{-1} ± 0.5 (9 replicates) which confirms that mineralisation between 4 and 20 weeks was minimal.

We can thus use the proportions of C from the soil and from latex in Table 5 with some confidence. Most of the activity of the microbial population in the soils was complete after 4 weeks, leaving the proportions of C in the latex-amended soil with 2/3 from indigenous C and 1/3 from latex. This means that about one half of the carbon from latex was mineralised, i.e. released as CO_2, the other half either in undecomposed latex or in microbial biomass and microbial metabolites. Based on decomposition experiments with a range of other materials, we can assume that most of the original latex was probably altered in some way and most of it utilised by microorganisms; otherwise 50% of the C would not have been mineralised.

The rate of decomposition of latex was similar to that of cow manures, which have also been found to lose about half the C within 20 weeks of incubation (Martin and Haider, 1986). Thus latex would not be expected to accumulate in, or pollute, soils and clearly there were no toxic effects as far as grasses were concerned (c.f. Chapter 6). Some other, synthetic soil conditioners are not decomposed in soils, and these cause concerns in terms of their accumulation. Others may decompose and lead to materials which are toxic. For example Sojka and Lentz (1994) showed that the monomer resulting from polyacrylamide was toxic to plants, which is why this polymer is only considered safe if it contains less than 0.05% monomer.

7.4 Conclusions

The decomposition of latex in soils matches that of other natural organic materials. The indications are that during 4 weeks the decomposition of latex was probably almost complete as shown by release of about half the C as CO_2.

From this experiment and that with the growth of grasses it can be concluded that latex would not be expected to accumulate in soils nor produce compounds toxic to plants.

The experiments indicate that monitoring of $\delta^{13}C$ values can be used to follow decomposition and mineralisation of C compounds in soils where the $\delta^{13}C$ values of the C in the soil and the organic material under study are different.

CHAPTER 8

General Discussion And Conclusions

8.1. General Discussion

Once soils are tilled, bonds between soil particles are destroyed and it takes weeks or months to recover these bonds. The bonding processes in natural conditions (Tisdall and Oades, 1982 and De Boodt, 1993) include:

1. flocculation of clay particles, which forms quasi-crystals, domains or tactoids;
2. *in situ* production of organic matter such as polysaccharides, polyuronides, fungal hyphae, and roots which adhere to associated clays and larger soil particles; and
3. the deposition of cements like iron and aluminium oxides and oxyhydroxides, calcium carbonates, calcium sulphate, and silica crystals around associated clay structures..

Soil conditioners as emulsions or solutions can react quickly with soil particles, providing rapid stabilisation.

Both latex as an aqueous emulsion and poly-DADMAC in aqueous solution have been shown in this study to have abilities as soil conditioners, ie through increased water stable aggregation (Chapter 2), decreases in mechanically dispersible clay (Chapter 4); decreased erosion (Chapter 6); no increases in soil hydrophobicity and water content at different water suctions in the range of tolerance to the growth of plants; no negative effects on the growth of grass; and no tendency to enhance crust formation on soil surfaces. Latex, an uncharged hydrophobic natural polymer, and poly-DADMAC, a positively charged hydrophilic, stabilised aggregates in different ways. Both polymers may be considered as soil conditioners depending on the soil and the particular problem to be ameliorated.

8.1.1. Natural rubber latex as a soil conditioner

Natural rubber latex when physically adsorbed on soil particles will be a good stabiliser in all soil types from sands to clays, or in soils dominated by either positively, negatively, or non charged components. Thus latex can be applied on all soil types. Latex can also be applied in a range of environments, from drier to humid tropical areas.

As a hydrophobic material, it may also be used as a soil conditioner in tropical areas or where rainfall is intense, as water was able to penetrate into soils at an application rate ≤ 1.5 g kg^{-1}. However, at higher application rates, it may increase run-off and may be employed to increase the water yield to supply water storage in ponds.

Since latex can be prepared as an aqueous emulsion, its use as a soil conditioner has the potential to be cheaper (than when mixed with synthetic emulsifiers), and thus more readily available in producer countries. Thus estate plantations and small holder farms can apply it at low cost. In developing countries like Malaysia, Indonesia and Thailand; the extent of intensive agriculture such as rubber plantations, oil palm plantations, or crop plantations increases every year. As these countries are in tropical areas which have intense rainfall, they always face a high risk of erosion. Erosion usually is very rapid once the land is cleared for agriculture, even though tropical soils are relatively stable due to having high iron and aluminium contents. Even though a cover crop is established, a soil conditioner is required before the cover crop is grown; this is especially necessary during the first 2 months, where the canopy of cover crops is still not enough to protect soil surfaces.

Shifting cultivation is still practiced in Indonesia, Malaysia, and the Philippines; this usually occurs on small farms, where the area is not more than 3 ha. Small farmers commonly clear the land and abandon it after 2 or 3 years of cultivation, due to a deterioration in the fertility of the soils. One of the reasons is the high erosion in the first year of cultivation, when the top few cm of fertile soil are eroded. Thus after the 2nd and 3rd year, the soils can no longer support crops, especially upland rice, cassava, vegetables crops, and yam (Librero, 1984; Morgan, 1986). The only weed which can grow on the remaining infertile soils at first is a grass called "alang-alang" (*Imperata cylendrica* L.). Latex, which is cheap and easily available from surrounding rubber farms, may be applied with this type of cultivation, so that small farmers might be able to grow crops on their farms for several years. This also means that a lot of land can be made safe, and the energy of farmers or their power resources used to clear new land or saved for other work.

The application of latex on engineering constructions such as road sides, sand dunes, and stabilised steep slopes is also recommended, at least for a few months before the growth of plants occurs. The application of latex as a permanent stabiliser is not proposed, since latex decomposes and has a short half life in soil (Chapter 7).

8.1.2. Poly-DADMAC as a soil conditioner

In the case of this positively charged and hydrophilic polymer, application may also vary depending on purposes. However, it will not be effective on sands or in soils which are dominated by positively charged materials. Since it is positively charged and hydrophilic, it cannot adhere to sand particles, and it will be repelled by positively charged particles. Schamp *et al.* (1975) recommended mixing negatively charged clay with pure sands before the positively charged polymer was added, thus water stable aggregates can be obtained.

Poly-DADMAC has a potential for application to sodic soils, which commonly form a crust when dry. As a large polymer, it may displace sodium on the exchange sites of minerals, replacing the need for gypsum. The high molecular weight polymer may adsorb more strongly than gypsum on clay mineral surfaces, therefore it is more difficult to remove by leaching. Thus the application of this polymer would need to be less frequent than that of gypsum. It also can decrease crust formation on sodic soils, as it was shown that it decreased tensile strength at a high application rates (Chapter 3). As a hydrophilic polymer, it can be mixed with water for irrigation, thus it is easy to apply.

In very unstable soils, i.e. those which slake easily and form crusts on their surface, such as Red-brown earth (Baldock and Oades, 1990), the application of positively charged poly-DADMAC is also recommended even though these soils commonly occur on gently sloping areas, where erosion risk is low. This polymer can overcome slaking and crust formation as a result of creating aggregates (>0.125-2 mm).

A positively charged polymer may not be used on soils at low pH which contain high contents of iron and aluminium oxides, because these soils are dominated by positive charges on the surfaces of active soil materials. Since tropical soils are highly leached, these soils have a relatively low pH and thus are highly positively charged. If poly-DADMAC is applied on these soils, it will be repelled and then washed out from the soil. This polymer also displace nutrient cations and thus induce further leaching in soils. In tropical areas, this polymer may be applied on soils which are dominated by montmorillonite clays or on soils which have a high cation exchange capacity e.g. Vertisols and some Mollisols, thus it may be adsorbed on active soil surfaces and will not be washed out by water through overland flow or percolation.

8.2. General conclusions

8.2.1. Latex as a soil conditioner

As a result of several experiments, it may be concluded that latex without the use of aromatic oils and stabilisers:

1. increased and stabilised >2 mm water stable aggregates by up to 80% on all soils at relatively low application rates (ie between 0.5 and 1.5 g kg^{-1})
2. significantly decreased mechanically dispersible clay on the two contrasting soils examined
3. did not affect water retention on both of these soils
4. increased the M.E.D. to moderate values which would not affect the available water for plant growth on both soils
5. did not affect the tensile strength and friability of both soils
6. did not affect water run-off and infiltration but significantly decreased erosion on both soils
7. did not produce any negative effects on the growth of grass
8. can be used as a soil conditioner which is environmentally safe.

8.2.2. Poly-DADMAC as a soil conditioner

Poly-DADMAC also showed a capability to be as soil conditioner since it:

1. increased and stabilised >0.125-2 mm water stable aggregates and significantly decreased the amount of <0.125 mm aggregates on all soils

2. increased the tensile strength of a weak soil (Red-brown earth or Alfisol) and, at higher rates, decreased the tensile strength of a Wiesenboden (Mollisol)
3. significantly decreased the proportion of mechanically dispersible clay on both soils
4. did not affect water retention by both soils within the range of water available to plants
5. did not affect water infiltration and run-off on the Red-brown earth and increased infiltration on the Wiesenboden; however, it decreased erosion significantly on both soils
6. did not have any negative effects on the growth of grass

8.3. Future work

Experiments are suggested on the application of latex and poly-DADMAC in the field eg. to investigate the depth that latex penetrates into soils and to discover the best time to apply them in soils ie after tillage, before tillage or at the time of tillage.

Since latex is a tropical product, an investigation of the effectiveness on tropical soils in the field is also suggested because these soils have a relatively higher moisture content than Mediterranean climate soils.

The effects of the two polymers on various crops also need to be investigated. The residual effects of the poly-DADMAC also require investigation.

REFERENCES

Allison, L.E. and D.C. Moore, 1956. Effect of VAMA and HPAN soil conditioners on aggregation surface crusting, and moisture retention in alkali soils. *Soil Science Society of America Proceedings* 20, 143-146.

Allison, L.E., 1956. Soil and plant reponses to VAMA and HPAN soil conditioners in the presence of high exchangeable sodium. *Soil Science Society of America Proceedings*, 20, 147-151.

Amato, M., R.B. Jackson, J.H.A. Butler and J.N. Ladd, 1984. Decomposition of plant material in Australian soils. II. Residual organic ^{14}C and ^{15}N from legume plant parts decomposing under field and laboratory conditions. *Australian Journal of Soil Research*, 22, 331-41.

Armbrust, D.V. and Dickerson, J.D. 1971. Temporary Wind Erosion control: Cost and effectiveness of 34 commercial materials. *Journal of Soil Conservation*, 26:154-157.

Ambrust, D.V. and Lyles, L. 1975. Soil stabilizers to control wind erosion. In: "Soil Conditioners" *Soil Science Society of America* Special Publication No.7: pp 77-82.

Ayanaba, A. and D.S. Jenkinson, 1990. Decomposition of carbon-14 labled Rye grass and Maize under tropical conditions. *Soil Science Society of American Journal,* 54, 112-115.

Bachik, A.T., C.S. Yeoh, Y.K. Chee, F.K. Yew and G. Haridas, 1985. New formulations and recomendations in the use of natural rubber for soil stabilisation and erosion control. *Proceeding of International Rubber Conference*, Kuala Lumpur, 701-709.

Baldock, J.A. and J.M. Oades, 1990. Structural amelioration of a South Australian Red-brown earth using clacium and organic amendments. pp 131-41. In "Soil Structure Research in Eastern Canada: Proceedings of the Eastern Canada Soil Structure Workshop". Eds. J.A. Stone; B.D. Kay and D.A. Angers. 236p.

Balesdent, J. and A. Mariotti, 1987. Natural ^{13}C abundance as a tracer for studies of soil organic matter dynamics. *Soil Biology and Biochemistry*, 19(1), 25-30.

Barvenik, F.W. 1994. Polyacrylamide characteristics related to soil applications. *Soil Science*, 158(4), 235-243.

Ben-Hur, M. 1994. Run-off, erosion, and polymer application in moving-springkler irrigation. *Soil Science*, 158(4), 283-290.

Ben-Hur, M. and J. Letey, 1989. Effect of polysaccarides, clay dispersion, and impact energy on water infiltration. *Soil Science*, 53, 233-238.

Ben-Hur, M.; M. Malik; J. Letey, and U. Mingelgrin, 1992. Adsorption of polymers on clays as affected by clay charge and structure, polymers properties, and water quality. *Soil Science*, 153, 349-356.

Black, A.P., F.B. Birkner, and J.J. Morgan, 1966. The effect of polymer adsorption on the electrokinetic stability of dilute clay suspensions. *Journal of Colloid and Interface Science*, 21, 626-648.

Bohne, H. and R. Lessing, 1988. Stability of clay aggregates as a function of water regimes. *In* "Impact of water and external forces on soil structure" (Drescher, Horn and De Boodt editors). Catena supplement II, 29-34. Catena Verlag, W. Germany.

Bradford, J.M. and C. Huang, 1993. Comparison of interill soil loss for laboratory and field procedures. *Soil Technology*, 6,145-156.

Braunack, M.V., J.S. Hewitt and A.R. Dexter, 1979. Brittle fracture of soil aggregates and the compaction of aggregate beds. *Journal of Soil Science*, 30, 653.

Bruce-Okene,I. and Lal, R. 1975. Soil erodibility as determined by raindrop technique. *Soil Science*, 119,149-157.

Carr, C.E. and D.J. Greenland, 1975. Potential application of polyvinyl acetate and polyvinyl alcohol in the structural improvement of sodic soils. pp: 47-63. *In* Soil Conditioners. (ed. W.C. Moldenhaver). 1975. SSSA spec publ. Madison, Wisconsin.

Chittleborough, D.J. and J.M. Oades., 1980. The development of a red brown earth. III. The degree of weathering and translocation of clay. *Australian Journal of Soil Research* 19,383-93.

Collins, H.P., L.F. Elliott, R.W. Rickman, D.F. Bezdicek, and R.I. Papendick, 1990. Decomposition and interactions among wheat residue components. *Soil Science Society of American Journal,* 54,780-785.

Cornish, K., D.J. Siler, O. Grosjean and N. Goodman, 1993. Fundamental similarities in rubber particle architecture and function in three evolutionarily divergent plant species. *Journal of Natural Rubber Research*, 8(4), 275-285.

Danneels, P., Q. Vyvey, C. Beel and W. Van Gotthem, 1992. Use of mini-rhizotrons to study effects of soil conditioners on root growth. *Soil Technology*, 5, 97-100.

Davis, C.C. , 1937. "The Chemistry and Technology of Rubber." Reinhold, New York.

De Boodt, M. 1975. Use of soil conditioners around the world. *In* "Soil Conditioners". *Soil Science Society of America*, special Pub. No 7. Wisconsin, USA. 1-12.

De Boodt, M.F., Hayes, M.H.B. and Herbillion, A. 1990. Soil colloids and their associations in aggregates. Nato Series. Series B: Physics Vol. 215. Plenum Press. New York. 520-528.

De Boodt, M.F. 1993. Soil conditioning, a modern procedure for restoring physical soil degradation. *Pedologie*, 43(1), 157-195.

Dexter A.R. and B. Kroesbergen, 1985. Methodology for determination of tensile strength of soil aggregates. *Journal of Agricultural Engineering Research*, 31, 139-147.

De Ploey, J. and J. Poeson, 1985. Aggregate stability, run off generation and interill erosion. *In* K.S. Richard; R.R. Arnett and S. Ellis (Eds). Geomorphology and soils. George Allen & Unwin, London.

Dixon, J.K., V.K. La Mer, Cassian LI, S. Messinger, and H.B. Linford, 1967. Effect of the structure of cationic polymers on the flocculation and the electrophoretic mobility of crystalline silica. *Journal of Colloid and Interface Science*, 23, 465-473.

Dowdy, R.H. 1975. The effect of organic polymers and hydrous iron oxides on the tensile strength of clays. pp: 25-33. *in* Soil Conditioners. SSSA special pub. No 7. Madison, Wisconsin.

Dowdy, R.H. and M.M. Mortland, 1967. Alcohol-water interactions on montmorrillonite surfaces I Ethanol. *Clays and Clay Minerals*, 15, 259-271.

Dowdy, R.H. and W.E. Larson, 1971. Tensile strength of montmorillonite as a function of saturating cation and water content. *Soil Science Society of America Proceedings* 35, 1010-1014.

Ekwue, E.I. 1991. The effects of soil organic matter content, rainfall duration, and aggregate size on soil detachment. *Soil Technology*, 4,197-207.

Emerson, W.W. and Raupach, M. 1964. The reaction of polyvinyl alcohol with montmorillonite. *Australian Journal of Soil Research,* 2, 46-55.

Franson, M.A.H., 1980. Standard methods for the examination of water and wastewater. 15th ed. APHA-AWWA-WPCF, Washington.pp.253-257.

Gabriels, D and de Boodt, 1978. Evaluation of soil conditioners for water erosion control and sand stabilization. *In* Emerson, W.W.; R.V. Bond and A.R. Dexter. 1978. Modification of soil structure. John Wiley and Sons. Chichester.

Gabriels, D, 1990. Application of soil conditioners for agriculture and engineering. pp. 557-576. In'Soil Colloids and Their Associations in Aggregates'. (Eds. M.F. De Boodt, M.H.B. Hayes and A. Herbillon). NATO ASI Series B: Physics Vol.215. Plenum, New York.

Glanville, S.F. and G.D. Smith, 1988. Aggregate breakdown in clay soils under simulated rain and effects on infiltration. *Australian Journal of Soil Research,* 26,111-20.

Golchin, A., J.M. Oades, J.O. Skjemstad, and P. Clarke, 1995. Structural and dynamic properties of soil organic matter as reflected by ^{13}C natural abundance, pyrolysis mass spectrometry and solid-state ^{13}C NMR spectroscopy in density fractions of an Oxisol under forest and pasture. *Australian Journal of Soil Research*, 33, 59-76.

Greene, R.S.B., A.M. Posner and J.P. Quirk, 1978. Interactions of suspensions of Ca-illite with PVA and $Ca(OH)_2$. pp: 157-163. In 'Modification of Soil Structure' ed W.W. Emerson, R.D. Bond and A.R. Dexter. John Wiley and Sons, Chichester.

Greenland, D.J. 1963. Adsorption of polyvinyl alcohols by montmorillonite. *Journal of Colloid Science.*,18, 647-664.

Greenland, D.J. 1965a. Interaction between clays and organic compound in soils. I. Mechanisms of interaction between clays and defined organic compounds. *Soils and Fertilizers*, 28, 415-425.

Greenland, D.J. 1965b. Interaction between clays and organic compounds in soils II. Adsorption of soil organic compounds and its effect on soil properties. *Soils and Fertilizers*, 28, 521-532.

Greenland, D.J. 1972. Interactions between organic polymers and inorganic soil particles. State Univ, Ghent, Belgium, 37(3), 897-906.

Hartmann, R. and De Boodt, M. 1974. The influence of the moisture content, texture and organic matter on the aggregation of sandy and loamy soils. *Geoderma*. 11,53-62.

Hayes, M.H.B. and U. Mingelgrin, 1991. Interactions between small organic chemicals and soil colloidal constituents. *In* H. Bolt, M.F. De Boodt, M.H.B. Hayes and M.B. McBride (eds). "Interactions at the soil colloid-soil solution interface", pp. 323-407. Kluwer Ac. Pub. The Netherlands.

Herman, W.A., W.B. McGill and J.F. Dormaar, 1977. Effects of initial chemical composition on decomposition of roots of three grass species. *Canadian Journal of Soil Science*, 57, 205-215.

Hillel, D. 1980. Introduction to soil physics. Academic Press. London, 44-45.

Iler, R.F. 1971. Relation of particle size of colloidal silica to the amount of a cationic polymer required for flocculation and surface coverage. *Journal of Colloid and Interface Science*, 37, 364-373.

Jager, G and E.H. Bruins, 1975. Effect of repeated drying at different temperatures on soil organic matter decomposition and characteristic, and on the soil microflora. *Soil Biology and Biochemistry*, 7, 153-159.

Jenkinson, D.S., 1977. Studies on the decomposition of plant material in soil V. The effect of plant cover and soil type on the loss of carbon from 14C labelled Rye grass decomposing under field conditions. *Journal of Soil Science, 28, 424-434.*

Kavanagh, B.V.; A.M. Posner, and J.P. Quirk. 1978. Adsorption of PVA on soil colloids. *In* Modification of soil structure, 1978, by W.W. Emersion, R.D. Bond and A.R. Dexter. John Wiley and Sons, Chichester, p165-173.

Kay, B. D. and A. R. Dexter, 1992. The influence of dispersible clay and wetting/drying cycles on the tensile strength of a red brown earth. *Australian Journal of Soil Research,* 30,297-310.

Kemper, W.D., and Rosenau, R.C., 1986. Aggregate stability and size distribution. In Klute, A., 1986. Methods of Soil Analysis. Part 1in The series Agronomy. Madison, Wisconsin. pp:425-461.

Kemper, W.D., Rosenau, R.C., and Dexter,A.R. 1987. Cohesion development in disrupted soils as affected by clay and organic matter content and temperature. *Soil Science Society of American Journal*, 51, 860-867.

Kemper, W.D., M.S. Bullock; I.D. Kimberly; and A.R. Dexter, 1989. Soil cohesion changes. pp. 81-95. *In* "Mechanics and related processes in structured agricultural soils". Editors: W.E. Larson et al. Kluwer Academic.

Khorasani, M.T., G.R. Bakhshandeh and A.A. Katbab, 1993. Synthesis, characterisation and activity of two new phenol antioxidants in natural rubber. *Journal of Natural Rubber Research*, 8(4), 253-259.

Kijne, J.W. 1967. Influence of soil conditioners on infiltration and water movement in soils. *Soil Science Society of America Proceedings*, 31(1), 8-13.

King, P.M. 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assesment of some factors that affect its measurement. *Australian Journal of Soil Research,* 19,275-85.

Klute, A. 1986. Methods of soil analysis. Part 1 in The Series Agronomy. Madison, Wisconsin.

Lagaly, G. 1987. Clay-organic interactions: Problems and recent results. Proc. Int. Clay Conf. Denver, 1985 (Eds. L.G. Schults, H. van Olphen, and F.A. Mumpton). The Clay Minerals Society, 343-351.

Lax, A. and F. Garcia-Orenes, 1993. Carbohydrates of municipal solid wastes as aggregation factor of soils. *Soil Technology*. 6,157-162.

Letey, J. 1994. Adsorption and desorption of polymers on soil. *Soil Science*, 158, 244-248.

Letterman, R.D. and Pero, R.W. 1990. Contaminants in polyelectrolytes used in water treatment. *Journal of American Water Works Association.*, 82(11), 87-97.

Levin, J.; M. Ben-Hur; M. Gal and G.J. Levy. 1991. Rain energy and soil amendments effects on infiltration and erosion of three different soil types. *Australian Journal of Soil Research*, 29,455-65.

Libero, A.R. 1984. Socioeconomic considerations in a soil erosion managemant program: Case study of the two provinces in the Phippines. pp. 90-101. In "Soil Erosion Managemant: ACIAR Proceedings Series 6. 132p.

Loch, R.J. and J.L. Foley, 1994. Measurement of aggregate breakdown under rain: comparison with tests of water stability and relationships with field measurements of infiltration. *Australian Journal of Soil Research,* 32,701-720.

Malinda, D.K., B.M. Dubois, R.N. Pederson, W.R. Darling and R.G. Fawcett, 1992. Improved equipment and methods for the study of rainfall infiltration, run-off, soil and nutrient losses. Dept. of Agric. South Australia. Technical Paper 33, 26p.

Malik, M. and J. Letey, 1991. Adsorption of polyacrylamide and polysaccharide polymers on soil materials. *Soil Science Society of American Journal,* 55, 380-383.

Martin, J.P. and K. Haider, 1986. Influence of mineral colloids on turnover rates of soil organic matter. pp: 283-304. In 'Interactions of Soil Minerals with Natural Organics and Microbes', Editors P.M. Huang and M. Schnitzer. SSSA Spec. Pub. no. 17. Madison.

Martin, W.P., 1953. Status report on soil conditioning chemicals. I. *Soil Science Society of America Proceedings,* 17(1), 1-16.

Mathers, A.C., F.B. Lotspeich, G.R. Laase, and G.C. Wilson, 1966. Strength of compacted Amarillo fine sandy loam as influenced by moisture, clay content, and exchangeable cation. *Soil Science Society of America Proceedings,* 30, 788-791.

Mausbach, J.J. and W.D. Shrader, 1975. Influence of surface treatment of selected subsoil materials on infiltration and erosion. In Soil Conditioners No-7. *Soil Science Society of America.* Special Publ. Series, 8393, pp.83-93.

Mitchell, A.R. 1986. Polyacrylamide application in irrigation water to increase infiltration. *Soil Science*, 141, 353-358.

Molyneux, P. 1984. Water-soluble synthetic polymers: Properties and Behavior. Vol. II. C.R.C. Florida.

Morgan, R.P.C. 1986. Soil erosion and conservation. Longman, U.K. 298p.

Morin, J., D. Goldberg and I. Seginer. 1967. A rainfall simulator with a rotating disc. *Transactions of the ASAE* 10 (1), 74-79.

Mukhopadhyay, R., P.R. Gajri and M.R. Chandhary. 1994. Synthesis of a soil conditioner from acrylic waste and its effect on aggregate stability and moisture retention in two soils. *Arid Soil Research and Rehabilitation*, 8,178-186.

Nadler, A. and J. Letey, 1989. Organic polyanions' effect on aggregation of structurally disrupted soil. *Soil Science*, 148, 346-354.

Nadler, A., M. Malik, and J. Letey, 1992. Desorption of polyacrylamide and polysaccharide polymers from soil materials. *Soil Technology*, 91-95.

Oades, J.M. 1976. Prevention of crust formation in soils by poly(vinyl alcohol). *Australian Journal of Soil Research*, 14, 139-148.

Oades, J.M. 1989. An introduction to organic matter in mineral soils. pp 89-160. In "Minerals in Soil Environments". eds: J.B. Dixon and S.B. Weed. 2nd edition. SSSA Book Series 1. Madison, Wisconssin. 1244p.

Parr, J.F. and R.I. Papendick, 1978. Factors affecting the decomposition of crop residues by microorganisms. p. 101-129. In W.R. Oschwald (ed.) Crop residue management systems. ASA Spec. Publ. 31, ASA, CSA, and SSSA, Madison, WI.

Pla, I. 1975. Effect of bitumen emulsion and polyacrylamide on some physical properties of Venezuelan soils. pp.35-46. In "Soil Conditioners". *Soil Science Society of America,* special Pub. No 7. Wisconsin, USA.

Polhamus, L.J. 1962. Rubber botany, production, and utilization. Leonard Hill, London.

Quessar, M.; R. Hartmann, and J. De Smet. 1993. Modification of the aggregate stability indices for the wet sieving method and the water drop technique. *Soil Technology*, 6,329-336.

Quirk, J.P. and C.R. Panabokke, 1962. Incipient failure of soil aggregates. *Journal of Soil Science*, 13, 60-70.

Reischert, J.M. and L.D. Norton, 1994. Aggregate stability and rain-impacted sheet erosion of air-dried and prewetted clayey surface soils under intense rain. *Soil Science*, 158(3), 159-169.

Rengasamy, P. , Greene,R.S.B., Ford, G.W., and A.H. Mehanni. 1984. Identification of dispersive behaviour and the management of Red-brown earth. *Australian Journal of Soil Research*, 22, 413-31.

Rogowski, A.S., W.C. Moldenhauer, and D. Kirkham, 1968. Rupture parameters of soil aggregates. Richards, L.A. 1956. Modulus of rupture as an index of crusting of soil. *Soil Science Society of America Proceedings,* 32, 720-724.

Roberts, K., J. Kowalewska, and S. Friberg, 1974. The influence of interactions beween hydrolyzed aluminum ions and polyacrylamides on the sedimentation of kaolin suspensions. *Journal of Colloid and Interface Sciences*, 48, 361-367.

Rubber Research Institute of Malaysia, 1962. Annual Report. Kuala Lumpur. p:81-83.

Rubber Research Institute of Malaysia, 1970. Annual Report. Kuala Lumpur p:48.

Rubio, H.O., M.K. Wood, M. Cardenas, and B.A. Buchanan, 1989. Effect of polyacrylamide on seedling emergence of three grass spcecies. *Soil Science*, 148, 355-360.

Schamp, N., Huyebroek, J., and Sadones, M. 1975. Adhesion and adsorption phenomena in soil conditioning. In "Soil Conditioners". *Soil Science Society of America*, special Pub. No 7. Wisconsin, USA. 13-23.

Seybold, C.A. 1994. Polyacrylamide review: Soil conditioning and environtal fate. *Communication in Soil Science and Plant Analysis*, 25(11&12), 2171-2185.

Shainberg, I., G.J. Levy, P. Rengasamy, and H. Frenkel, 1992. Aggregate stability and seal formation as affected by drops' impact energy and soil amendments. *Soil Science*, 154(2), 113-119.

Skjemstad, J.O., R.P. Le Feuvre and R.E. Prebble, 1990. Turnover of soil organic matter under pasture as determined by ^{13}C natural abundance. *Australian Journal of Soil Research*, 28, 267-76.

Smith, B.N. and S. Epstein, 1971. Two categories of 13C/12C ratios for higher plants. *Plant Physiology*, 47, 380-384.

Snyder, V.A. and R.D. Miller, 1985. Tensile strength of unsaturated soils. *Soil Science Society of AmericanJournal*, 49, 58-65.

Sojka, R.E. and R.D. Lentz, 1994. Time for yet another look at soil conditioners. *Soil Science*, 158, 233-234.

Soong, N.K. and C.S. Yeoh. 1974. The use of NR emulsions for stabilising sandy soils. Proc. Rubb. Res. Int. Kuala Lumpur, Malaysia. 127-137.

Soong, N.K. and C.S. Yeoh. 1975. Latex oil emulsions for controlling soil erosion on exposed soil surfaces. *Proceedings of Insternational Rubber Conference*, Kuala Lumpur, 51-66.

Soong, N.K. 1979. The prospects of using natural rubber for conditioning tropical soils. *In* Lal, R. and Greenland, D.J. 1979. "Soil physical properties and crop production". pp 105-110. John Wiley and Sons. Chichester.

Stace, H.C.T., Hubble, G.D., and Brewer, R., Northcote, K.H., Sleeman, J.R., Mulcahy, M.J., and Hallsworth, E.G. 1972. "A Handbook of Australian Soils". Rellim, Glenside, S.A.

Steel, R.G.D. and J.H. Torrie, 1960. Principles and procedures of statistics. McGraw-Hill. New York. 481p.

Stefanson, R.C. 1974. Soil stabilization by polyvinyl alcohol and its effect on the growth of wheat. *Australian Journal of Soil Research*, 12, 59-62.

Stern, R.; M.C. Laker and A.J. Van der Merwe. 1991. Field studies on effect of soil conditioners and mulch on runOff from kaolinitic and illitic soils. *Australian Journal of Soil Research*, 29, 249-261.

Tennant, D. 1975. A test of a modified line intersect method of estimating root length. *Journal Of Ecology*, 63, 995-1001.

Theng, B.K. 1979. Formation and properties of clay-polymer complexes. Developments in Soil Science 9. Elsevier. 362p.

Tisdall, J.M. and J.M. Oades, 1982. Organic matter and water stable aggregates in soils. *Australian Journal of Soil Research*, 33, 141-63.

Ueda, T. and S. Harada, 1968a. Effect of the structure of cationic polysulfone on the flocculation of kaolinite. *Journal of Applied Polymer Science*, 12, 2383-2394.

Ueda, T and S. Harada, 1968b. Adsorption of cationic polysulfone on bentonite. *Journal of Applied Polymer Science* ,12, 2395-2401.

Utomo, W.H. and Dexter, A.R. 1981. Soil friability. *Journal of Soil Science*, 32, 203-213.

Wah, H.C. and A.T. Bachik, 1985. Commercial application in the use of natural rubber latex emulsions for hydroseeding. *Proceedings International Rubber Conference*, Kuala Lumpur, 710-722.

Wallace, A. and A.M. Abouzamzam, 1984. Nitrogen and bicarbonate relationships with iron nutrition in plants. *Journal of Plant Nutrition*, 7, 587-594.

Wallace, A; G.A. Wallace; A.M. Abouzamzam, and J.W. Cha, 1986c. Effects of polyacrylamide soil conditioner on the iron status of soybean plants. *Soil Science*, 141, 368-369.

Wallace, A., G.A. Wallace, and A.M. Abouzamzam, 1986a. Effects of soil conditioners on water relationships in soils. *Soil Science*, 141, 346-352.

Wallace, G.A. and A. Wallace, 1986. Control of soil erosion by polymeric soil conditioners. *Soil Science*, 141, 363-367.

Wallace, A., G.A. Wallace, and A.M. Abouzamzam, 1986b. Amelioration of sodic soils with polymers. *Soil Science*, 141, 359-362.

Williams, B.G., D.J. Greenland, and J.P. Quirk, 1967. The tensile strength of soil cores containning polyvinyl alcohol. *Australian Journal of Soil Research*, 5, 85-92.

Wood, J.D. and J.D. Oster, 1985. The effect of cellulose xanthate and polyvinyl alcohol on infiltration, erosion, and crusting at different sodium levels. *Soil Science*, 139, 243-249.

APPENDIX

1. Comparison of the effects of latex and poly(DADMAC) on structural stability and strength of soil aggregates.
   S.M. Bernas, J.M. Oades, G.J. Churchman and C.D. Grant.
   Australian Journal of Soil Research
   Vol. 33 (1995) 369-80.
2. Effects of latex and poly-DADMAC on erosion, hydrophobicity and water retention on two different soils.
   S.M. Bernas, J.M. Oades and G.J. Churchman.
   Australian Journal of Soil Research
   Vol. 33 (1995) 805-816.

Bernas, S. M., Oades, J. M., Churchman, G. J. & Grant, C. D. (1995). Comparison of the effects of latex and poly(DADMAC) on structural stability and strength of soil aggregates. *Australian Journal of Soil Research, 33*(2), 369-380.

Bernas, S. M., Oades, J. M. & Churchman, G. J. (1995). Effects of latex and poly-DADMAC on erosion, hydrophobicity and water retention on two different soils. *Australian Journal of Soil Research, 33*(5), 805-816.